

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



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

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 [1] to concentration by

$$A = \frac{A_0 + A_1 \frac{(H)}{K_{a2}} + A_2 \frac{(H)^2}{K_{a2}K_{a1}}}{1 + \frac{(H)}{K_{a2}} + \frac{(H)^2}{K_{a2}K_{a1}}} \quad (3)$$

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

$$A = \frac{A_{N-n} + A_{N+1-n} \frac{(H)}{K_{an}}}{1 + \frac{(H)}{K_{an}}} \quad (4)$$

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

$$\begin{aligned} f_2 &= \frac{[H_2R]}{C_R} = \frac{[H_2R]}{[H_2R] + [HR] + [R]} = \frac{1}{1 + \frac{[HR]}{[H_2R]} + \frac{[R]}{[H_2R}}} = \\ &= \frac{1}{1 + \frac{K_{a1}}{(H)} + \frac{K_{a1}K_{a2}}{(H)^2}} = \frac{1}{1 + \frac{K_{a1}}{K_{a2}} \left(\frac{K_{a2}}{(H)} + \left(\frac{K_{a2}}{(H)} \right)^2 \right)} \\ &= \frac{1}{1 + 10^{\Delta pK_a} (10^{-z} + 10^{-2z})} \end{aligned} \quad (5)$$

Where

$$\Delta pK_a = pK_{a2} - pK_{a1} = \log \frac{K_{a1}}{K_{a2}} \quad (6)$$

and

$$z = pK_{a2} - pH = \log \frac{(H)}{K_{a2}} \quad (7)$$

The molarity fraction of R species can be indeed expressed as

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$$f_0 = \frac{[R]}{C_R} = \frac{[R]}{[R] + [HR] + [H_2R]} = \frac{1}{1 + \frac{[HR]}{[R]} + \frac{[H_2R]}{[R]}} \quad (8)$$

$$= \frac{1}{1 + \frac{(H)}{K_{a2}} + \frac{(H)^2}{K_{a2}K_{a1}}} = \frac{1}{1 + \frac{K_{a1}}{K_{a2}} \left(\frac{(H)}{K_{a1}} + \left(\frac{(H)}{K_{a1}} \right)^2 \right)}$$

$$= \frac{1}{1 + 10^{\Delta pK_a} (10^{-y} + 10^{-2y})}$$

being in this case

$$y = pH - pK_{a1} = \log \frac{K_{a1}}{(H)} \quad (9)$$

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

$$\frac{1}{f_2} - 1 = 10^{\Delta pK_a} (10^{-z} + 10^{-2z}) \quad (10)$$

which may be ordered as a second degree equation

$$10^{-2z} + 10^z - \frac{(1/f_2 - 1)}{10^{\Delta pK_a}} = 0 \quad (11)$$

Solving Eqn. (11) for fixed values of f_2 and different values of ΔpK_a we have

$$z = pK_{a2} - pH = -\log \left(\frac{-1 + \sqrt{1 + 4 \left(\frac{1}{f_2} - 1 \right) 10^{-\Delta pK_a}}}{2} \right) \quad (12)$$

Values of $pK_{a2} - pH = z$ (or $pH - pK_{a1} = y$) for different values of $\Delta pK_a = pK_{a2} - pK_{a1}$ and f_2 or $\log f_2$ (or f_0 and $\log f_0$) are depicted in Figures 1 and 2, respectively. Figure 3 shows $pK_{a2} - pH = z$ (or $pH - pK_{a1} = y$) values against ΔpK_a for varying f_2 (or f_0) values.

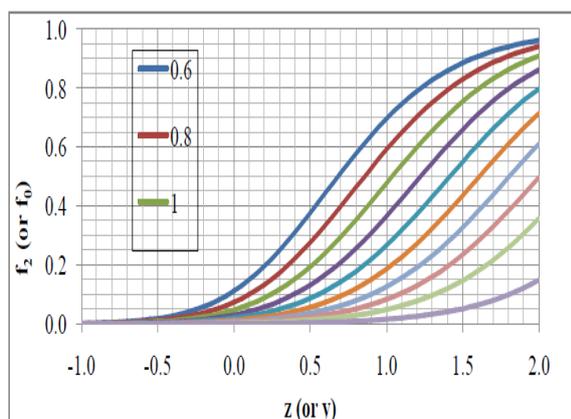


Figure1. Molar fractions of f_2 (or f_0) as a function of $z = pK_{a2} - pH$ (or $y = pH - pK_{a1}$) at varying values of ΔpK_a .

