Rate Law Determination of the Crystal Violet Reaction

In this experiment, you will observe the reaction between crystal violet and sodium hydroxide. One objective is to study the relationship between concentration of crystal violet and the time elapsed during the reaction. The equation for the reaction is shown here.

\[
\begin{align*}
\text{C}^+ \text{N(CH}_3\text{)}_2 & + \text{OH}^- \rightarrow \text{CVOH} \text{ (aq)} \\
\text{N(CH}_3\text{)}_2 & \text{N(CH}_3\text{)}_2
\end{align*}
\]

A simplified (and less intimidating!) version of the equation is:

\[
CV^+ (aq) + OH^- (aq) \rightarrow CVOH (aq)
\]

(crystal violet) (hydroxide)

The rate law for this reaction is in the form: \(\text{rate} = k[CV^+]^m[OH^-]^n\), where \(k\) is the rate constant for the reaction, \(m\) is the order with respect to crystal violet \((CV^+)^m\), and \(n\) is the order with respect to the hydroxide ion. Because the hydroxide ion concentration is more than 1000 times as large as the concentration of crystal violet, \([OH^-]\) will not change appreciably during this experiment. Thus, you will find the order with respect to crystal violet \((m)\), but not the order with respect to hydroxide \((n)\).

As the reaction proceeds, a violet-colored reactant will be slowly changing to a colorless product. You will measure the color change with a Vernier Colorimeter or a Vernier Spectrometer. The crystal violet solution used in this experiment has a violet color, of course, thus the Colorimeter users will be instructed to use the 565 nm (green) LED. Spectrometer users will determine an appropriate wavelength based on the absorbance spectrum of the solution. We will assume that absorbance is proportional to the concentration of crystal violet (Beer’s law). Absorbance will be used in place of concentration in plotting the following three graphs:

- Absorbance vs. time: A linear plot indicates a zero order reaction \((k = -\text{slope})\).
- \(\ln\) Absorbance vs. time: A linear plot indicates a first order reaction \((k = -\text{slope})\).
- \(1/\text{Absorbance}\) vs. time: A linear plot indicates a second order reaction \((k = \text{slope})\).

Once the order with respect to crystal violet has been determined, you will also be finding the rate constant, \(k\), and the half-life for this reaction.
OBJECTIVES

In this experiment, you will

- Observe the reaction between crystal violet and sodium hydroxide.
- Monitor the absorbance of the crystal violet solution with time.
- Graph Absorbance vs. time, ln Absorbance vs. time, and 1/Absorbance vs. time.
- Determine the order of the reaction.
- Determine the rate constant, $k$, and the half-life for this reaction.

MATERIALS

<table>
<thead>
<tr>
<th>Item</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>computer</td>
<td>0.10 M sodium hydroxide, NaOH, solution</td>
</tr>
<tr>
<td>Vernier computer interface*</td>
<td>2.5 × 10$^{-5}$ M crystal violet solution</td>
</tr>
<tr>
<td>Logger Pro</td>
<td>ice</td>
</tr>
<tr>
<td>Colorimeter or Spectrometer</td>
<td>two 10 mL graduated cylinders</td>
</tr>
<tr>
<td>Temperature Probe or thermometer</td>
<td>two 100 mL beakers</td>
</tr>
<tr>
<td>5 plastic cuvettes</td>
<td>50 mL beaker</td>
</tr>
<tr>
<td>1 liter beaker</td>
<td>watch with a second hand</td>
</tr>
</tbody>
</table>

*No interface is required if using a Spectrometer

PROCEDURE

Both Colorimeter and Spectrometer Users

1. Obtain and wear goggles.

2. Use a 10 mL graduated cylinder to obtain 10.0 mL of 0.10 M NaOH solution. **CAUTION:** Sodium hydroxide solution is caustic. Avoid spilling it on your skin or clothing. Use another 10 mL graduated cylinder to obtain 10.0 mL of 2.5 × 10$^{-5}$ M crystal violet solution. **CAUTION:** Crystal violet is a biological stain. Avoid spilling it on your skin or clothing.

3. Prepare a blank by filling a cuvette 3/4 full with distilled water. To correctly use cuvettes, remember:

   - Wipe the outside of each cuvette with a lint-free tissue.
   - Handle cuvettes only by the top edge of the ribbed sides.
   - Dislodge any bubbles by gently tapping the cuvette on a hard surface.
   - Always position the cuvette so the light passes through the clear sides.

Spectrometer Users Only (Colorimeter users proceed to the Colorimeter section)

4. Use a USB cable to connect the Spectrometer to your computer. Choose New from the File menu.

5. To calibrate the Spectrometer, place the blank cuvette into the cuvette slot of the Spectrometer, choose Calibrate ► Spectrometer from the Experiment menu. The calibration dialog box will display the message: “Waiting 90 seconds for lamp to warm up.” After 90 seconds, the message will change to “Warmup complete.” Click OK.
6. Determine the optimum wavelength for examining the crystal violet solution and set up the mode of data collection.
   a. Empty the blank cuvette and rinse it twice with small amounts of 2.5 × 10^{-5} M crystal violet solution. Fill the cuvette about 3/4 full with the crystal violet solution and place it in the spectrometer.
   b. Click [Collect]. A full spectrum graph of the solution will be displayed. Note that one area of the graph contains a peak absorbance. Click [Stop] to complete the analysis.
   c. To save your graph of absorbance vs. wavelength, select Store Latest Run from the Experiment menu.
   d. To set up the data collection mode and select a wavelength for analysis, click on the Configure Spectrometer Data Collection icon, on the toolbar.
   e. Click Abs vs. Time (under the Set Collection Mode). The wavelength of maximum absorbance (λ_max) will be selected. Click OK]. Remove the cuvette from the spectrometer and dispose of the crystal violet solution as directed. Save the cuvette for Step 7.
   f. Proceed to Step 7.

