Experiment 7C

DETERMINATION OF THE K_A OF A SLIGHTLY SOLUBLE WEAK ACID[A]

MATERIALS: Spectronic 20, cuvettes, buffer solutions, 1.0 M HCl, 1.0 M NaOH, 10 mL pipet, 1 mL pipet, bromcresol green, pH meter, three large test tubes.

DISCUSSION: In Experiment 18 (Acid-Base Titration Curves) the K_a of a very soluble weak acid or base was determined by means of a titration curve. However, if the acid or base is only slightly soluble such a procedure becomes impractical. Fortunately, there are other techniques which can be used. One such technique involves a spectrophotometric method and is the one which we shall use in this experiment. Since the spectrophotometers in our laboratory are limited to investigating compounds that absorb in the visible range of the spectrum, we will need to use a weak acid which is colored. We have chosen bromcresol green, a very sparingly soluble weak acid,[B] the protonated and anionic forms of which both absorb strongly in the visible region of the spectrum[1].

Let us now consider the equilibrium

$$\underset{\text{yellow}}{HB} + H_2O \rightleftarrows H_3O^+ + \underset{\text{blue-green}}{B^-} \qquad (1)$$

Notice that the colors of the two forms are different. One form or the other will predominate depending on the concentration of H_3O^+. We can determine the equilibrium constant for this reaction (K_a of bromcresol green) by making appropriate spectral measurements followed by an application of Beer's Law[2] to this data.

When two light-absorbing species are present, as indicated in equation (1), the absorbencies of the two species are additive and the total absorbance, A, is given by

$$A = e_{HB}[HB] + e_{B-}[B^-] \qquad (2)$$

where [HB] and [B^-] are the respective concentrations of protonated and anion forms and ϵ_{HB} and ϵ_B the respective molar absorptivities. If the pH of the solution is adjusted over a wide range, then the following three equations apply. (<u>NOTE</u>: [HB] + [B^-] = [bromcresol green]$_{total}$)

$$A_{mix} = \text{absorbance of the mixture} = e_{HB}[HB] + e_{B^-}[B^-] \qquad (3)$$

$$A_{alk} = \text{absorbance of alkaline form} = e_{B^-}\left([HB] + [B^-]\right) \qquad (4)$$

$$A_{acid} = \text{absorbance of acid form} = e_{HB}\left([HB] + [B^-]\right) \qquad (5)$$

---

[1] Note: Most organic acids, which appear colorless, actually absorb in the U.V. region and thus with a slightly more sophisticated spectrophotometer, this technique becomes applicable to a large number of compounds.

[2] See Appendix I.

Now if the total concentration of bromocresol green remains constant, by referring to *Figure 1* we have

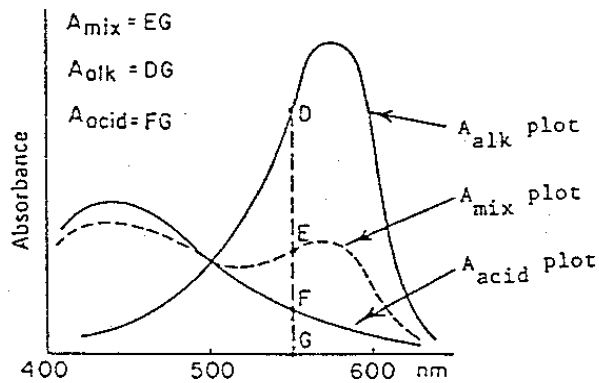

Figure 1

$$DE = A_{alk} - A_{mix}$$

$$DE = \left[e_{B^-}\left([HB]+[B^-]\right)\right] - \left[e_{HB}[HB] + e_{B^-}[B^-]\right]$$

Therefore,

$$DE = \left[\left(e_{B-} - e_{HB}\right)[HB]\right] \tag{6}$$

$$EF = A_{mix} - A_{acid}$$

$$EF = \left(e_{HB}[HB] + e_{B^-}[B^-]\right) - \left[e_{HB}\left([HB]+[B^{-]}\right)\right]$$

Therefore,

$$EF = \left(e_{B^-} - e_{HB}\right)\left[B^-\right] \tag{7}$$

Combining equations (6) and (7):

$$\frac{EF}{DE} = \frac{\left(e_{B^-} - e_{HB}\right)\left[B^-\right]}{\left(e_{B^-} - e_{HB}\right)[HB]} = \frac{\left[B^-\right]}{[HB]} \tag{8}$$

Thus, by obtaining your own data and constructing a plot similar to Figure 1, you can determine the concentration <u>ratio</u> of $[B^-]/[HB]$ in your solution.

