Ionization Constant of Weak Acid

PURPOSE

The purpose of this experiment is to determine the ionization constant of an organic acid, or indicator. The techniques to be used include using a pH meter and spectrophotometry.

DISCUSSION

An acid-base indicator is a weak acid and ionizes according to the equation:

$$\mathrm{HIn}\ (\mathrm{Color\ 1}) \leftrightarrow \mathrm{H}^{+} + \mathrm{In}^{-}\,(\mathrm{Color2})$$

The ionization constant may be expresses as:

$$K = \frac{\left[\mathrm{H}^{+}\right]\left[\mathrm{In}^{-}\right]}{\left[\mathrm{HIn}\right]}$$

If we let *x* represent the fraction of indicator in the ionized form, then:

$$\frac{x}{1-x} = \frac{\left[\mathrm{In}^{-}\right]}{\left[\mathrm{HIn}\right]}$$

Thus we may use this expression for *K*.

$$K = \frac{x}{1-x}\left[\mathrm{H}^{+}\right]$$

or

$$p\mathrm{K} = p\mathrm{H} - \log\frac{x}{1-x}$$

pH can be determined using a pH meter. The ratio ${x}/{1-x}$ can be determined using a spectrophotometer and Beer's Law, which states that absorbance is proportional to concentration.

In an acid solution most of the indicator will be in the form HIn. In a basic solution nearly all of the indicator will be in the form In^-. At intermediate pH there will be some HIn and some In^-.

If we choose a wavelength where either HIn or In^- absorbs strongly the total absorbance will be made up of absorbances contributed from each form.

If we let A_a represent the absorbance in the most acid solution and A_b the absorbance in the most basic solution, then at intermediate pH the absorbance is:

$$A = (1 - x)A_a + xA_b$$

Solving for *x* we find:

$$x = \frac{A_a - A}{A - A_b}$$

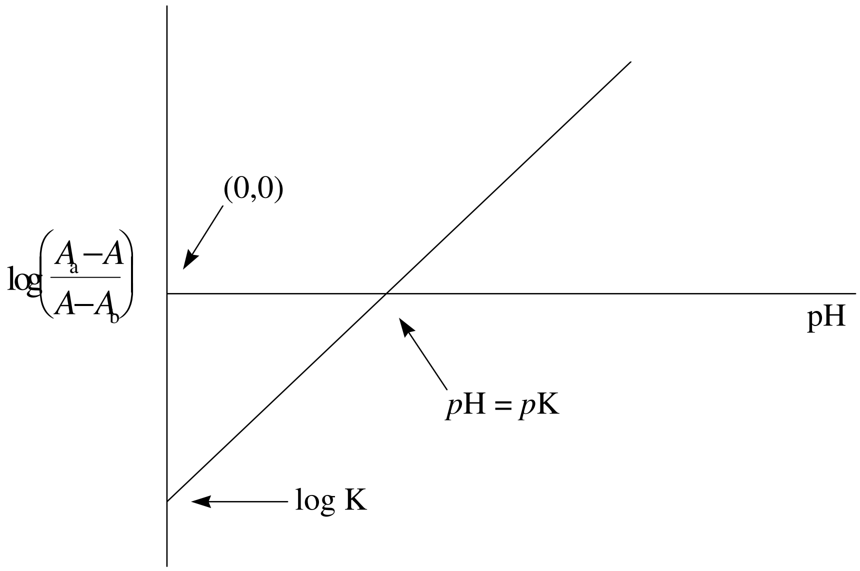
If we substitute this into the equation for pK, we obtain:

