

## Experiment 12

### Kinetics of the Decolorization of Crystal Violet by Sodium Hydroxide

#### Introduction

Crystal violet is a brightly colored organic compound which is used as a dye. One common use of the dye is in purple ditto masters used to make the purple copies often distributed to students (in the old days!). Crystal violet is also used as a pH indicator because its color depends upon the acidity of the solution. Its deep purple color is removed by reaction with hydroxide ion. In the experiment the reaction order with respect to each reactant and the value of the rate constant,  $k$ , will be determined.

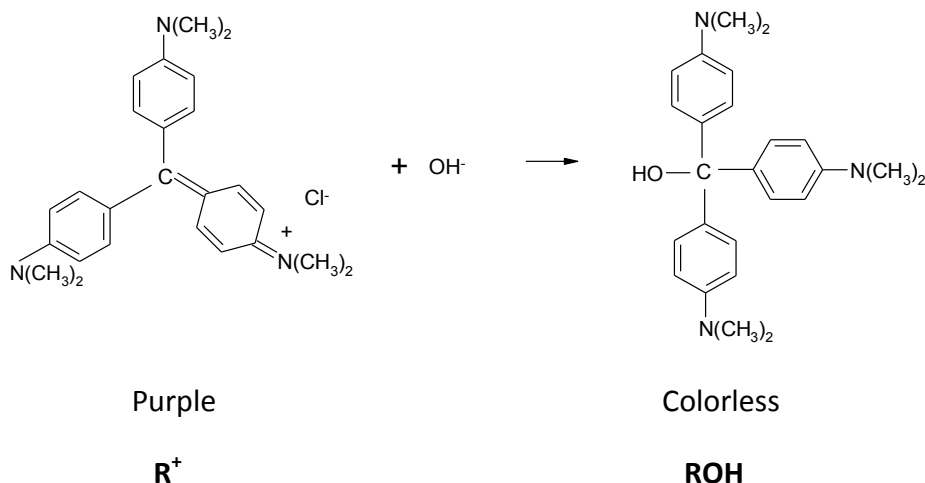
#### Safety

Wear safety goggles at all times. Sodium hydroxide solutions are caustic. In the event of contact with your skin or eyes, wash the affected area immediately with lots of water. If necessary, seek qualified medical assistance. To clean up, crystal violet and sodium hydroxide solutions can go down the drain with running water. Use acetone from a squirt bottle to remove the crystal violet stain from the volumetric flasks and the other glassware [**Do Not rinse the cuvettes with acetone** - try rinsing with water only – few drops of the NaOH solution will help here]. Keep rinsing until the violet color is gone.

When finished, please turn OFF the source by choosing **(deselecting) Spectrometer/Enable Strobe**. Your TA may take off points if you do not turn off the source!!!!

#### Concepts (To be discussed during lab)

The equation shown below shows the Lewis structures of the compounds involved in the reaction.



Because the reaction occurs at a relatively slow rate, we can use the spectrometer to monitor its progress. From the absorbance values, we can determine the concentration of crystal violet at various times after the reaction has begun.

The rate law for the decolorization reaction has the form:

$$\text{Rate.} = -\Delta[\text{R}^+]/\Delta t = k[\text{R}^+]^n[\text{OH}^-]^m \quad \text{(Eqn. 1)}$$

where

$k$  is the rate constant of the reaction at a particular temperature

$n$  is the order of the reaction with respect to crystal violet

$m$  is the order of the reaction with respect to sodium hydroxide

The reaction order with respect to  $\text{R}^+$  will be determined first. The concentration of sodium hydroxide in the reaction mixture used is much greater than that of the crystal violet. It is so much larger, that even after all of the crystal violet has reacted, the sodium hydroxide concentration has not changed very much.

$$[\text{OH}^-]_o \gg [\text{R}^+]_o$$

$$[\text{OH}^-]_{\text{initial}} \approx [\text{OH}^-]_{\text{final}} \approx \text{constant}$$

The rate law may be rewritten

$$\text{Rate} = k' [\text{R}^+]^n \quad \text{(Eqn. 2)}$$

where  $k'$  is a new constant having the value

$$k' = k [\text{OH}^-]^m \quad \text{(Eqn. 3)}$$

To determine the reaction order, the concentration of the crystal violet is followed over time. The Spectrometer is used to follow the concentration of the crystal violet as it changes during the reaction. The reaction order with respect to crystal violet can then be determined graphically using integrated forms of the rate law for a zero, first or second order reaction.

If the order of the reaction with respect to crystal violet is zero ( $n = 0$ ) then

$$[\text{R}^+]_t = -k't + [\text{R}^+]_o$$

Plotting  $[\text{R}^+]_t$  vs.  $t$  yields a straight line with a slope =  $-k'$ .

