

## CHEM113L - Determination of Ka of an Indicator by Visible Spectrophotometry

An exercise involving a colorful equilibrium, spectrophotometry, Beer's Law, and the Henderson-Hasselbalch Equation all rolled into one. Who could ask for anything more?

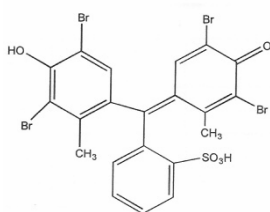
### Instrumentation:

Ocean Optics ChemUSB Spectrophotometer  
Spectronic 20 D  
Denver Scientific Basic pH meter

### Chemicals Needed:

#### 1.0 x 10<sup>-4</sup> M Sodium Salt of Bromocresol Green.

Molar Mass = 720 g/mol -  
Solution prepared by dissolving 40.0 mg of the salt in enough water to make 500 mL of solution (Provided)



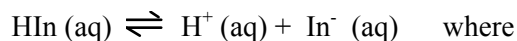
250 mL of 0.50 M NaOH (aq) - Prepared by diluting 2 M NaOH(aq) with DI H<sub>2</sub>O. (enough for group)

250 mL of 0.50 M HCl (aq) - Prepared by diluting 2 M HCl (aq) with DI H<sub>2</sub>O. (enough for group)

0.50 M NaC<sub>2</sub>H<sub>3</sub>O<sub>2</sub> (aq) - Solution prepared by dissolving enough of Anhydrous Sodium Acetate (Molar Mass = 82.03 g/mol) in sufficient water to make 250 mL of solution. (prepared by group . . . remember to weigh to the nearest 0.1 mg)

### Introduction

Acid-Base indicators are actually dyes that are weak acids or bases. Their equilibria may be represented by the following equation:



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

In this experiment, the Bromocresol green (BCG) is an indicator that shifts between a yellow color (HIn) and a blue color (In<sup>-</sup>) in the pH range of (3.8 -5.4).

The acid form (HIn) absorbs visible light near 440 nm and the base form (In<sup>-</sup>) absorbs visible light near

615 nm. These absorbances can be observed by obtaining a visible spectrum. By forcing the equilibrium to the base form, it is possible to estimate the molar absorptivity for the base form,  $\epsilon_{\text{In}^-}$ , by measuring the absorbance A and using the relationship

$$A = \epsilon_{\text{In}^-} b [\text{In}^-] \quad \text{or} \quad \epsilon_{\text{In}^-} = A / (b [\text{In}^-])$$

This can also be done with the acid form except the acid peak is observed to shift somewhat with pH.

Therefore, its concentration will be determined by difference from the known total concentration of BCG.

In this experiment a buffer (HC<sub>2</sub>H<sub>3</sub>O<sub>2</sub>/C<sub>2</sub>H<sub>3</sub>O<sub>2</sub><sup>-</sup>) will be used to fix the ratio of the ratio of In<sup>-</sup> (aq) to HIn (aq). From a pH measurement, [H<sup>+</sup>] will be determined.

$$[\text{H}^+] = 10^{-\text{pH}}$$

Then, from the visible spectrum of the buffered solution (at a given wavelength,  $\lambda$ ),

$$[\text{In}^-] = A / \epsilon_{\text{In}^-} b$$

and

$$[\text{HIn}] = [\text{BCG}](0.25)^* - [\text{In}^-]$$

These values are then substituted into the expression for K<sub>a</sub> and the value for K<sub>a</sub> may be calculated. This may then be compared with the theoretical value, 1.6 x 10<sup>-5</sup> (at 25° C).

\* For comparison the BCG concentration is the diluted value (i.e. 25 mL diluted to 100 mL.)

## Procedure

### A. Preparation of Solutions

Prepare all solutions (**except blanks**) in 100 mL volumetric flasks according to the **Table 1 and Table 2. Blanks can be prepared in 250 mL beakers.**

For the preparation of all solutions, deliver BCG using a buret. All other solutions (HCl, NaOH, and NaC<sub>2</sub>H<sub>3</sub>O<sub>2</sub>) may be delivered using labeled 50-mL graduated cylinders or burets. In all cases, dilute to final volume with distilled water.

