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Playing Around with "Kaleidagraph" Program for Determination of pK_a Values of Mono, Di and Tri Basic Acids in a Physical-Organic Chemistry Laboratory

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A simple and easy laboratory protocol for the determination of the pK_a of mono, di and tri-basic weak acids is described in this paper by using arbitrarily simulated data as a function of pH. An equation compatible to Kaleidagraph program is derived and used in the program to determine the pK_a. The present protocol for the determination of the pK_a is useful in teaching chemistry experiments in a Physical-Organic Chemistry Laboratory.

Keywords: pK_a; Kaleidagraph; Acid-Base Equilibriums

Introduction

The acid-base ionization/dissociation constant, pK_a, is a measure of the tendency of a molecule or ion to keep a proton (H^+) at its ionization center(s), and is related to the ionization ability of the acid or base. pK_a is the core property of an electrolyte that defines chemical and biological behavior. In biological terms, pK_a is important in determining whether a molecule will be taken up by aqueous tissue components or lipid membranes and is related to log *p* (where *p* the partition coefficient). Water is a very polar solvent (dielectric constant ε_{20} = 80), so facile ionization will increase the likelihood of a species to be taken up into aqueous solution. If a molecule does not readily ionize, it will tend to stay in a non-polar solvent such as cyclohexane (ε_{20} = 2) or octanol (ε_{20} = 10). Separation and analytical scientists require an understanding of pK_a because it impacts the choice of techniques used to identify and isolate the compound of interest. pK_a is also closely related to the concept of pH (the acidity of the solution). Hence the knowledge of pK_a values is useful to the majority of the pharmaceutical companies worldwide. Also knowing the acidity constant value (K_a) of an acid and its associated pK_a value is important for medical students for different reasons. The first reason is that the knowledge of pK_a of a drug allows predicting the absorption, bio-reactivity and tissular accumulation as a function of the pH of the medium (Brunton, Lazo, & Parker, 2006). Another reason is that the pK_a values of the amino acids of a polypeptide chain are related to the function and structure of the protein (Stryer, 2003). In addition, the pK_a values of different chemical species will help understanding the biological systems (Devlin, 2003; Guyton, 2006).

Experimental

The software program used for the curve fitting of the simulated data versus pH was a "Kaleidagraph" from Synergy Software, Reading, PA, USA.

Results and Discussion

Theoretical Basis: The students must be familiar with the acid-base equilibriums. Population of dissociated and un-dissociated species of weak acids changes with pH.

Consider the dissociation of a mono-basic weak acid in aqueous solution,

$$HA + H_2O \underset{}{\overset{K}{\rightleftharpoons}} H_3O^+ + A^- \quad (1)$$

The equilibrium constant *K* could be written as

$$K = \frac{[H_3O^+][A^-]}{[HA][H_2O]} \quad (2)$$

or

$$K[H_2O] = \frac{[H_3O^+][A^-]}{[HA]} \quad (3)$$

or

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} \quad (4)$$

where K_a is the acid dissociation constant, $[H_3O^+]$ is the concentration hydrogen ion, $[A^-]$ is concentration of salt, and [HA] is that of un-dissociated acid. Taking the logarithms of Equation (4), we get

$$\log K_a = \log[H_3O^+] + \log[\text{salt}] - \log[\text{acid}] \quad (5)$$

or

$$pK_a - pH = \log\frac{[\text{acid}]}{[\text{salt}]} \quad (6)$$

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Equation 6 contains total of three variables, the pH which is an independent variable and [acid] and [salt] which are two different dependent variables. The two dependent variables must be transformed in to one dependent variable in terms of the simulated data points of the species preferably the anion of the weak acid, so that eventually the equation could best be transformed in to an equation of a locus with two variables. This is done as follows:

Equation (6) is rewritten as

$$(c-x)=\log\left(\frac{a-y}{y-b}\right) \tag{7}$$

Where "c" is pK_a, "x" is pH, "y" is simulated data points which change with pH, "a" and "b" are the average simulated data points of the salt at highest pH say after the pH where only salt of the week acid exits and at the lowest pH say where a species exits totally as acid. Therefore $(a - y)$ and $(y - b)$ are the concentrations of the acid and the salt in terms of one variable that is "y", the simulated data which changes as a function of pH. Therefore Equation (7) now contains eventually only two variables "x" and "y". And this could be further transformed in to the equation of a locus with two variables as follows:

