Limits of Acidity Constants Validity of Diprotic Acids with $K_1/K_2<10^4$
Calculated from Potentiometric Data

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Algorithms of acidity constants of diprotic acids have been established on the grounds of a global protonation of active centers within the molecule of these chemical species. The values of the acidity constants, calculated from the measured pH values, have not been altered by the involvement of the ampholytes as macrospecies, compared to two other macrospecies: the diprotic acid and the neutral salt of diprotic acid. The validity of these constants is not absolute, because they were influenced by energies, resulted from interactions, determined by the ampholyte division in two microspecies, differentiated according to the occupied protonation center.

Keywords: acidity constants; Potassium hydrogen phthalate; Phthalate standard solution pH

The acidity constants of diprotic acids have been determined by the free energy, including not only the free energy necessary to bind the protons to the active centers, but also the interaction energy between the protons bonding centers [1, 2]. The potentiometer measurements can determine the pH values of the resulted buffer solutions. Such measurements consist in adding different volumes of heavy acids and bases to ampholyte solutions [3,4]. Irrespective of the algorithm established for the calculation of acidity constants from the measured pH values, and irrespective of the volume and solution concentrations, the above mentioned interaction energies cannot be calculated in such a way as to allow us to establish accurate acidity constants values. Interaction energies can be deducted only from the equilibrium microconstants, i.e. two placed between the diprotic acid and the two microspecies, where the ampholyte has been divided according to the occupied protonation center, and two between these microspecies and the neutral diprotic acid salt. Microconstants shall be determined only by means of NMR[5-7] titrations, representing the ampholyte constants of the monoprotic acid [1]. Equilibrium microconstants refer to those formed between macrostates such as: diprotic acid, ampholyte as unit species and the diprotic acid joint base.

The calculation of acidity macroconstants of diprotic acid, determined with the help of the proposed algorithm, by taking into consideration the global protonation, shall exclude the effect of the ampholyte involvement in two competitive macrospecies, but shall not include the effect of the interactions energies determined by the presence of microspecies where the ampholyte is divided. The differences between the acidity constants of orthophthalic acid on different pH values indicate the presence of different interaction energy in the buffer solutions, resulted by adding different quantities of hydrochloric acid or hydroxide sodium to the potassium hydrogen orthophthalate.

The acidity macroconstants of the algorithm has been applied to the pH standard resulted from potassium hydrogen orthophthalat [3, 4], because the permanent interest in thermodynamic interpretation has been determined by the orthophthalic acidity constants, resulting into former [8-10] and recent [11-12] scientific papers.

Experimental part
Methods used in establishing the algorithms of diprotic acids acidity macroconstants

In order to calculate the acidity macroconstants of one diprotic acid independent of competitive protonation and deprotonation of macrocenters, we have used complete equations of diprotic acid titration curves with heavy base [13] together with its neutral state, in combination with heavy acid [14] expressed by the following equations (1) and (2):

$$
\Phi = 2 - \bar{n} + \frac{\alpha_o + \alpha_1}{C_o V_0} \left( \frac{K_{H,O}'}{[H^+]} - [H^+] \right) \tag{1}
$$

$$
\Phi = \bar{n} + \frac{\alpha_o + \alpha_1}{C_o V_0} \left( [H^+] - \frac{K_{H,O}'}{[H^+]} \right) \tag{2}
$$

These equations represent the fraction significant for a certain pH value, written as the sum of the dissociated fraction, no. 2-$\bar{n}$ and the fraction resulted from the difference between the following ions concentrations [OH-] and [H+], respectively, as the sum of the protonated fraction $\bar{n}$ and the fraction resulted from the difference between the following ions concentrations [H+] and [OH-].

The dissociation and protonation global fractions expressed on the basis of the species fractions, characterized by different protonation degrees originating from the diprotic acid, have been expressed by the following equations (3) [15] and (4) [16]

$$
2 \cdot \bar{n} = 2\alpha_o + \alpha_1 \tag{3}
$$

$$
\bar{n} = 2\alpha_o + \alpha_1 \tag{4}
$$

Taking into account that at the first equivalence point, the value of the significant fraction is 1, so that it could express the ampholyte significant fractions, we subtract the 1st value from both members of equations (1) and (2). Moreover, the dissociated fraction $\alpha_o + \alpha_1 + \alpha_2 = 1$, namely, the protonated fraction resulted from the equations (1) and (2) become: $\alpha_o - \alpha_2$ respectively $\alpha_2 + \alpha_o$. 

