An Annotation on Normalized Diagrams for the Existence of Two Species of a Diprotic Acid in Solution

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ABSTRACT

The aim of this annotation is to find out in which experimental conditions a diprotic acid may be treated as a monoprotic one, the drawing of normalized diagrams helping on this context, facilitating the choice of pH ranges in which there are only two species in solution from a practical point of view.

Keywords: Diprotic acid, Monoprotic acid, normalized diagrams, number of species

INTRODUCTION

The acidity constants corresponding to the equilibria of diprotic acids may be described by

$$ H_{n-1}R \rightleftharpoons H_nR + H \quad (N \geq n \geq 1) $$

$$ K_{an} = (H) \left[ \frac{H_nR}{H_{n-1}R} \right] \quad (N = 2, \ n = 1, \ or \ 2) $$

At low enough pH values we get the equilibrium $H_2R=HR+H$ governed by $K_{a1}$, whereas at high enough pH values is the equilibrium $HR=R+H$, governed by $K_{a2}$, which prevails. The absorbance for a diprotic acid is related to concentration by

$$ A = \frac{A_0 + A_1(H) + A_2(H^3)}{1 + \frac{(H)}{K_{a2}K_{a1}}} $$

where $A_0$, $A_1$, and $A_2$ are the limit absorbance of $R$, $HR$ and $H_2R$ species, respectively. Then, when only two species $H_2R$ and HR, or HR and R are present, Eqn. (3) takes the form

$$ A = \frac{A_{n-1} + A_{n-1}(H)}{K_{an}} $$

Being susceptible of linear transformation [2]. In order to ascertain in which conditions Eqn. (3) is applicable we may make of normalized diagrams as follows.

NORMALIZED MOLARITY FRACTION OF THE $H_2R$ AND $R$ SPECIES: NORMALIZED DIAGRAMS

The molarity fraction of the $H_2R$ species of a dibasic acid can be expressed as

$$ f_2 = \frac{[H_2R]}{[H_2R] + [HR] + [R]} = \frac{1}{1 + \frac{K_{a1}}{H_{a1}^2} + \frac{K_{a2}}{H_{a2}^2} + \frac{K_{a1}K_{a2}}{H_{a1}H_{a2}}} $$

(5)

Where

$$ \Delta pK_a = pK_{a2} - pK_{a1} = \log \frac{K_{a1}}{K_{a2}} $$

and

$$ z = pK_{a2} - pH = \log \frac{H}{K_{a2}} $$

(6)

The molarity fraction of $R$ species can be indeed expressed as
F_{a} = \frac{[R]}{C_{a}} = \frac{[R]}{[R]+[HR]+[H_{2}R]} = \frac{1}{1 + \frac{[HR]}{[R]} + \frac{[H_{2}R]}{[R]}} = \frac{1}{1 + \frac{K_{a1}}{K_{e}} \left( \frac{[H]}{[R]} \right) + \frac{K_{a2}}{K_{e}} \left( \frac{[H]}{[R]} \right)^{2}} = \frac{1}{1 + 10^{\Delta pK_{a}} \left( 10^{-z} + 10^{-2z} \right)}

being in this case

\[ y = pK_{a1} - \log \frac{K_{a1}}{(H)} \tag{9} \]

Taking reciprocals in Eqn. (5), subtracting 1, we get

\[ \frac{1}{f_{2}} - 1 = 10^{\Delta pK_{a}} \left( 10^{-z} + 10^{-2z} \right) \tag{10} \]

which may be ordered as a second degree equation

\[ 10^{-2z} + 10^{z} - \frac{1}{f_{2}} - 1 = 0 \tag{11} \]

Solving Eqn. (11) for fixed values of \( f_{2} \) and different values of \( \Delta pK_{a} \), we have

\[ z = pK_{a1} - pH = -\log \left( -1 + \frac{1 + 4 \left( \frac{1}{f_{2}} - 1 \right) 10^{\Delta pK_{a}}}{2} \right) \tag{12} \]

Values of \( pK_{a1} - pH = z \) (or \( pH - pK_{a1} = y \)) for different values of \( \Delta pK_{a} \) are depicted in Figures 1 and 2, respectively. Figure 3 shows \( pK_{a1} - pH = z \) (or \( pH - pK_{a1} = y \)) values against \( \Delta pK_{a} \) for varying \( f_{2} \) (or \( f_{0} \)) values.

