Study of Electrode Mechanism by Cyclic Voltammetry

Please note that this experiment is NOT in the P. Chem lab in Mergenthaler. Students doing this experiment should go directly to NCB 228.

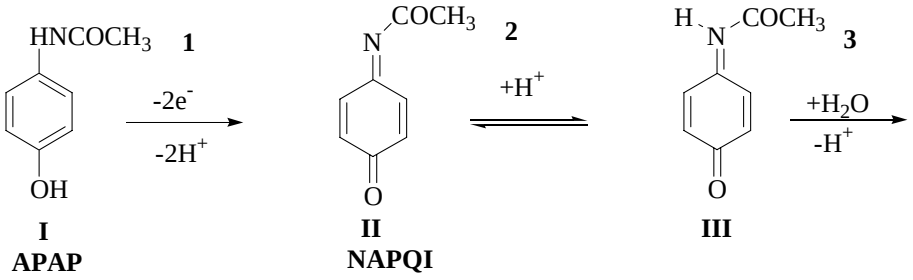
Purpose

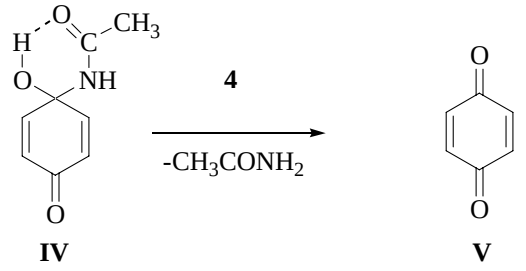
1). Use cyclic voltammetry to determine the concentration of acetaminophen in a children's pain relief elixir.
2). Study the mechanism of acetaminophen oxidation, which involves both pH dependent and coupled chemical reactions.

Theory

Cyclic voltammetry (CV) is considered to be the versatile electroanalytical technique currently available. It is generally the first experiment to be run when dealing with any electrochemically active species. The basic theory behind CV is to measure the current response at an electrode surface to a specific range of potentials in an unstirred solution. Please read the attached article from the Journal of Chemical Education on Cyclic Voltammetry by Kissenger and Heineman for a more complete understanding of this technique.

This laboratory exercise studies the oxidation mechanism of 4-acetminophenol, otherwise known as acetaminophen, the active ingredient in Tylenol. It will be refered to as APAP from this point. The oxidation mechanism of APAP is as follows:





This process can be electrochemically "mapped out" by varying the pH of the supporting electrolyte and the scan rate in cyclic voltammetry.

At a pH of 6, APAP is oxidized in a quick pH dependent step involving the loss of two electrons and two protons to give N-acetyl-*p*-quinoneimine (NAPQI) as shown in step 1 of the above mechanism. At a pH greater than or equal to pH 6.0 NAPQI (II) exists in its stable, unprotonated form.

Under more acidic conditions (ex. pH 2.2), NAPQI is readily protonated to give species III, which is a less stable, but electrochemically active species. Species III then rapidly yields a hydrated species (IV), which is electrochemically inactive in the examined potentials.

Finally, under increasingly more acidic conditions the hydrated species (IV) converts to benzoquinone (V). Only under extremely acidic conditions will the reduction of benzoquinone observed with cyclic voltammetry.

PRE LAB QUESTIONS:

To make sure that you understand the experiment, please answer following questions in the prelab. **These questions must be completed before lab and handed in to the TA before beginning any experiments.**

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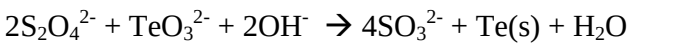
1. Does O_2 need to be accounted for in this experiment? Why or why not?
2. Why is cyclic voltammetry an unstirred voltammetry technique?
3. Why is a triangular waveform used as the excitation waveform in cyclic voltammetry rather than a square waveform?
4. Identify the oxidizing and reducing agents and write a balanced half cell reaction for each:



$$2S_2O_4^{2-} + TeO_3^{2-} + 2OH^- \rightarrow 4SO_3^{2-} + Te(s) + H_2O$$

Materials

- Pine AFCB1 Bipotentiostat
- Three electrode Cell
- Glassy carbon electrode
- Platinum auxiliary electrode
- Ag/AgCl reference electrode
- pH 2.2 and pH 6.0 McIlvaine Buffer with 0.5 M ionic strength
- 1.8 M sulfuric acid
- 0.070 M 4-acetamidophenol in perchloric acid (stock solution)
- Children's Tylenol Elixir

Experimental Procedure

Note: All glassware used for electrochemistry experiments must be as clean as possible. The solvents and reagents used to prepare solutions should be pure. Additionally, ultrapure (MilliQ) water is required for all dilutions and final rinsing of glassware.

A. Solution Preparation

The TA will prepare the stock solution of 4-acetamidophenol (APAP), both McIlvaine buffer solutions, and the sulfuric acid. The children's Tylenol will also be provided.