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The neutral salt fraction shall be marked with a zero index, while the diprotic acid fraction shall be marked with index two; the equations left member (1) and (2) represent the balance of potassium hydrogen orthophthalate converted from the initial quantity.

The data used to calculate the acidity constants are the ones specified in table 1 for the buffer solutions prepared by Clark [3] and pH values measured by Bower [4]. By analyzing the data specified in table 1, we notice that \( V_0 + V = 100 \), \( C_0V_0 = 5 \), representing the \( \text{pH} \) highest value is 5.90 with over two orders of magnitude higher than the corresponding \( \text{pOH} \). After a reordering process, the equations (1) and (2) become (5) and (6):

\[
K_0, K_2 = \frac{\Psi}{\Psi} - 1[H^+] \quad K_0 = \frac{1+\Psi}{\Psi} - 1[H^+] \\
K_0, K_2 = \frac{\Psi}{\Psi} + 1[H^+] \quad K_0 = \frac{1+\Psi}{\Psi} + 1[H^+] 
\]

In equation (5) \( \Psi = \Phi + 20[H^+] \) and in equation (6)

\[
\Psi = \Phi - 20[H^+] \quad \Phi = \frac{C_1V_1}{C_2V_2} \quad V \text{ being equal with } x \text{ from table } 1, \quad \text{and } C = 0.1 \text{ M, representing the concentration of HCl solutions respectively, the NaOH added.}
\]

Equations (5) and (6) represent the proposed algorithms which have been adapted to the data mentioned in table 1. By resorting to this type of equations it is possible to calculate the constants by resorting to an algebra formula in order to solve the two equations systems with two unknown elements, namely, \( K_0 \) and \( K_0K_2 \) for two successive \( \text{pH} \).

**Results and discussions**

Table 2 presents the acidity constants values calculated by resorting to an algebra method and nevertheless, by taking into consideration the ions strengths. Taking into account that the ions maximum strength slightly exceeds 0.1, the equation Debye Hückel has been applied only in case of \( \text{pH} \) 5.00-5.90 (0.1020-0.1378) interval, in order to be able to calculate the acidity coefficient.

\[
\lg \gamma = \frac{-0.51z^2\sqrt{\mu}}{1 + (\alpha\sqrt{\mu}/305)}
\]

Where 0.51 and 305 represent constants for an aqueous medium at a temperature 25°C, \( \alpha \) represents the hydrated ion, \( z \) represents the ions charge, and \( \mu \) represents the ions strength [17]. By calculating the hydrogen orthophthalate and neutral orthophthalate activity coefficients we have obtained the activities of these species. More specifically, the orthophthalic acid activity coefficient has been considered one, while the concentrations of hydronium ions calculated from the measured \( \text{pH} \) values represent activities.
K1 and K2K2 values could be obtained as roots of two equation systems with two unknown elements. In table 2, the roots negative values are missing, being present on dependences non linear fields

$$-\frac{1+\Psi_1}{\Psi_1-1}[H^+]\times10^{-x}\text{vs.}\frac{\Psi_1}{\Psi_1+1}[H^+]$$ respectively

$$-\frac{1-\Psi_1}{\Psi_1+1}[H^+]\times10^{-y}\text{vs.}\frac{\Psi_1}{\Psi_1+1}[H^+]$$

The right hand equations describing the right field of those dependences are the following:

$$y = 2.3942x + 9.1357 \quad (8)$$

$$R^2 = 0.9936 , \text{ df } = 4 , \ p \ < 0.01 \ (\text{two tailed}) \ \text{for NaOH addition}$$

$$y = 1.3824x + 0.0157 \quad (9)$$

$$R^2 = 0.9993 , \text{ df } = 16 , \ p \ < 0.01 \ (\text{two tailed}) \ \text{for HCl addition}$$

In equations (8) and (9) the intersections with the ordinate represent K1K2 and the slope K1.

Equation (8) is valid for a pH interval of 4.10-4.60, K1 = 2.39 . 10^{-3}, K1K2 = 9.14 . 10^{-6}, K2 = 3.82 . 10^{-6}.

Equation (9) is valid for a pH field of 2.20-3.90, K1 = 1.38 . 10^{-3}, K1K2 = 0.0157 . 10^{-6}, K2 = 11.3 . 10^{-6}.

