EXPERIMENT 2

pH Indicators

Discussion

Acid-base indicators are weak organic acids and bases whose colors change with the pH of their environment. The general equation for their dissociation is illustrated below.

$$HIn \rightleftharpoons H^+ + In^- \qquad \textbf{(EQ 2.1)}$$

$$K_{HIn} = \frac{[H^+][In^-]}{[HIn]} \qquad \textbf{(EQ 2.2)}$$

The acid form, HIn, and the conjugate base, In^-, each have distinctive color characteristics and light absorption properties. The human eye averages the color of transmitted light and observes the acid color when the $[HIn]/[In^-]$ ratio is ten or greater and the color of the basic form when the $[In^-]/[HIn]$ is greater than or equal to 10. The intermediate color is observed when $[HIn]/[In^-]$ is close to one. Your eye can be used to approximate these ratios. A more objective method would use a spectrophotometer.

Beer's Law

A spectrophotometer is an instrument that measures the absorbance of light (usually visible and ultraviolet) when passed through an aqueous solution. This absorbance is proportional to the concentration of the absorbing species.

The relationship between the concentration of a species and the absorbance is given by Beer's Law.

$$A = \varepsilon bc \qquad \textbf{(EQ 2.3)}$$

In this equation A is the absorbance, ε is the molar absorptivity constant, b is the path length, and c is the molar concentration of absorbing species. Often % transmittance is measured rather than absorbance. The following is the relationship between A and % T.

$$A = \log\left(\frac{100}{\%T}\right) \qquad \textbf{(EQ 2.4)}$$

In the Beer relationship ε and *b* are constants, making absorbance and concentration directly proportional. Exploiting this relationship allows us to determine the K_a for an indicator knowing the pH and the ratio, $[HIn]/[In^-]$.

For phenolphthalein the only absorbing species is In^-. At pH 11 essentially all of the indicator is in the form of In^-. At pH 11,

$$A_{11} = \varepsilon b[In^-]_0 \qquad \textbf{(EQ 2.5)}$$

where $[In^-]_0$ equals the total concentration of the indicator. In the pH 9 buffer, some of the indicator is in the form HIn and some is in the form In^-. If the concentration of In^- in the buffer is called $[In^-]_9$, then in the pH 9 buffer,

$$A_9 = \varepsilon b[In^-]_9 \qquad \textbf{(EQ 2.6)}$$

Now let us consider the ratio, $[In^-]/[HIn]$ at pH 9. We know that the $[In^-]$ is proportional to the absorbance, A_9. [HIn] at this pH will take a bit more reasoning. At pH 11 we can assume that all the HIn has been converted to In^-. This means that the $[In^-]$ at pH 11 is equal to the initial $[HIn]_o$. Therefore, the difference in the absorbance at pH 11 and the absorbance at pH 9 represents the [HIn] at pH 9. This gives the following relationship.

$$[In^-]_9 = \frac{A_9}{A_{11}}[In^-]_0 \qquad \textbf{(EQ 2.7)}$$

$$[HIn] = [In^-]_0 - [In^-]_9$$

$$\frac{[In^-]}{[HIn]} = \frac{[In^-]_9}{([In^-]_0 - [In^-]_9)} = \frac{A_9}{A_{11} - A_9} \qquad \textbf{(EQ 2.8)}$$

Determination of the K_a of an Indicator

Colors of Indicators. In the first part of this experiment you will observe the color of 5 indicator solutions. Four of the indicators will be prepared for you, the fifth, a universal indicator, you will prepare from cabbage leaves.The following are the four prepared indicator solutions.

TABLE 2.1

Indicator	pH Range
congo red	2–6
methyl orange	2–6
methyl red	3–7
cresol red	5–9

You will observe the colors of each of these to determine the K_a of the indicator.

Preparation of Cabbage Juice Indicator

1. Break a leaf of red cabbage into small pieces and place them in a 250 mL beaker.
2. Add enough distilled water to cover the cabbage leaf, and heat the mixture to boiling. The indicator will be extracted from the leaves.
3. Set up a series of pH buffers of 2, 4, 6, 8, 10, and 12 by adding 3 to 4 mL of buffer solutions to separate test tubes. Add 1 mL of the extract to the 6 test tubes, and record the color of each.

Determine the K_a of the cabbage juice indicator in the same manner as the other prepared indicator solutions. That is, by inspection of their color relative to the pH of the solution.

Determination of the K_a of an Indicator Using the Spectronic 20

The method of K_a determination in the first part of this experiment is capable of yielding data that is no better than 1 significant figure in precision. In order to obtain more precise data, a spectrophotometer will be used to determine the K_a of phenolphthalein. A spectrophotometer is necessary for phenolphthalein, as there is no discernible intermediate color. This is due to the fact that the only absorbing species (in the visible spectrum) is the In^- in phenolphthalein.

Phenolphthalein Solution Preparation.

1. Obtain approximately 20 mL of phenolphthalein solution in a clean, dry test tube.
2. Using a 10.0 mL graduated cylinder, transfer 1.0 mL of the indicator solution into each of three clean, dry containers. Label each container with the pH of the buffer to be added (9, 9.5, 10, and 11).
3. Add 50.0 mL of buffer solution to each container. Each container should contain 1.0 mL of phenolphthalein, and 50.0 mL of a single buffer.
4. Rinse and fill an empty cuvette with each of the indicator solutions.

> ! Make sure that you make up the pH 11 phenolphthalein indicator solution fresh.

Finding the λ of Max Absorbance. Refer to the instructions with your instrument to make sure that it is properly calibrated before performing the next steps.

1. Set the wavelength to 380nm and place the pH 10 solution of the indicator sample into the spectrophotometer.
2. Record the absorbance of the sample from 380nm to 660nm in 15nm increments. Take three to four extra reading near the maximum absorbance to better define the peak.
3. Plot the absorbance measurements vs. the wavelength. Determine the wavelength range in which the colored species is most sensitive from the maximum absorbance peak.

Absorbance for the Indicator Solutions. Once the wavelength of maximum absorbance is obtained measure the *A* for each of the indicator solutions at this wavelength. When you are finished you should have measured the absorbance of the pH 9, 9.5, 10, and 11 solutions at the wavelength that you determined to have the highest absorbance.

Calculations and Results

1. Calculate the value of K_{HIn} and p$K_{HIn.}$

$$K_{HIn} = \frac{[H^+][In^-]}{[HIn]}. \qquad \textbf{(EQ 2.9)}$$

2. Look up the p*K* for the indicator in the *CRC* Handbook, and calculate your percent error.
3. Calculate the pH of your indicator when the ratio of In^-/HIn in solution is:
   a. 10 to 1
   b. 1 to 10
   c. 1 to 1