### B. pH Measurement

1. Standardize your pH meter with pH 4 and pH 7 buffers following the manual provided. Pour about 25 mL each of solutions (not the blanks) into separate 50 mL beakers.
2. Rinse the pH probe with distilled water, pat dry with a “Kimwipe” tissue, and place it into a beaker. Swirl the solution gently and then wait for the pH reading to stabilize. Record the reading.
3. Repeat this procedure with the remaining solutions. Remember to rinse and dry the probe between beakers.
4. Calculate [H<sup>+</sup>] for each solution using the equation,

$$\text{pH} = -\log [\text{H}^+]$$

### C. Visible Spectrum Measurements

*(These instructions may change depending on what spectrophotometers are used.)*

1. Use a scanning spectrophotometer, scan standard solutions for the acid (#7) and base (#4) forms of the indicator using appropriate blanks. If this instrument is not available, your instructor will

provide these spectra. (see **Figure 1.**) Use these spectra to set wavelengths ( $\lambda_{\text{max}}$ ) for future measurements. . Make a baseline measurement with two empty cuvetts in the sample holders.

2. Set Spectronic 20 to a wavelength of 615 nm (unless another wavelength is provided). Set the 0% and 100% transmittances following instructions on the instrument and using appropriate blanks.

- a. Measure absorbances for standards #2, #3, #4, and #5 using a single blank. These data will be used for making a **standard curve plot.**

- b. Measure the absorbances of the buffered indicators #8, #10, and #12. Make sure you use the appropriate blanks for each for each buffered indicator.

## Calculations

Perform calculations as described in the

introduction. 1. Calculate the [H<sup>+</sup>] for data collected in Part B.

2. Plot Absorbance vs Dilute Molarity of BCG for data in Part C (2a). The slope of the fitted line will be the molar absorptivity ( $\epsilon_{\text{in}}$ ) for the base form of the indicator.

3. Calculate values of [HIn] and [In<sup>-</sup>] for each of the three buffered indicators.

4. Calculate the average K<sub>a</sub> for the BCG indicator, its standard deviation, and its percent difference. compared with the theoretical value,  $1.6 \times 10^{-5}$  (at 25° C).

5. Turn in Data Page, Standard Curve Plot, and Calculations page.

**For Further Information consult:** General Chemistry Text on Acid Base Equilibrium and Buff

**Table 1 – Standard BCG Solutions Preparation**

Solution <sup>a</sup>	0.5 M HCl (mL)	0.5 M NaOH (mL)	BCG (mL)	Diluted Molarity of BCG	A, measured
<b>Base Form<sup>b</sup></b>					
#1 Base Blank	0	25.0	0		
#2 Base Std 1	0	25.0	10.0		
#3 Base Std 2	0	25.0	15.0		
#4 Base Std 3	0	25.0	25.0		
#5 Base Std 4	0	25.0	40.0		
<b>Acid Form<sup>c</sup></b>					
#6 Acid Blank	25.0	0	0		
#7 Acid Std.	25.0	0	25.0		

<sup>a</sup>These solutions are diluted to a total volume of 100 mL

<sup>b</sup>Base Form of Indicator (Set spectrophotometer to  $\lambda_{\max}$  =615 nm)

<sup>c</sup>Acid Form of Indicator (Set spectrophotometer to  $\lambda_{\max}$  =440 nm), This will not be used for calculations.

**Table 2 – Buffered BCG Solutions**

Solution <sup>a</sup>	0.5 M HCl (mL)	0.5 M NaOH (mL)	BCG (mL)	0.5 M NaC <sub>2</sub> H <sub>3</sub> O <sub>2</sub> (mL)	A <sup>b</sup> ,	pH
#8 Buffer 1	10.0	0	25.0	30.0		
#9 Buf 1 blank	10.0	0	0	30.0	xx	xx
#10 Buffer 2	15.0	0	25.0	30.0		
#11 Buf 2 blank	15.0	0	0	30.0	xx	xx
#12 Buffer3	20.0	0	25.0	30.0		
#13 Buf 3 blank	20.0	0	0	30.0	xx	xx