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 ΔpK_a is known, one can read directly from the diagram the value of f_2 for each value of x ; ii) as $z + y = \Delta pK_a$

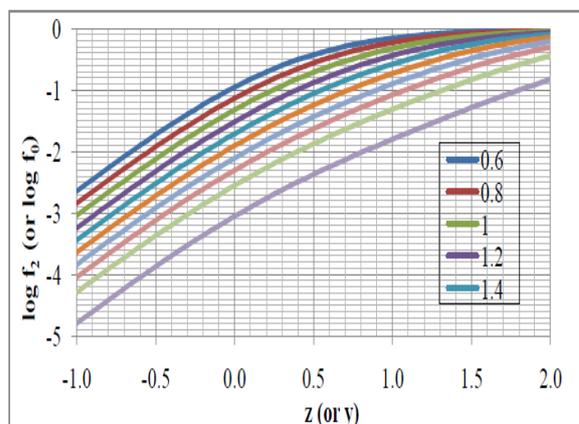


Figure2. $\log f_2$ (or $\log f_0$) values as a function of $z = pK_{a2} - pH$ (or $y = pH - pK_{a1}$) at varying ΔpK_a values.

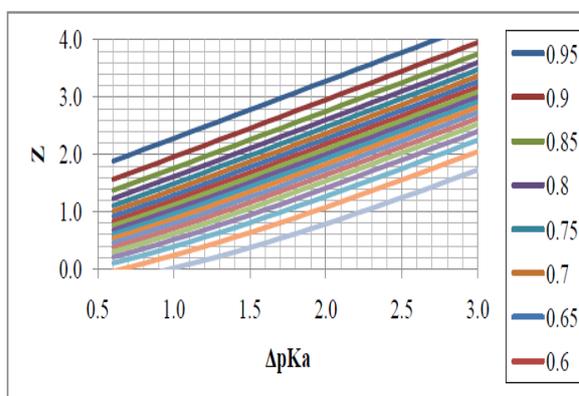


Figure3. Values of $z = pK_{a2} - pH$ (or $y = pH - pK_{a1}$) as a function of ΔpK_a at varying molar fractions f_2 (or f_0) values

Table 1 shows the values of z (or y) against ΔpK_a for given low values of f_2 (or f_0). In cases in which the contribution of the H_2R (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 ΔpK_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 zero ($f_0 \leq 0.01$). The interval of pH usable depends on the value of ΔpK_a . For well-separated acidity constants this pH range is $pK_{an} \pm 1$ ($n=1, 2$) because the quotient $[H_{N-n}R]/[H_{N+1-n}R]$ ($N=2$) would be varied between 10

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and 0.1. In the limit case [3] $K_{a1}/K_{a2}=4$, and then the evaluation of the first acidity constant, and $\Delta pK_a=0.6$ 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 ($pK_{a2}+0.65, pK_{a2}+1$) for the second.

Table 1. Values of z (or y) for different values of ΔpK_a and f_2 (or f_0)

ΔpK_a	f_2 (or f_0)			
	0.01000	0.005	0.0040	0.0025
0.6	-0.6543	-0.7964	-0.9707	-0.9788
0.8	-0.5431	-0.6881	-0.7636	-0.8732
1.0	-0.4291	-0.5777	-0.6547	-0.7661
1.2	-0.3115	-0.4646	-0.5435	-0.6573
1.4	-0.1896	-0.3481	-0.4294	-0.5461
1.6	-0.0623	-0.2276	-0.3118	-0.4322
1.8	-0.0712	-0.1021	-0.1899	-0.3147
2.0	-0.2121	0.0294	-0.0627	-0.1929
2.2	-0.3613	0.1679	0.0708	-0.0658
2.4	-0.5192	0.3144	0.2117	0.0676
2.6	-0.6858	0.4696	0.3609	0.2083
2.8	0.8605	0.6335	0.5187	0.3572
3.0	1.0421	0.8059	0.6853	0.5148

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 specie. This allows us to check when the contribution of H_2R or R species can be neglected.

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