The family of curves \( f_{2} = F(z, \Delta pK_{a}) \) permits the construction of the distribution diagrams of the different species of a diprotic acid. In fact: i) once \( \Delta pK_{a} \) is known, one can read directly from the diagram the value of \( f_{2} \) for each value of \( x \); ii) as \( z+y=\Delta pK_{a} \).

**Figure 1.** Molar fractions of \( f_{2} \) (or \( f_{0} \)) as a function of \( z=pK_{a1}-pH \) (or \( y=pH-pK_{a1} \)) at varying values of \( \Delta pK_{a} \).

**Figure 2.** \( \log f_{2} \) (or \( \log f_{0} \)) values as a function of \( z=pK_{a1}-pH \) (or \( y=pH-pK_{a1} \)) at varying \( \Delta pK_{a} \) values.

**Figure 3.** Values of \( z=pK_{a1}-pH \) (or \( y=pH-pK_{a1} \)) as a function of \( \Delta pK_{a} \) at varying molar fractions \( f_{2} \) (or \( f_{0} \)) values

Table 1 shows the values of \( z \) (or \( y \)) against \( \Delta pK_{a} \) for given low values of \( f_{2} \) (or \( f_{0} \)). In cases in which the contribution of the \( H_{2}R \) (or \( R \)) species is valueless, Eqns. (4) is valid, being possible in consequence to apply slope-intercept procedures to the evaluation of acidity constants from spectrophotometric measurements. The range of \( pH \) usable in the evaluation of \( pK_{a1} \) and \( pK_{a2} \) depends both on the value of \( \Delta pK_{a} \) and the restriction imposed to the value of \( f_{2} \) (and \( f_{0} \)).

Therefore, in order to evaluate the \( pK_{a1} \) by the singular straight line (logarithmic) method \([R]\) should be close to cero \((f_0 \leq 0.01)\). The interval of \( pH \) usable depends on the value of \( \Delta pK_{a} \). For well-separated acidity constants this \( pH \) range is \( pK_{a1} + 1 \) \((n=1, 2)\) because the quotient \( [H_{N_{a-1}}]/[H_{N_{a+1}}] \) \((N=2)\) would be varied between 10
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and 0.1. In the limit case [3] $K_{a1}/K_{a2}=4$, and then $\Delta pK_a=0.6$ and the range of pH usable ($f_2$ or $f_0\approx 0.01$, respectively) is ($pK_{a1}-1.0$, $pK_{a1}-0.65$) for the evaluation of the first acidity constant, and ($pK_{a2}+0.65$, $pK_{a2}+1$) for the second.

Table 1. Values of $z$ (or $y$) for different values of $\Delta pK_a$ and $f_2$ (or $f_0$)

<table>
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<tr>
<th>$\Delta pK_a$</th>
<th>0.01000</th>
<th>0.005</th>
<th>0.0040</th>
<th>0.0025</th>
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<tr>
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</tr>
<tr>
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<tr>
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<tr>
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<tr>
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<tr>
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<td>1.0421</td>
<td>0.8059</td>
<td>0.6853</td>
<td>0.5148</td>
</tr>
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</table>

**FINAL COMMENTS**

The family of curves $f_2=F(z, \Delta pK_a)$ where $f_2$ is the mole fraction of $H_2R$ species, $\Delta pK_a=pK_{a2}-pK_{a1}$, and $z=pK_{a2}-pH$ allows the construction of the normalized distribution diagrams of the $H_2R$ species. In the same way, the family of curves $f_0=F(y, \Delta pK_a)$ where $f_0$ is the mole fraction of $R$ species, and $y=pH-pK_{a1}$ allows the construction of the normalized distribution diagrams of the $R$ species. This allows us to check when the contribution of $H_2R$ or $R$ species can be neglected.

**REFERENCES**