The following solutions must be prepared before beginning the cyclic voltammetry experiments:

1. 10 mL of 3mM APAP in each supporting electrolyte (pH 2.2 and 6.0 buffer solutions and sulfuric acid)
2. Four additional APAP solutions in pH 2.2 buffer spanning the range of 0.10 to 5.0 mM.

B. Cyclic Voltammograms

Several cyclic voltammograms are obtained with solutions of varying concentrations, supporting electrolytes. The five standard solutions in the pH 2.2 buffer will be run with a scan rate of 40 mV/sec. The 3-3mM solutions with different supporting electrolytes (pH 2.2 buffer, pH 6.0 buffer, and 1.8M sulfuric acid) will each be run at scan rates of 40 mV/sec and 250 mV/sec. General instructions for cyclic voltammetry are as follows:

1. Equip a clean electrochemical cell with a Ag/AgCl reference electrode, a platinum auxiliary electrode, and a glassy carbon reference electrode.
2. Fill the cell with the solution to be analyzed (lowest concentration first), making sure that all three electrodes are immersed in solution.
3. Before making electrical connections between the cell and the potentiostat, assure that the instrument is in DUMMY mode. This is accomplished by adjusting the controls on the INSTRUMENT STATUS panel to match the settings in Figure 1. At this point, the electric connections between the potentiostat and the cell may be made.
4. Select the **Analog Sweep Voltammetry** option from the **Experiment** menu and adjust the experiment settings so that they match Figure 2. (One exception to the parameters in this figure is the scan rate. The scan rate should either be set to 40 or 250 mV/sec as discussed above.)
5. Click the PERFORM button to initiate the experiment. A fairly prominent anodic wave should appear during the sweep from 0 mV to +1000 mV. On the return sweep, no cathodic wave should be apparent. Figure 3 shows a cyclic voltammogram typical of APAP. Note that as displayed by the software, positive potentials are plotted to the right and anodic currents are plotted to the top of the graph, which is the opposite of conventional electrochemical techniques.
6. After acquiring a satisfactory voltammogram, save it under C/pchem/yourgroupnumber and print. Note that if more than one cyclic voltammogram of the same solution is required slightly move the working electrode to agitate the solution and replenish the analyte.
7. Plot the voltammogram as a current versus time graph by choosing the **I1 vs. t** option from the **Plot** menu. Then, use the **Peak Height Tool** found in the **Toolbox** menu to measure the height of the anodic peak as shown in Figure 4. Record peak height.

8. Acquire similar cyclic voltammograms for the remaining standard solutions and different supporting electrolyte solutions in order of increasing concentration APAP solutions. Adjust the sweep rate as necessary.
9. Finally acquire a voltammogram of the *Elixir Test Solution* using the same experimental parameters as for the standard solutions.

C. Data Analysis

Using the anodic peak currents for the series of standard solutions, construct a calibration curve of peak current versus concentration. Perform a least squares analysis on the data to find the equation of best straight line which fits the data. Be sure to include error analysis with the least squares fit.

Using the equation of the calibration curve line, compute the concentration of acetaminophen (APAP) in the elixir. Remember to take into account any dilution of the original elixir during solution preparation process (TA will inform of any dilutions). Report the acetaminophen concentration in grams per liter using three significant figures. Convert the acetaminophen concentration listed on the manufacturer's label to units of grams per liter using three significant figures. Compare your calculated value to the label value.

