Using Spectrophotometry to Determine the Equilibrium Constant, K_a, and pKa of an Acid-Base Titration Indicator

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1 Introduction

Products and reactants do not stop forming when a reversible chemical reaction reaches equilibrium. Rather, the rate at which reactants create products k_f and the rate at which products create reactants k_r are equal and thus have zero net effect on each compound's concentration. Knowing the equilibrium constant K_a is useful in evaluating the ratio between k_f and k_r. This experiment attempted to use spectrophotometry and pH data of an acid-base titration indicator (bromothymol blue) to determine the equilibrium constant of the acid-base reaction and calculate its pK_a.

2 Materials and Methods

In order to safely and properly perform this experiment, our team utilized the following materials: (a) one 250 mL beaker to act as a waste container; (b) one 150 mL beaker for preparing the initial buffer solution; (c) three 50 mL beakers for preparing the individual bromothymol blue solutions of varying pH; (d) one 5.0 mL serological pipet for transferring solution from the 150 mL beaker to the 50 mL beakers; (e) four 1.0 cm path length cuvettes for analyzing each solution in the 50 mL beakers in the spectrometer; (f) two burets for transferring water, 1.0 M HCl, and 1.0 M NaOH to the 50 mL beakers; and lastly (g) one SpectroVis Plus spectrometer for collecting data.

2.1 Preparing the Spectrophotometric Samples

First, three phosphate buffer solutions were prepared containing equal concentrations of the acid-base titration indicator bromothymol blue (HBB). A 150mL beaker was filled with 50mL of phosphate buffer solution, the pH of the buffer solution was recorded, then 20 drops of a 0.04% HBB solution was added. This primary solution was then transfered to three separate 50mL beakers in 5.0mL quantities, where each beaker then recieved either 1.00 mL of 1.0 M HCl (hydrogen chloride), 1.00mL of 1.0 M NaOH (sodium hydroxide), or 1.00 mL of distilled water; these beakers were then labeled "yellow", "blue", and "green" respectively. Lastly, three cuvettes were filled with the three different solutions in the 50mL beakers resulting in a cuvette for each "yellow", "blue", and "green" solution.

2.2 Collecting the Spectrophotometric Data

The spectrometer was connected to the computer via USB, the software, Logger *Pro*, was started and the experiment file "Equilibrium" from eCampus was opened. The software was then calibrated using a cuvette filled with distilled water, making sure the clear side of the

cuvette faced the white arrow on the spectrophotometer. After calibration, three total trials were ran for the three solutions ("yellow", "blue", and "green") in the 400-700 nm wavelength range. Each cuvette was placed in the spectrometer with proper orientation (the clear side facing the white arrow) and the spectromter was allowed to run for three seconds after clicking the "Collect" button in Logger *Pro*. If a dialogue box appeared asking to delete or keep the previous trial's data, our team would click on "Store Latest Run" to keep each trial's data. Once the three different spectra was colleced on the same plot, the file was saved with a '.cmbl' extension. Lastly, the workstation was cleaned, all materials were emptied and washed, and all waste was poured into the designated waste container.

2.3 Data Analysis

Using the .cmbl file containing the three different spectra, a graph was produced containing the absorbance vs. wavelength plots for each sample. The maximum wavelength λ_{max} was recorded from the graphs for bromothymol blue (HBB) and bromothymol blue anion (BB^-). For each λ_{max} found, the absorption of each solution was recorded using the data table in the left-hand pane of Logger *pro*. Any existing isobestic points were found and recorded using the same procedure as the last step. Lastly, the absorption for each sample was found at the wavelength 616 nm using the data table in the left-hand pane of Logger *Pro*.

3 Results and Discussion

3.1 Data Summary

For section 2.2, we found the pH of the phosphate buffer solution to be 6.76. For section 2.4, we found the λ_{max} for HBB to be 433.4 nm, and the λ_{max} for BB^- to be 614.4 nm. We found an isobestic point at the coordinate (489.0, 0.0515) corresponding to an absorbance of a wavelength of 489 nm and an absorbance of 0.0515. The absorption values in the table below are based on the cleanliness of the cuvettes placed in the spectrometer. If the cuvettes were dirty when being placed in the spectrometer, it would hinder the light from passing through and the spectrometer would record a lesser value of absorbance. This would reduce the K_a value because the absorption values would be less.

	Absorbance, λ_{max} for Acidic Form, HBB (nm)	Absorbance, λ_{max} for Basic Form, BB^- (nm)
Yellow Solution	0.1193	-0.009947
Green Solution	0.1087	0.08393
Blue Solution	0.03086	0.3331

Table 1: The absorbance of each solution for the λ_{max} of both HBB and BB^-.