Colorimeter Users Only

4. Connect the Colorimeter to the computer interface. Prepare the computer for data collection by opening the file “30b Rate Crystal Violet” from the Advanced Chemistry with Vernier folder of LoggerPro.

5. Open the Colorimeter lid, insert the blank, and close the lid.

6. To calibrate the Colorimeter, press the < or > button on the Colorimeter to select the wavelength of 565 nm (Green). Press the CAL button until the red LED begins to flash and then release the CAL button. When the LED stops flashing, the calibration is complete. Remove the cuvette from the Colorimeter and save it for Step 7.

Both Colorimeter and Spectrometer Users

7. Do this quickly! To initiate the reaction, simultaneously pour the 10 mL portions of crystal violet and sodium hydroxide solutions into a 250 mL beaker and stir the reaction mixture with a stirring rod. Empty the water from the cuvette. Rinse the cuvette twice with ~1 mL amounts of the reaction mixture, fill it 3/4 full, and place it in the device (Colorimeter or Spectrometer). Close the lid on the Colorimeter. Click [Collect].

8. Absorbance data will be collected for three minutes. Discard the beaker and cuvette contents as directed by your instructor.

9. Analyze the data graphically to decide if the reaction is zero, first, or second order with respect to crystal violet.
   - Zero Order: If the current graph of absorbance vs. time is linear, the reaction is zero order.
   - First Order: To see if the reaction is first order, it is necessary to plot a graph of the natural logarithm (ln) of absorbance vs. time. If this plot is linear, the reaction is first order.
   - Second Order: To see if the reaction is second order, plot a graph of the reciprocal of absorbance vs. time. If this plot is linear, the reaction is second order.
10. Follow these directions to create a calculated column, ln Absorbance, and then plot a graph of ln Absorbance vs. time:
   a. Choose New Calculated Column from the Data menu.
   b. Enter “ln Absorbance” as the Name, and leave the unit blank.
   c. Enter the correct formula for the column into the Equation edit box by choosing “ln” from the Function list, and selecting “Absorbance” from the Variables list. Click Done.
   d. Click on the y-axis label. Choose ln Absorbance. A graph of ln absorbance vs. time should now be displayed. Change the scale of the graph, if necessary.
   e. Click the Linear Regression button, Graph 1. Write down the slope value in your data table as the rate constant, \( k \).
   f. Close the Linear Regression box by clicking the X in the corner of the box.

11. Follow these directions to create a calculated column, 1/Absorbance, and then plot a graph of 1/Absorbance vs. time:
   a. Choose New Calculated Column from the Data menu.
   b. Enter “1/Absorbance” as the Name, “1/Abs” as the Short Name, and leave the unit blank.
   c. Enter the correct formula for the column into the Equation edit box. To do this, type in “1” and “/”. Then select “Absorbance” from the Variables list. In the Equation edit box, you should now see displayed: 1/“Absorbance”. Click Done.
   d. Click on the y-axis label. Choose 1/Absorbance and uncheck any other boxes. A graph of 1/Absorbance vs. time should now be displayed. To see if the relationship is linear, click the Linear Fit button, Graph 1.

12. Print a copy of the graph in Steps 9-11 that was linear (Absorbance, ln Absorbance, or 1/Absorbance vs. time).
   a. Click the vertical-axis label of the graph.
   b. Of “Absorbance”, “ln Absorbance”, or “1/Absorbance”, choose only the data that gave a linear plot. Click OK.
   c. Print a copy of the graph. Enter your name(s) and the number of copies of the graph you want printed. Note: Be sure the linear regression curve is displayed on the graph, as well as the regression statistics box.

13. Print a copy of the table. Enter your name(s) and the number of copies of the table.

14. Optional: Print a copy of the two non-linear graphs.
PROCESSING THE DATA

1. Was the reaction zero, first, or second order, with respect to the concentration of crystal violet? Explain.

2. Calculate the rate constant, \( k \), using the slope of the linear regression line for your linear curve (\( k = -\text{slope} \) for zero and first order and \( k = \text{slope} \) for second order). Be sure to include correct units for the rate constant. Note: This constant is sometimes referred to as the \textit{pseudo rate constant}, because it does not take into account the effect of the other reactant, OH⁻.

3. Write the correct rate law expression for the reaction, in terms of crystal violet (omit OH⁻).

4. Using the printed data table, estimate the half-life of the reaction; select two points, one with an absorbance value that is about half of the other absorbance value. The \textit{time} it takes the absorbance (or concentration) to be halved is known the \textit{half-life} for the reaction. (As an alternative, you may choose to calculate the half-life from the rate constant, \( k \), using the appropriate concentration-time formula.)
Vernier Lab Safety Instructions Disclaimer

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