$$p\mathrm{K} = p\mathrm{H} - \log\left(\frac{A_a - A}{A - A_b}\right)$$

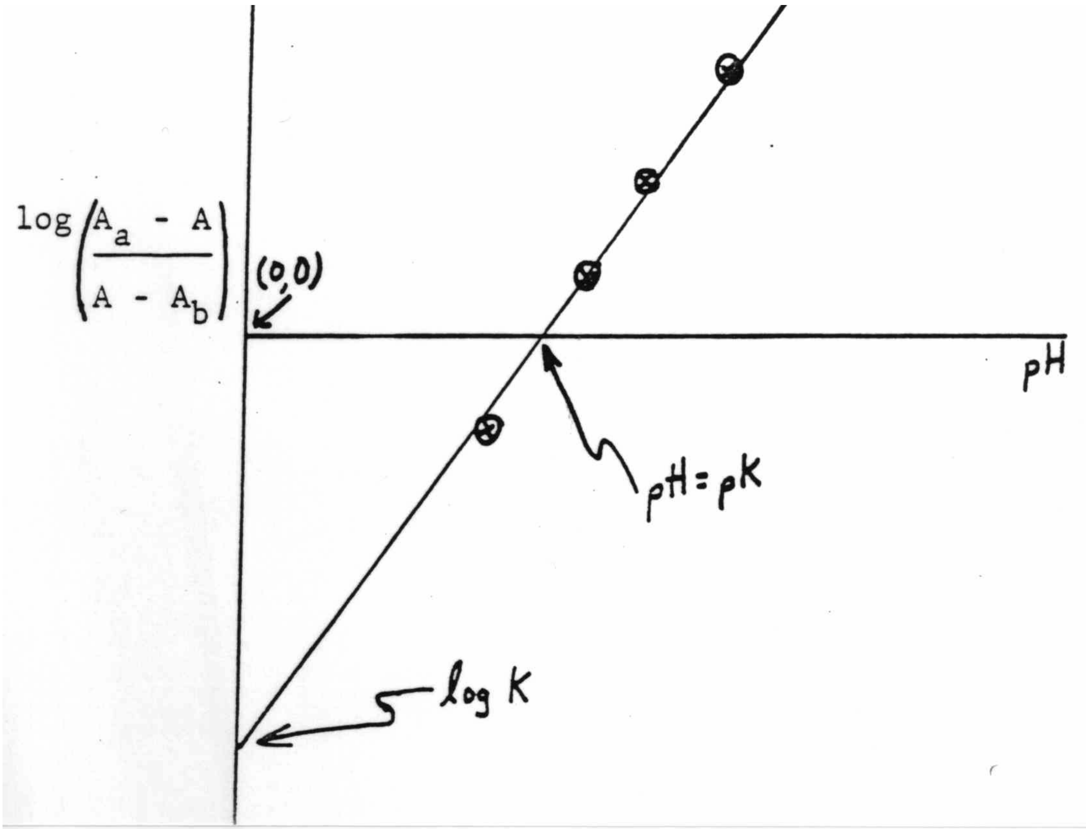
If we plot $\log\left(\frac{A_a - A}{A - A_b}\right)$ vs. pH we should obtain a straight line.

At the intercept where $\log\left(\frac{A_a - A}{A - A_b}\right)$ is zero, the pH is pK.

Also, where pH = 0, $-\log\left(\frac{A_a - A}{A - A_b}\right) = p\mathrm{K}$



$\log\left(\frac{A_a - A}{A - A_b}\right)$
(0,0)
pH
pH = pK
log K



$\log\left(\frac{A_a - A}{A - A_b}\right)$
(0,0)
pH
pH = pK
log K

EQUIPMENT AND CHEMICALS

Spectrohotometer (visible, such as Spectronic 20, Turner 350, or Coleman 124)
pH meter
1 *M* HCl, small amount
1 *M* Sodium Acetate, 50 *ml*

Indicator stock solution to be made up as follows:

(a) approx. one-half gram indicator
(b) 15 *ml* 0.1 *M* NaOH
(c) Sufficient distilled water to make one liter.

Indicator may be methyl orange, methyl red, bromphenal blue, or bromcresol green.

PROCEDURE

Add 2 *ml* indicator to 50 *ml* sodium acetate in a 250 *ml* volumetric flask. Fill to the mark with distilled water.

Find the absorbance of this solution in the range 350 - 650 *nm*. Use a recording spectrophotometer, such as Coleman 124 or P. E. Lambda 3.

Determine the pH of the solution. (Be sure the pH meter is calibrated!)

Add a small amount of 1*M* HCl to reduce pH and again determine absorbance as a function of wavelength. Measure the pH of the solution.

Repeat the procedure over the range pH 2-6 for a total of at least five absorption curves. When using Coleman 124 all runs may be made using same recorder paper.

At a wavelength corresponding to one of the absorption maxima, plot $\log\left(\frac{A_a - A}{A - A_b}\right)$ against pH. The graph should be linear. At either intercept, determine pK. Note: The number of points on your graph will be the number of runs minus 2.