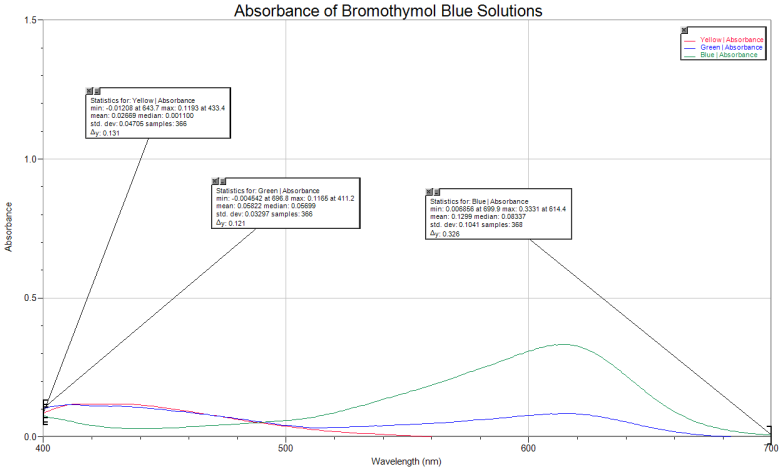

Figure 1: The absorbance vs. wavelength plots for each solution "yellow", "blue", and "green".

3.2 Data Analysis

In order to calculate the equilibrium constanant K_a and $\mathrm{p}K_a$, it is necessary to first calculate the $[\mathrm{H_3O^+}]$ of the green solution: $[\mathrm{H_3O^+}] = 10^{-\mathrm{pH}} = 10^{6.76} \approx 1.738 \cdot 10^{-7}$. This can then be used to calculate K_a: $K_a = [\mathrm{H_3O^+}]_{\mathrm{green}} \cdot \left(\frac{\mathrm{A}^g_{616}}{\mathrm{A}^B_{616} - \mathrm{A}^g_{616}}\right) = \left(1.738 \cdot 10^{-7}\right) \cdot \left(\frac{0.08373}{0.3326 - 0.08373}\right) \approx 5.862 \cdot 10^{-8}$. Next, we can find $\mathrm{p}K_a$: $\mathrm{p}K_a = -\log(K_a) = -\log(5.862 \cdot 10^{-8}) \approx 7.232$. Lastly, using literature values of $1.120 \cdot 10^{-7}$ for K_a and 7.232 for $\mathrm{p}K_a$ [Klotz et al., 2011],we can compute the percentage difference: $\%$ diff $K_a = \frac{|1.120 \cdot 10^{-7} - 5.862 \cdot 10^{-8}|}{1.120 \cdot 10^{-7}} \cdot 100 \approx 47.66\%$; $\%$ diff $\mathrm{p}K_a = \frac{|6.950 - 7.232|}{6.950} \cdot 100 \approx 4.058\%$.

This method of determing the equilibrium constant only works if one reaction is happening. If there was no isobestic point then that would indicate that bromothymol blue would be involved in another reaction, which would thus invalidate this method of determining the equilibrium constant. In addition, this method would work for other acid/base indicators such as thymol blue, cresol red, and phenolphthalein. The only difference is other acid/base indicators have different pH activation levels and that must be accounted for. For example, during acidic conditions, the concentration of phenolphthalein anions is too low for the magenta color to be observed, so this acid/base indicator could only work in alkaline conditions.

A few possible sources of errors include (a) not being precise with the amount of solution being put into beakers in section 2.2, (b) accidently contaminating one solution with another with a couple of drops, (c) not properly cleaning the cuvettes when placing them into the spectrometer, (d) not cleaning the lens on the spectrometer where the light is shot out of, and (e) having contaminates inside of the solutions such as small dirt particles or other things that would hinder the passage of light through the solution.

4 Conclusion

Computing the equilibrium constant K_a and $\mathrm{p}K_a$ of the acid-base titration indicator bromothymol blue with spectrophotometry methods was fairly successful. Our results for K_a and $\mathrm{p}K_a$ had a 47.66% and 4.058% error compared to the current literature values for these parameters.

References

[Klotz et al., 2011] Klotz, E., Doyle, R., Gross, E., and Mattson, B. (2011). The equilibrium constant for bromothymol blue: A general chemistry laboratory experiment using spectroscopy. *Journal of Chemical Education*, 88(5):637–639.