The pH intervals specified in table 2, column 2, correspond to the equations forming two equation systems with two unknown elements; the K1, K1K2 and K2 values proved to be equal for both pH values if the figures are real. The K1 and K2 values, which have been calculated by resorting to an algebra formula, indicate modification at the interaction energy level, within the studied diprotic system for different pH values. Specialized studies have published values of those constants obtained from the pH value measurements in potassium hydrogen orthophthalate [18]. By adding hydrochloric acid and sodium hydroxid on potassium hydrogen orthophthalate, the ratio between fractions with different protonation degrees and implicitly, and the average protonation corresponding to a certain pH, has been modified. The different values of diprotic acid acidity constants resulting from average protonations have been determined with the help of interaction energies existing between protons and protonation centers. If it were possible to determine the energy values within the free protonation energy, we would be able to establish the real and free protonation energies, which would give us the opportunity to calculate the acidity constants real values.

**Comparison of acidity constants values, calculated by means of an algebra formula and graphic method on pH 2.20-3.90 interval with the published values. [18]**

The K1 values, which have been calculated with the help of an algebra formula, seem to be closer to the published value of K1 = 1.112 . 10^{-3} on a pH 2.20-2.70 K1 = (1.16 ± 0.06) . 10^{-3} interval for df = 5, with a reliability level of 95%, as compared to the entire field of pH 2.20-3.90 K1 = (1.29 ± 0.06) . 10^{-3} for df = 15, with a confidence level of 95%. K1 = 1.38 . 10^{-3}, obtained with the help of the graphic method, proving that the above mentioned value does not correspond to any reliability levels. Moreover, the difference between the above mentioned value and the published value seems to exceed the average values of 1.16 . 10^{-3}, respectively 1.29 . 10^{-3}. The K2 values on this pH interval, calculated with the help of an algebra formula, but also with the help of the graphic method differs sensibly from the published value of 3.906 . 10^{-6}, and moreover, their pH value variation is more pronounced.

**Comparison of acidity constants values, calculated by an algebra and graphic method on pH 4.10-4.60 interval with the published values of [18]**

The K1 values resulted on this pH interval, calculated with the help of both algebra and graphic methods, seem to differ sensibly from the published value, and the reproducibility values calculated with the help of an algebra formula seems to be lower than the K1 values. Due to the fact that the value of the measurements used to calculate the acidity constants have been rounded up to

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**Table 2**

<table>
<thead>
<tr>
<th>Nr.</th>
<th>pH</th>
<th>K1*10^{-3}</th>
<th>K1K2*10^{-6}</th>
<th>K2*10^{-3}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.20-2.30</td>
<td>0.94</td>
<td>0.78</td>
<td>4.10-4.20</td>
</tr>
<tr>
<td>2</td>
<td>2.40-2.50</td>
<td>1.31</td>
<td>0.06</td>
<td>4.30-4.40</td>
</tr>
<tr>
<td>3</td>
<td>2.60-2.70</td>
<td>1.22</td>
<td>0.15</td>
<td>4.50-4.60</td>
</tr>
<tr>
<td>4</td>
<td>2.80-2.90</td>
<td>-</td>
<td>-</td>
<td>4.70-4.80</td>
</tr>
<tr>
<td>5</td>
<td>3.00-3.10</td>
<td>1.22</td>
<td>0.04</td>
<td>4.90-5.00</td>
</tr>
<tr>
<td>6</td>
<td>3.20-3.30</td>
<td>1.37</td>
<td>0.01</td>
<td>5.10-5.20</td>
</tr>
<tr>
<td>7</td>
<td>3.40-3.50</td>
<td>1.43</td>
<td>0.01</td>
<td>5.30-5.40</td>
</tr>
<tr>
<td>8</td>
<td>3.60-3.70</td>
<td>1.42</td>
<td>0.01</td>
<td>5.50-5.60</td>
</tr>
<tr>
<td>9</td>
<td>3.80-3.90</td>
<td>1.40</td>
<td>0.01</td>
<td>5.70-5.80</td>
</tr>
</tbody>
</table>
two decimals, there is in some cases a great difference between the $K_1$ value specified in table 2 and the one calculated in the $K_1/K_2$ values ratio.

**Conclusions**

By using established algorithms, we obtained positive values for $K_1$ and $K_2$ on the pH 2.20-2.70, 3.00-3.90 and 4.10-4.60 intervals.

On the pH 2.20-2.70, 3.00-3.90 intervals, the $K_1$ values proved to be constant and closer to the real value than the $K_2$ values.

On the pH 4.10-4.60 interval, the $K_2$ values proved to be constant and closer to the real value than the $K_1$ values.

**References**


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