

THE SPECTROPHOTOMETRIC DETERMINATION OF pH

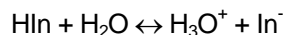
Adapted from Skoog, West, Holler and Crouch, 7th ed. Pg 767.

Background reading: Harris, 7th ed., Ch. 19. Skoog et al., Ch. 27, "Analysis of Mixtures,"

Introduction

The pH of an unknown solution can be determined by addition of an acid/base indicator of known K_a and spectrophotometric measurement of the relative concentrations of the acid and base forms of the indicator. This method has been used as a basis for continuous shipboard monitoring of seawater pH.¹

The relationship between the two forms of the indicator in an aqueous solution is described by the equilibrium



for which

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{In}^-]}{[\text{HIn}]}$$

and

$$\text{pH} = \text{p}K_a + \log \frac{[\text{In}^-]}{[\text{HIn}]}$$

Thus if $\text{p}K_a$ is known and $[\text{In}^-]/[\text{HIn}]$ is measured, the pH of the solution can be calculated.

In this exercise the indicator is bromocresol green, with $K_a = 1.6 \times 10^{-5}$. The spectra of the acid and base forms of bromocresol green overlap. The absorbance of the solution at a given wavelength is equal to the sum of the absorbances of the individual components in a mixture. For two overlapping components the absorbance must be measured at two wavelengths.

$$A_1 = \epsilon_{a1}bC_a + \epsilon_{b1}bC_b$$

$$A_2 = \epsilon_{a2}bC_a + \epsilon_{b2}bC_b$$

where the subscripts 1 and 2 indicate the two wavelengths and the subscripts a and b indicate the acid and base forms of the indicator.

To determine the amount of each form in a mixture from the measured absorbances requires knowledge of the molar absorptivity of each form. In a preliminary experiment the absorption spectra of the acid and base forms of the indicator are measured separately. The wavelength of maximum absorbance for each component is identified, and the molar absorptivities of each component at these two wavelengths are determined. The absorbance of the solution of unknown pH is measured at the same two wavelengths, and the concentrations of the two forms of the indicator in this solution are calculated by solving the two simultaneous equations describing the solution absorbances at the two wavelengths.

Procedure

Solutions

1. Bromocresol green. Dissolve 40.0 mg (to the nearest 0.1 mg) of the sodium salt of bromocresol green (720 g/mol) in water and dilute to 500 mL in a volumetric flask.

¹ R. S. Pomeroy, M. E. Baker, M. B. Denton and A. G. Dickson, *Appl. Spectrosc.* **49**, 1729 (1995).

2. HCl, 0.5 M. Dilute about 4 mL of concentrated HCl to approximately 100 mL with water. (You can prepare this and the NaOH solution in a graduated cylinder, since you do not need to know the exact concentrations. Why do you not need the exact concentrations?)
3. NaOH, 0.4 M. Dilute about 7 mL of 6 M NaOH to about 100 mL with water.

Determination of Individual Absorption Spectra

Transfer 25.00-mL aliquots of the bromocresol green indicator solution to two 100-mL volumetric flasks. To one, add 25 mL of 0.5 M HCl; to the other, add 25 mL of 0.4 M NaOH. Dilute to the mark with water and mix well.

Obtain the absorption spectra for the acid and conjugate-base forms of the indicator between 400 and 650 nm, using water as a blank. Record absorbance values at 10-nm intervals routinely and as needed to define maxima and minima. Evaluate the molar absorptivity for HIn and In⁻ at wavelengths corresponding to their absorption maxima.

Determination of pH of an Unknown Solution

Transfer 25.00 mL of the stock bromocresol green indicator to the 100-mL volumetric flask containing 50.0 mL of the unknown solution, dilute to the mark with water, and mix well. Measure the absorbance of the diluted solution at the wavelengths for which absorptivity data were calculated.

Report

1. Print a graph showing the spectra of only the acid and base forms of bromocresol green. The graph should be of a reasonable size and appropriately labeled—see the example provided in the pre-lab problem.
2. In tabular form show the wavelengths selected for measurements, the molar absorptivities of the acid and base forms of bromocresol green at these wavelengths, and the absorbances for the solution of unknown pH.
3. Calculate and report the [In⁻]/[HIn] ratio and pH for your unknown solution.