If the order of the reaction with respect to crystal violet is one ( $n = 1$ ) then

$$\ln [\text{R}^+]_t = -k't + \ln[\text{R}^+]_o$$

Plotting  $\ln[R^+]_t$  vs.  $t$  yields a straight line with a slope =  $-k'$ .

If the order of the reaction with respect to crystal violet is two ( $n = 2$ ) then

$$1/[R^+]_t = k't + 1/[R^+]_o$$

Plotting  $1/[R^+]_t$  vs.  $t$  yields a straight line with a slope =  $+k'$ .

Once the order of the reaction is determined, the slope of the line is calculated to obtain  $k'$ . Recall  $k'$  is not a true constant. Its value depends on the initial hydroxide ion concentration, according to Eq. 3. We will measure  $k'$  at two different hydroxide ion concentrations,  $[OH^-]_A$  and  $[OH^-]_B$ . We can then write:

$$k'_A = k[OH^-]_A^m \quad \text{(Eqn. 4)}$$

$$k'_B = k[OH^-]_B^m.$$

Because  $k'_A$ ,  $k'_B$ ,  $[OH^-]_A$ , and  $[OH^-]_B$  are known values and  $k$  and  $m$  are constants, we have a system of two equations and two unknowns. This can easily be solved to give the values of  $k$  and  $m$ .

(Hint: It helps to use logarithms)

$$\ln k'_A = \ln k + m \ln[OH^-]_A \quad \text{(Eqn. 5)}$$

$$\ln k'_B = \ln k + m \ln[OH^-]_B$$

subtract B from A

$$\ln(k'_A/k'_B) = m \ln([OH^-]_A/[OH^-]_B)$$

$$m = \frac{\ln(k'_A/k'_B)}{\ln([OH^-]_A/[OH^-]_B)}$$

The true rate constant,  $k$ , can be calculated by substituting values into either equation 4 or equation 5.

### **Materials**

#### From the Storeroom

5 - 100 mL volumetric flasks

1 - 10 mL Mohr pipet

1 - pipet pump

#### From Your Locker

50 mL beaker

100 mL beaker

medicine dropper

5- cuvettes


test tube rack

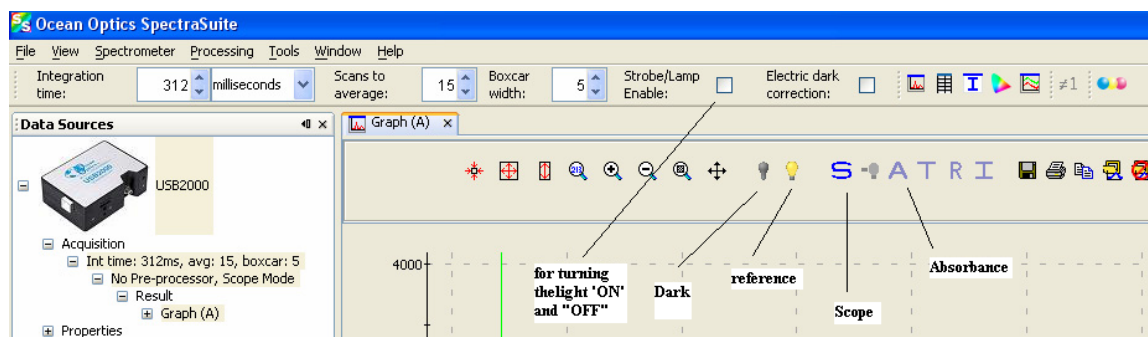
pH meter





## Procedure

### Part I: Crystal Violet Calibration Curve

Follow the steps below to take an absorbance measurement using SpectraSuite (please refer to the image below):

Connect the spectrometer to the laptop. Double click on the SpectraSuite icon .





Place SpectraSuite in Scope mode by clicking the Scope (  ) icon in the toolbar. Take and store a dark spectrum by clicking  (shaded or grey lamp icon). Check (select) the **Strobe/Lamp Enable** box to turn on the source. If required adjust the integration time, scans to average and boxcar width values on the software to get a good reference spectrum. Take and store the reference spectrum by clicking  (yellow lamp icon). Ensure that the *entire signal is on scale*. The intensity of the reference signal's peak differs depending on the device being used. (Seek help from your TA if necessary). Choose absorbance mode by clicking on  . The spectrometer is now ready to measure the spectrum of your samples in absorbance mode.

Obtain about 60 mL of  $1.00 \times 10^{-4}$  M crystal violet stock solution in a 100 mL beaker. Caution!! Crystal violet will stain hands and clothing! Wear vinyl gloves! Fill each volumetric flask about halfway with deionized water. Label the flasks with numbers 1-5 using a grease pencil. Use a Mohr pipet to add the volume of stock solution indicated to each flask. Dilute to the 100 mL mark with deionized water. Cover with parafilm and invert to mix the solution.