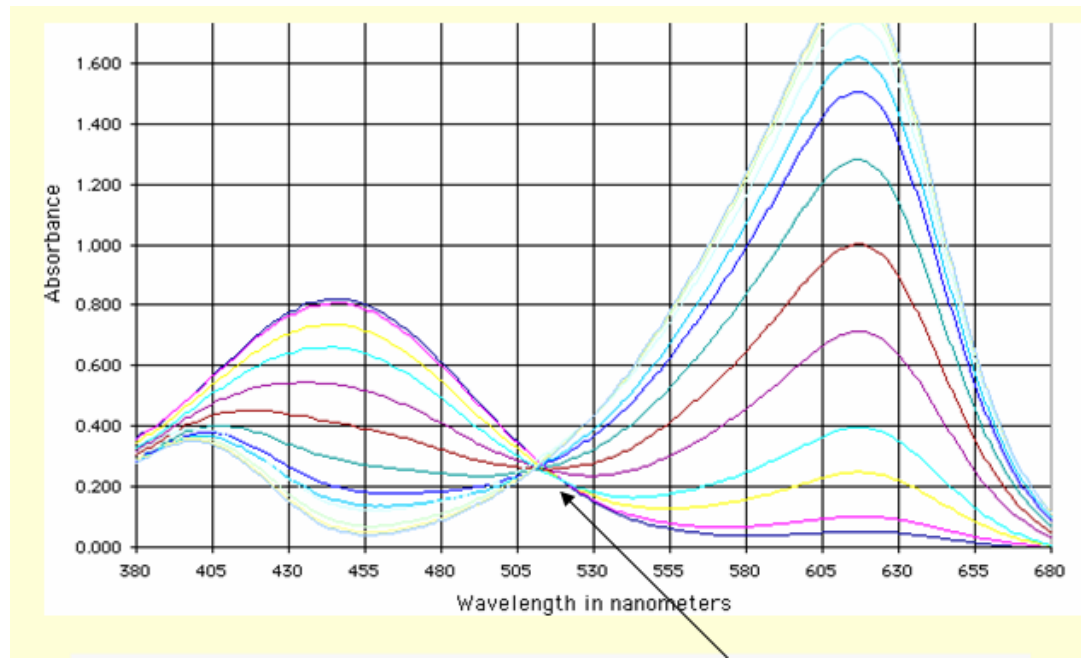
<sup>a</sup>These solutions are diluted to a total volume of 100 mL

<sup>b</sup>Measured for Base Form of Indicator (Set spectrophotometer to  $\lambda_{\max}$  =615 nm)

Other Notes

- All Buffered solutions contain the same “Total BCG Concentration”
- Buffered Indicator Solutions #8 , #10, and #12 have a mixture of the acid and base forms of your indicator. Buffered Blank Solutions #9, #11, and #13 are blanks for each of the buffered indicator, with no indicator present.

**Figure 1 - Visible Spectra of BCG at various pH's**



Disposal: All solutions can go down the drain with large amounts of water.

Safety: Wash hands after handling all chemicals.

Notes:

# CHEM113L - Determination of $K_a$ of an Indicator by Visible Spectrophotometry

Name: \_\_\_\_\_

## Concentrations of Provided solutions (from label):

Bromcresol Green (BCG) \_\_\_\_\_

### Observations:

Solution	pH	A
#2 Base Std1		
#3 Base Std2		
#4 Base Std3		
#5 Base Std4		
#6 Acid Std		
#8 Buffer #1		
#10 Buffer #2		
#12 Buffer #3		

### Calculations:

Solution	Diluted Molarity BCG	A (from above)
#2 Base Std1		
#3 Base Std2		
#4 Base Std3		
#5 Base Std4		

Variable from equation of line

From plot ( $y = mx + b$ )

$m =$  \_\_\_\_\_

$b =$  \_\_\_\_\_

Solution	$[H^+]$	$[HIn]$	$[In]$	$K_a$
Buffer #1				
Buffer #2				
Buffer #3				
Average	XXXXXXXX	XXXXXXX	XXXXXXX	