Since

$$K_a = \frac{[H_3O^+][B^-]}{[HB]} \tag{9}$$

by measuring the pH of your mixture solution and using <u>your</u> Figure 1 plot, you can determine the $[B^-]/[HB]$ ratio for a given $[H_3O^+]$ and thus the K_a of bromocresol green.

PROCEDURE: Prepare three separate solutions, in the three large test tubes provided, by placing *exactly* 1.0 mL of bromcresol green solution in each test tube. Then add *exactly* 10 mL of 1.0 M HCl to the first test tube, 1.0 M NaOH to the second test tube and a pH 4. buffer to the third test tube. Obtain an absorption spectrum for each of these three solutions using a distilled water blank as reference. The spectrophotometer 0% and 100% transmittance should be standardized **at each wavelength** and the percent transmittance measured at 10 nm intervals between wavelengths of 400 nm and 650nm. Finally, determine the exact pH of the buffer-bromcresol green solution, using a properly calibrated pH meter. Record all data on the data sheet provided.

Determine the actual pH of the solution containing pH 4. buffer using the pH meter. Record the value in the Data Section.

CALCULATIONS
Experiment 7c

Since the calculations are repetitive, a spreadsheet, such as QUATTRO PRO, is highly recommended.

First enter your experimental wavelengths and percent transmittances in titled columns in your spreadsheet. Convert percent transmittance to absorbance for each of your three solutions (consult Appendix I), and put these values in three additional titled columns. At each experimental wavelength, determine the values of the line segments EF and DE in Figure 1.

From the measured value of pH for the buffer-bromcresol green solution, calculate $[H_3O^+]$ in this solution. Show both pH and $[H_3O^+]$ values obtained in your spreadsheet. Use this $[H_3O^+]$ value and equations 8 and 9 to determine a value of K_a at each experimental wavelength. Scan the K_a values in your spreadsheet, and (after giving due consideration to question 2 on page 6) record in your spreadsheet what you consider to be the best value of K_a.

Finally, graph absorbance as a function of wavelength for each of the three solutions. Use one set of axes (as in Figure 1) but different data point symbols. Annotate your graph with an explanatory key, using Quattro PRO. Be sure the graph is titled and the axes properly labeled. Hand in spreadsheet and graph as part of your lab report.

NOTES:

A. See: Ramett, Journal of Chemical Education. 40, 252 (1963)

B. Actually bromcresol green is both a strong and weak acid. Figure 2 gives the structure of the compound.

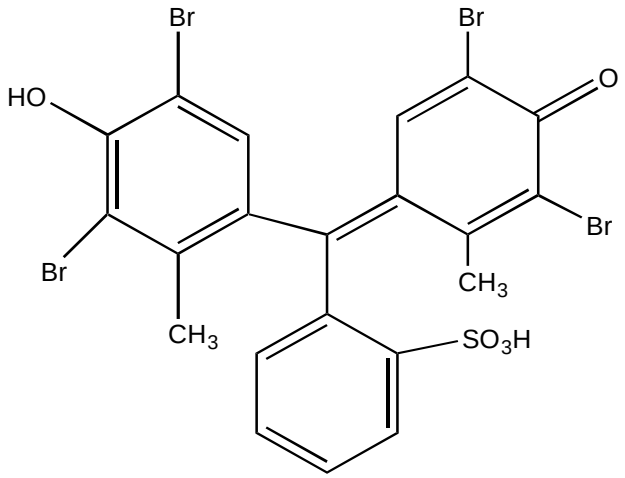

Figure 2

The $-SO_3H$ group is a strong acid group and its proton is completely ionized in aqueous solutions. This group is present in the molecule to give it some water solubility. The -OH group (phenolic) contains the weak acid proton. Its K_a is what we are measuring.

Name _____ Section _____

Partner _____ Date _____

DATA SECTION
Experiment 7C

pH of buffer-bromcresol green solution _____

Wavelength (nm)	Acid (Yellow) %T	Buffer (Green) %T	Base (blue) %T
400			
410			
420			
430			
440			
450			
460			
470			
480			
490			
500			
510			
520			
530			
540			
550			
560			
570			
580			
590			
600			
610			
620			
630			
640			
650			

QUESTIONS
Experiment 7c

1. Would bromocresol green make a good acid-base indicator? Why? In what pH range would it be effective? Why?

2. If you were dropping only one perpendicular (DG) on your graph, and determining a single value of K_a (vice the averaging technique actually employed), indicate what wavelength you would select and the reasons(s) why. (Hint: Consider Figure 1. Are K_a values determined at wavelengths close to the isosbestic point suspect[3]? Why?)

[3] The isosbestic point is the point in *Figure 1* where all three solutions have the same absorbance.