

## Experiment 4

### (i) Determination of the Equivalent Weight and $pK_a$ of an Organic Acid

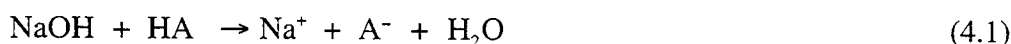
#### Discussion

This experiment is an example of a common research procedure. Chemists often use two or more analytical techniques to study the same system. These experiments can give complementary qualitative and quantitative information concerning an unknown substance.

#### I. Titration of Acids and Bases in Aqueous Solutions

The almost instantaneous reaction between acids and bases in aqueous solution produce changes in pH which one can monitor. Two techniques are useful for detecting the equivalence point: (1) colorimetry, using an acid-base color indicator - a dye which undergoes a sharp change in color in a region of pH covering the equivalence point and (2) potentiometry, using a potentiometer (pH meter) to record the sharp change at the equivalence point in the potential difference between an electrode (usually a glass electrode) and the solution whose pH is undergoing change as a result of the addition of acid or base.

For example, in the case of the titration of a weak monoprotic acid HA using sodium hydroxide solution we may write:



Applying the law of mass action to the ionization equilibrium for the weak acid in water:



we may write (in dilute solutions  $[\text{H}_2\text{O}]$  is essentially constant)

$$\frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} = K_a \quad (4.3)$$

where  $K_a$  is the acid ionization constant (constant at any given temperature). This expression is valid for all aqueous solutions containing hydronium ions ( $\text{H}_3\text{O}^+$ ),  $\text{A}^-$  ions, and the un-ionized molecules HA.

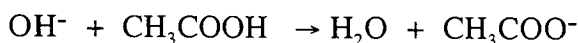
Introducing the quantities pH and  $pK_a$  defined by

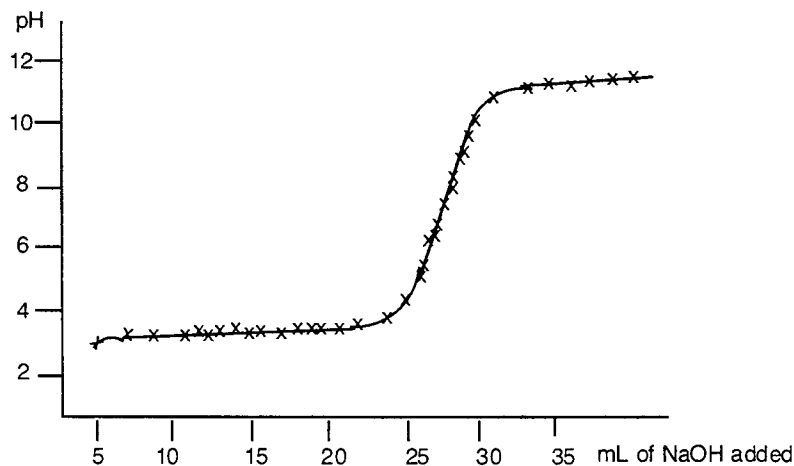
$$\text{pH} = -\log [\text{H}_3\text{O}^+] \quad \text{and} \quad \text{p}K_a = -\log K_a \quad (4.4)$$

the expression in (3) can then be rearranged to give:

$$\text{pH} = \text{p}K_a + \log \frac{[\text{A}^-]}{[\text{HA}]} \quad (4.5)$$

This is known as the Henderson-Hasselbalch equation. Let us apply this equation to the titration of a solution of the weak acid acetic acid using the strong base NaOH. As we add NaOH solution to the initial solution of acetic acid the concentration of  $[\text{H}^+]$  changes (and can be monitored by a pH meter). The overall titration reaction is:





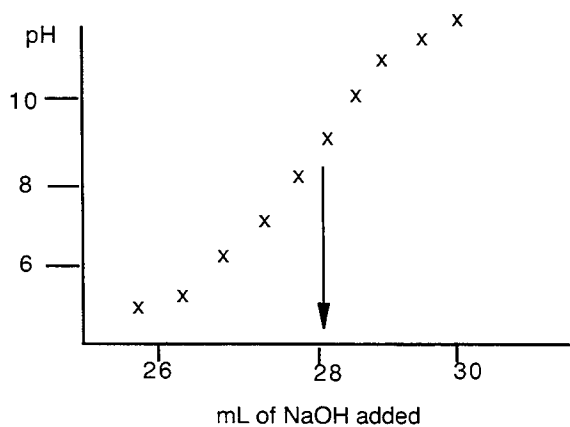
**Figure 1.** Complete titration curve

and the plot of pH versus volume sodium hydroxide added is of the form shown in Figure 1.