Equation (7) could be written as

$$\frac{(a-y)}{(y-b)}=10^{(c-x)}$$

or

$$(a-y)=(y-b)10^{(c-x)}$$

or

$$a-y=y\cdot 10^{(c-x)}-b\cdot 10^{(c-x)}$$

or

$$y\left(1+10^{(c-x)}\right)=a+b\cdot 10^{(c-x)}$$

or

$$y=\frac{a+b\cdot 10^{(c-x)}}{1+10^{(c-x)}} \tag{8}$$

And this is converted to an equation which could be understood by Kaleidagraph software to calculate the pK_a of the weak acid and is written as:

$$y=\frac{\left(0.55+0.05\times 10^{(m_1-m_0)}\right)}{\left(1+10^{(m_1-m_0)}\right)};\ m_1=2.5 \tag{9}$$

where m_1 = pK_a and $m_0 = x$ and 0.55 is "a" which is the average of data points at highest pH and 0.05 is "b" which is that of average at lowest the pH and m1 is arbitrarily given a value of 2.5. After several iterations the Kaleidagraph program calculates the pK_a value, which came out to be 2.71 and a locus is passing through the simulated data points which is a sigmoid. In Equation 7 the quantity on right hand side is put equal to 1 so that at half neutralization the pH = pK_a. With this condition y comes out to be 0.3 using the values 0.55 and 0.05 for "a" and "b" respectively, which is the simulated data point of the species at half neutralization. Identifying the value of 0.3 on the y-axis on the graph (**Figure 1**), proceeding to the locus perpendicularly to the y-axis and from there interpolating on to x-axis gives the pH for half neutralization which is the pK_a of the acid.

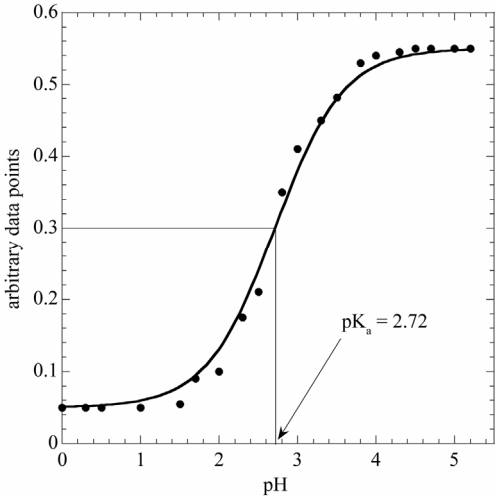

Figure 1.
pK_a of mono basic acid.

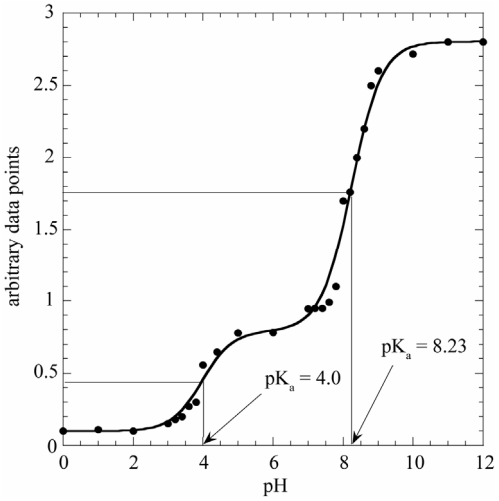

Figure 2.
pK_a of di-basic acid.

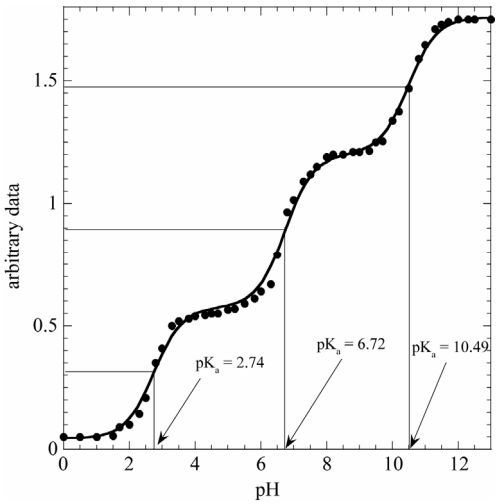

Figure 3.
pK_a of tri-basic acid.

Similarly the following equations were derived and used for di and tri-basic acids respectively:

$$y = \frac{a_1 + b_1 \cdot 10^{(c_1 - x)}}{1 + 10^{(c_1 - x)}} \cdot \frac{a_2 + b_2 \cdot 10^{(c_2 - x)}}{1 + 10^{(c_2 - x)}} \quad (10)$$

$$y = \frac{a_1 + b_1 \cdot 10^{(c_1 - x)}}{1 + 10^{(c_1 - x)}} \cdot \frac{a_2 + b_2 \cdot 10^{(c_2 - x)}}{1 + 10^{(c_2 - x)}} \frac{a_3 + b_3 \cdot 10^{(c_3 - x)}}{1 + 10^{(c_3 - x)}} \quad (11)$$

where, a_1, a_2, a_3, b_1, b_2, b_3, c_1, c_2, and c_3 have their usual significance analogous to Equation (8). Accordingly they were fit for the data and **Figures 2** and **3** were obtained.

Hence, the "Kaleidagraph" software is a "Hands On" tool for any graduate program laboratory.

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