Volumetric flask #	mL crystal violet stock solution
1	2.00
2	4.00

3	6.00
4	8.00
5	10.00

Pour solution #1 into the cuvette and insert it into the sample holder of the spectrometer appropriately i.e. with the light from the spectrometer passing through the clear transparent part of the cuvette and click . You may have to click on the autoscale  icon to see the spectrum. (If you have a problem in getting a good spectrum, please check with your TA). Record the absorbance value at  $\lambda_{\max}$  ( $\approx 590$  nm) and repeat steps for the other solutions (#2 to #5).

### Part I – Analysis

1. Calculate the concentration of each crystal violet standard solution. Show a sample calculation of the concentration for flask 4.
2. Prepare a plot of absorbance (y-axis) vs. concentration of crystal violet (x- axis).
3. Calculate the slope and y-intercept of the best straight line (manually or electronically).

### Part II : Kinetics Measurements

Using a clean pipet, transfer 8.00-10.00 mL of  $1.00 \times 10^{-4}$  M crystal violet stock solution into a clean 100 mL volumetric flask. Add about 75 mL of deionized water. Obtain about 30 mL of 0.1 M sodium hydroxide solution in a 50 mL beaker. Measure the pH of your sodium hydroxide solution. Clean the pipet with deionized water and then rinse it with a small amount of the sodium hydroxide solution in the beaker. **Working as quickly as possible**, pipet 10.00 mL of the 0.1 M sodium hydroxide solution into the volumetric flask. Fill the flask to the mark with deionized water. Cover and invert 2 or 3 times to mix. Pour some of the solution into a cuvette, and place it into the sample chamber of the Spectrometer. Take an initial ( $t=0$ ) absorbance reading at  $\lambda_{\max}$  ( $\approx 590$  nm ) and record on the results. Pour the rest of the solution in the flask to a 250 mL beaker and measure the initial pH. Continue taking absorbance and pH readings every 60 seconds for 10 minutes. Repeat steps, but this time pipetting 5.00 mL of 0.1 M sodium hydroxide solution into the volumetric flask instead of 10.00 mL.

## **Part II – Analysis**

1. Calculate the concentration of crystal violet  $[R^+]$ , remaining at each time interval from the equation for the straight line of the calibration curve,  $y = mx + b$  obtained in Part I. Calculate  $\ln[R^+]$  and  $1/[R^+]$  for each time interval.
2. Make plots of  $[R^+]$  vs. time,  $\ln[R^+]$  vs. time, and  $1/[R^+]$  vs. time for the kinetic data obtained when you used 10.00 mL of 0.1 M sodium hydroxide ( RUN A). Draw the best-fit line (or curve) through the data points. Which plot is the most linear?
3. What is the reaction order with respect to crystal violet concentration?
4. For the plotting variable ( $[R^+]$ ,  $\ln[R^+]$ , or  $1/[R^+]$ ) that gives the best straight line when plotted against time in Question #2, prepare the same plot for the kinetic data obtained when you used 5.00 mL of sodium hydroxide ( RUN B). Use the same piece of graph paper as the linear plot for RUN A i.e. the 10.00 mL sodium hydroxide data. Use different symbols for the runs - for example  $\bullet$  for the RUN A data and  $\square$  for the RUN B data.
5. Draw the best straight line through the RUN B data points of the plot in Question 4. Calculate the slope of both the RUN A and RUN B lines.
6. Calculate  $k'_A$  and  $k'_B$ ,
7. Calculate  $[OH^-]_A$  and  $[OH^-]_B$ . Show your work.
8. Set up the simultaneous equations described in the introduction. Solve for  $m$ , the order in  $[OH^-]$ , and  $k$ , the rate constant. (Round the exponent to the nearest whole number.) Show your work.
9. Write the reaction rate law showing all values ( $k$ ,  $n$  and  $m$ ).
10. What is the overall reaction order?
11. Calculate the reaction rates for RUN A and for RUN B. How do the two rates compare?

## **Post Laboratory Questions**

- 1) a) A solution is prepared by mixing 25.0 mLs of  $1.00 \times 10^{-4}$  M crystal violet solution with 25.0 mLs of 0.120 M sodium hydroxide solution and diluted to a final volume of 100.0 mLs. Determine the limiting reagent.  
  
b) After the reaction has gone to completion, calculate the concentration of all species in the reaction.

- c) How does the concentration of sodium hydroxide change over the course of the reaction?
- d) Explain your answer in question 1c in terms of the initial concentrations of reactants.