

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 (H_3O^+), A^- ions, and the un-ionized molecules HA.

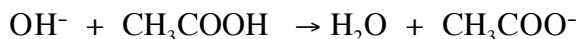
Introducing the quantities pH and pK_a defined by

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

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:



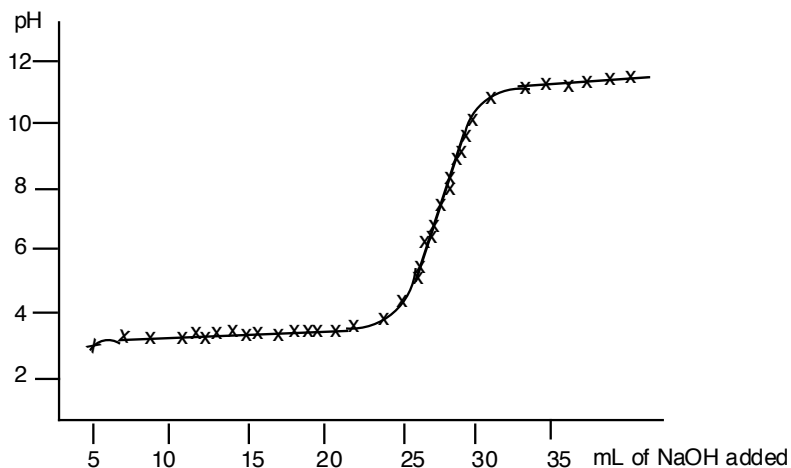


Figure 1. Complete titration curve

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 K_a for the acid (see Figure 3).

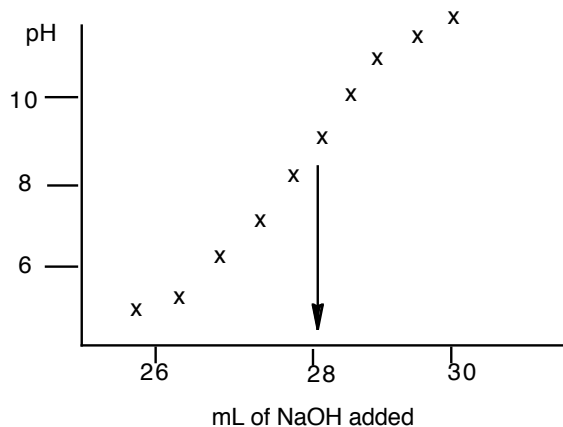


Figure 2. To determine equivalent weight

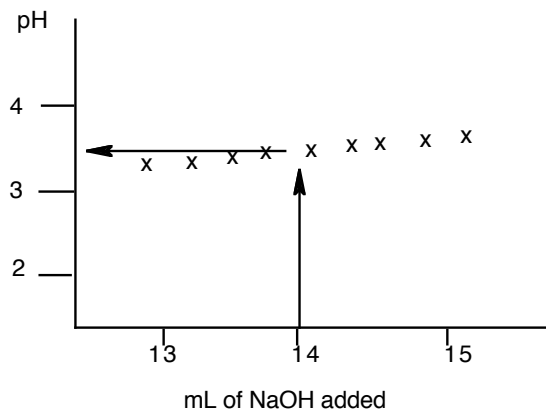
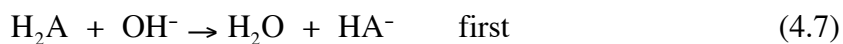


Figure 3. To determine pK_a

For diprotic acids (H_2A) 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.



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

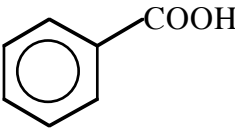
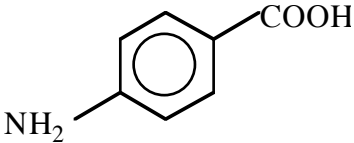
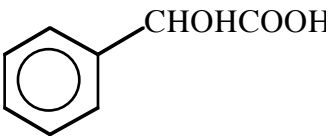
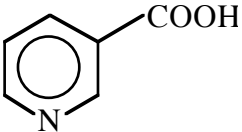
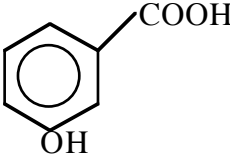


$$K_a'' = \frac{[\text{A}^{2-}][\text{H}_3\text{O}^+]}{[\text{HA}^-]} \quad (4.10)$$

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_a</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.

