





**Figure 2:** Visible absorbance spectra of bromothymol blue at low pH (yellow, solid line) and high pH (blue, dashed line).

The equilibrium expression,  $K_c$ , for this equilibrium (Eq. 1) is:

$$K_c = \frac{[BB^-][H_3O^+]}{[HBB]} \quad (2)$$

The value of  $K_c$  should be independent of all factors except a change in temperature. At high pH, the concentration of the blue form,  $[BB^-]$ , is large and  $[HBB]$  is small, and at low pH,  $[HBB]$  is large and  $[BB^-]$  is small. In this experiment, you will be working with a solution that is green in color, so that neither  $[HBB]$  nor  $[BB^-]$  is much larger than the other.

Both the yellow and blue forms of bromothymol blue have Beer's law expressions ( $A = \epsilon b c$ ) that relate absorbance ( $A$ ) to concentration ( $c$  or  $[ ]$ , in molarity) at their respective wavelengths:

$$\text{For the yellow form, HBB: } A_{453nm} = \epsilon_{453nm}^{yellow} \cdot b \cdot [HBB] \quad (3)$$

$$\text{For the blue form, BB-: } A_{616nm} = \epsilon_{616nm}^{blue} \cdot b \cdot [BB^-] \quad (4)$$

where  $\epsilon$  is the molar absorptivity ( $L \cdot mol^{-1} \cdot cm^{-1}$ ) and  $b$  is the pathlength in cm. By knowing the molar absorptivity of each form of bromothymol blue and the path length of our cuvette it is possible to use the measured absorbance to calculate the equilibrium concentrations of HBB and BB-. However, what is typically done is to make a calibration curve or Beer's law plot at the wavelength of interest using solutions of known concentration. This plot can then be used to determine the concentration of a species in an equilibrium solution.

There are five values that you must obtain to determine  $K_c$  for bromothymol blue equilibrium reaction. These are summarized in Table 1. You will measure three of these values for a solution that is green in color, meaning that both yellow HBB and blue BB- are present in reasonable quantities (not almost zero as would be the case in either

the blue or yellow solutions at high and low pH values, respectively).

Table 1: Measured quantities

Quantity	How do we measure it?
$[\text{H}_3\text{O}^+]_{\text{eq}}$	Use a pH meter to determine the pH of a green solution and convert value to concentration.
$A_{453}$	Measure the absorbance of a green solution at 453nm
$A_{616}$	Measure the absorbance of a green solution at 616nm
[HBB]	Beer's Law plot of yellow solution (See below)
[BB <sup>-</sup> ]	Beer's Law plot of a blue solution (See below)

The concentration of the yellow form [HBB], will be determined using a Beer's law plot that is obtained for solutions that are completely yellow (low pH; ~100% HBB and negligible BB<sup>-</sup>) and the concentration of the blue form [BB<sup>-</sup>] will be determined from another Beer's law plot that is obtained from solutions that are completely blue (high pH; ~100% BB<sup>-</sup>).

### Procedure:

#### Part 1: Making Beer's Law Plots

1. Obtain enough stock solution ( $4 \times 10^{-4}$  M) of bromothymol blue to make two sets of solutions with concentrations between  $4 \times 10^{-5}$  M and  $4 \times 10^{-6}$  M bromothymol blue. One set (low pH, yellow) will be made using 0.1 M HCl as the diluent and the other set (high pH, blue) will be made using 0.1 M NaOH as the diluent. Use 10 mL volumetric flasks and the appropriate pipets to make four solutions in the correct concentration range using 0.1 M HCl to dilute to the mark. Make a second set of four solutions in 10 mL volumetric flasks in the correct concentration range using 0.1 M NaOH to dilute to the mark.
2. Measure the absorbance of each solution (yellow at 453 nm and blue at 616 nm) and create two Beer's Law plots (absorbance vs. concentration). Fit the data with a linear least squares fit, if any data does not fit the trend re-measure absorbance and remake solutions as needed. The slopes of the best-fit linear equations will be used to obtain a value for the concentrations of HBB and BB<sup>-</sup> in the equilibrium solutions below.

#### Part 2: Equilibrium measurements

1. Add 40 drops of bromothymol blue indicator (stock solution) to 10.0 mL of the pH = 7 buffer solution in a small beaker and stir to mix the indicator uniformly through the solution. The solution should appear green in color.
2. If the solution is green, you can skip this step. If the solution is blue, add 1 M HCl(aq), a drop at a time, with thorough mixing, until you obtain a shade of green. If the solution is yellow, add 1 M NaOH (aq), a drop at a time, again with thorough mixing, until you obtain a shade of green.
3. Determine the pH of the green buffer solution using the pH probe. Record the pH value in your notebook.
4. Take a portion out of the beaker and place in a cuvette to measure the absorbance at 453 and 616 nm of this green solution and record the values in your notebook. Return the portion to the sample beaker.
5. Add a few drops of either 1 M NaOH or 1 M HCl to your mixture and repeat steps 3 and 4 until you have six trials for green solutions with different pH's (possibly 3 slightly more basic and 3 slightly more acidic).
6. Use the Beer's law plots to determine the concentration of HBB and BB<sup>-</sup> for each trial. Use the relation  $[\text{H}_3\text{O}^+] = 10^{-\text{pH}}$  to determine the concentration of hydronium ion.
7. Using the values determined calculate the equilibrium constant for the bromothymol blue reaction for each of your trials at different pH. Average the values to obtain a value of  $K_c$  for bromothymol blue reaction.

### References

Atkins, P.; Jones, L. "Chemical Principles: The Quest for Insight", 6th ed.; Freeman: New York. 2013.