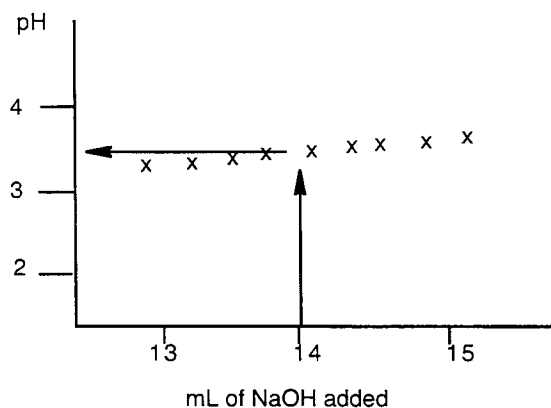
At the mid-point of the titration, when half the acetic acid has been neutralized  $[\text{CH}_3\text{COOH}] = [\text{CH}_3\text{COO}^-]$ . The Henderson-Hasselbalch equation then becomes

$$\text{pH} = \text{pK}_a \quad (4.6)$$

Thus, by carefully plotting a titration curve, it is possible to determine the equivalent weight of the acid in question (see Figure 2) as well as the  $\text{K}_a$  for the acid (see Figure 3).



**Figure 2.** To determine equivalent weight



**Figure 3.** To determine  $\text{pK}_a$

For diprotic acids ( $\text{H}_2\text{A}$ ) there may be two breaks or points of inflection, corresponding to the titration of the first and second acidic hydrogen if the two ionization constants are sufficiently different. The more prominent one represents the reaction of the second hydrogen.



$$\text{K}'_a = \frac{[\text{H}_3\text{O}^+][\text{HA}^-]}{[\text{H}_2\text{A}]} \quad (4.8)$$

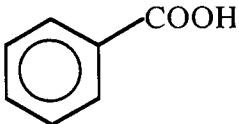
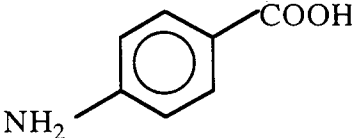
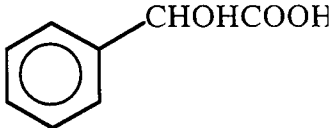
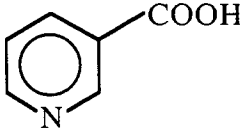
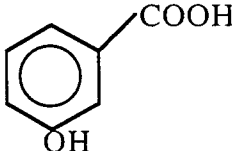


$$K_a'' = \frac{[\text{A}^{2-}][\text{H}_3\text{O}^+]}{[\text{HA}^-]} \quad (4.10)$$

### Procedure

Weigh out accurately three samples of approximately 0.1-0.2 g of the unknown acid into 250-mL beakers. DO NOT DRY. The first sample will serve for a trial run. Dissolve each sample in approximately 100 mL of water; use gentle warming on one of the hot plates on the side bench, if necessary, to achieve solution and cool back to room temperature. This process can take a few minutes. Is there something else you can do in the meantime? Check the calibration of the pH meter before you start using the pH=4.0 buffer. Titrate each of your samples using the sodium hydroxide solution that you standardized in Experiment 1; you can do one rough titration, followed by two careful titrations.

Your unknown is one of the five monoprotic organic acids listed below.

<u>Acid</u>	<u>Structure</u>	<u>Molecular Wt.</u>	<u>pK<sub>a</sub></u>
benzoic		122.1 g/mole	4.20**
p-aminobenzoic		137.2	4.79
mandelic		152.2	3.37
nicotinic		123.1	5.39
m-hydroxybenzoic		138.1	4.08

\* Values taken from CRC.

You will use the midpoint of the steepest portion of your titration curve to determine the volume at the equivalence point, and from the normality of your NaOH, calculate the equivalent weight of your acid. You can then divide the volume at the equivalence point by 2 to determine the dissociation constant of your acid. Repeat this analysis for your second sample. Use this information to identify your acid.