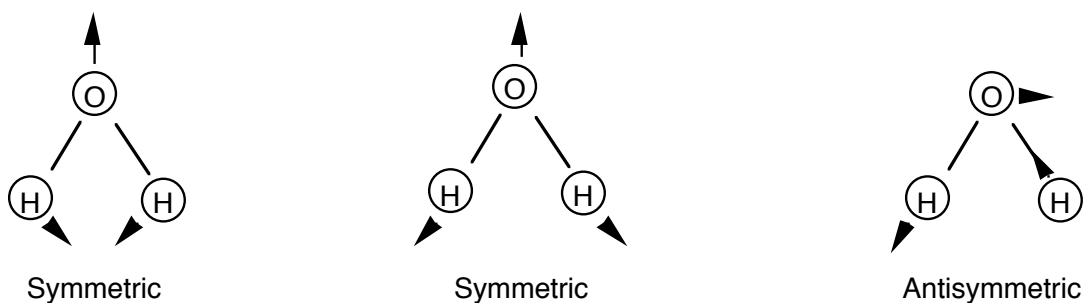
You will use the midpoint of the steepest portion of your titration curve to determine the volume at the equivalence point, and from the normality of your NaOH, calculate the equivalent weight of your acid. You can then divide the volume at the equivalence point by 2 to determine the dissociation constant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

(ii) Qualitative Identification of the Organic Acid Using Infrared Spectrometry

Discussion

If we regard a polyatomic molecule as being comprised of mass points (atoms) joined together with springs (chemical bonds), then you can imagine that the addition of energy to such a system results in a complicated vibrational motion. It is easy to show, however, that this complex motion is the result of the combination of a relatively small number of what are termed normal vibrations or normal modes. If a molecule contains n atoms, then there are $(3n - 6)$ distinct normal modes of vibration ($3n - 5$ modes for a linear molecule). Associated with each vibrational mode is a set of energy levels. Electromagnetic radiation in the infrared region of the spectrum can induce transitions between these vibrational levels which is the physical basis for an important analytical technique called infrared spectroscopy.

For example, in the case of a bent triatomic molecule such as the water molecule, the following diagram pictures the three normal modes of vibration.



	HOH bending	OH stretch	OH stretch
Vibrational Frequency*	1595 cm^{-1}	3652 cm^{-1}	3756 cm^{-1}
Absorption Wavelength*	6.28 μm	2.75 μm	2.67 μm

*1595 cm^{-1} means that there are 1595 waves per centimeter; 1 μm , micrometer, is 1.0×10^{-6} meters or 1.0×10^{-4} cm. The frequency $\tilde{\nu}$, measured in cm^{-1} , is related to the wavelength, λ : $\tilde{\nu} = 1/\lambda$.

The use of vibrational (infrared) spectroscopy to solve problems of molecular structure (bond energies, molecular shapes, etc.) is important but somewhat more complex than we wish to tackle here. A more simple use of vibrational spectra consists in verifying the identity of a compound by matching its spectrum with that of known compounds. Infrared spectra of molecules containing a large number of atoms, while being complicated, show unique “fingerprint” patterns characteristic of each molecule. (You might see whether you can pick out of the spectra absorption peaks attributable to specific groups using a table of characteristic bond-stretching frequencies.)

Most transitions between vibrational levels in molecules occur in the wavelength range 2-15 microns. The Perkin-Elmer spectrophotometer you will use enables you to cover the important parts of this region of the spectrum, and thus by comparison with the spectra available in the laboratory you should be able to confirm the identity of your unknown acid.

DETERMINATION OF INFRARED SPECTRUM

Sample preparation

Transfer a very small sample (20-30 mg.) of the acid to the agate mortar and grind it into a very fine powder. Add 2 or 3 drops of Nujol and continue grinding until the mull is smooth and homogeneous. Select a pair of NaCl plates from the desiccator. Handle them with a piece of Kimwipe to protect them from the moisture from your fingers. To clean them, put 1 or 2 drops of Nujol on each side and wipe off with Kimwipe. Transfer a portion of the mull to one salt plate with the bottom of the pestle. Put the other plate on top and press the plates together to obtain an even film. After running the IR spectrum (get help from your TA), clean the salt plates with a little methylene chloride, and return them to the desiccator.

Compare your spectrum to those your instructor provides. Note that the height of the absorption peaks will depend on the thickness of the film of mull. The concentration of the mull will affect the relative size of the "nujol peaks" with respect to the peaks from your sample. The wavelength of each peak and the relative heights of your sample peaks will be independent of sample preparation. Use this information to match reference and unknown spectra.

Experiment 4 Worksheet – Organic Acid (i & ii)

Name _____

Date of Experiment: ___/___/___

Date of Report: ___/___/___

Experimental Results

Number of Unknown _____

Titration of Unknown acid:

Give the average of your results with its standard deviation.

Molecular Weight (from your data) _____ \pm _____

pK_a (from your data) _____ \pm _____

Name of Unknown _____

Attach three graphs similar to those shown in Figs. 1, 2, and 3 for each titration. Analyze the plots graphically as demonstrated in those schematics. Mark significant points (equivalence point, half-equivalence point) on the axes. Use a small enough range for the axes to achieve the best resolution. Introduce symbols and use these in equations for your numerical analysis. Also attach your IR spectrum. Mark significant observations in your spectrum. List all your evidence (data), compare it to the literature values provided (using your experimental error to put possible deviations into perspective) and discuss how you reached your conclusion about the identity of the unknown acid (inference). If not all the evidence points in the same direction, explain why you place more weight on some results.