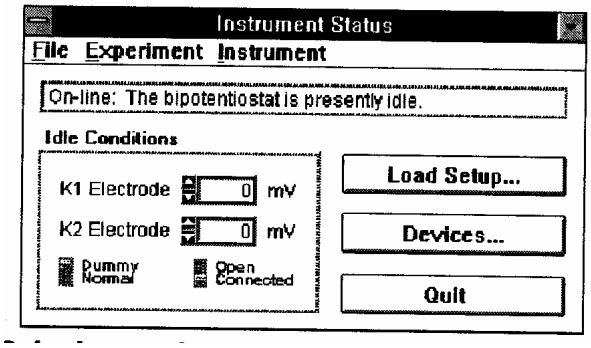


Figure 1: Initial Instrument Status Panel Settings

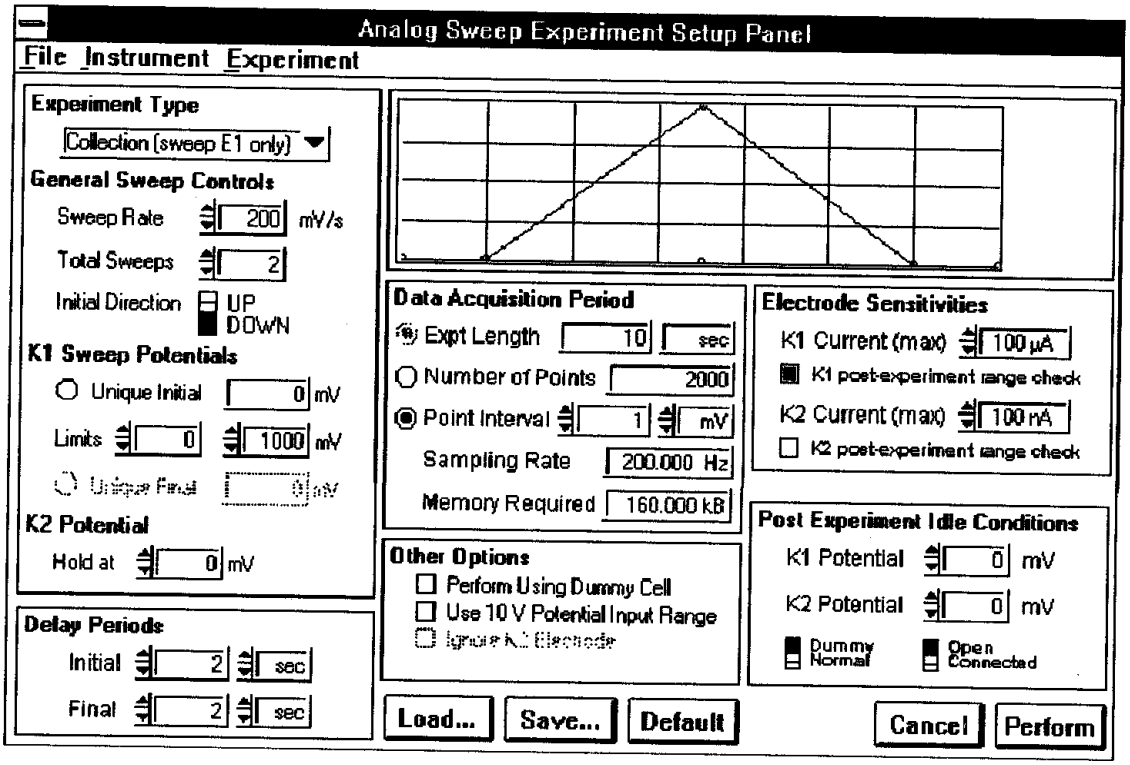


Figure 2: Experimental Setup for APAP Voltammetry

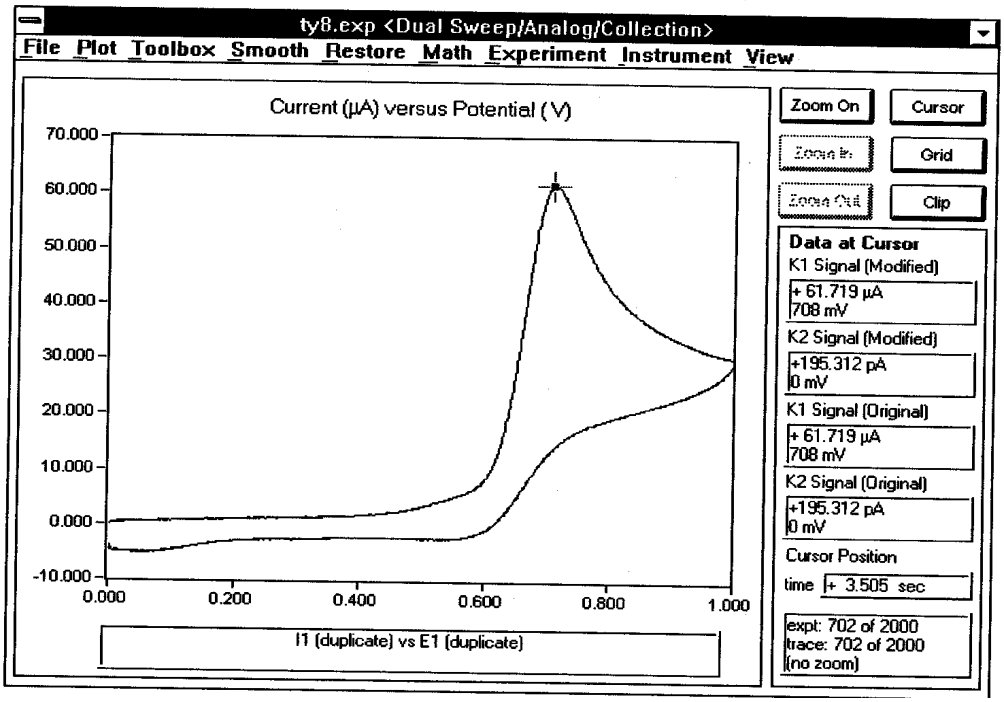


Figure 3: Typical APAP Voltammogram

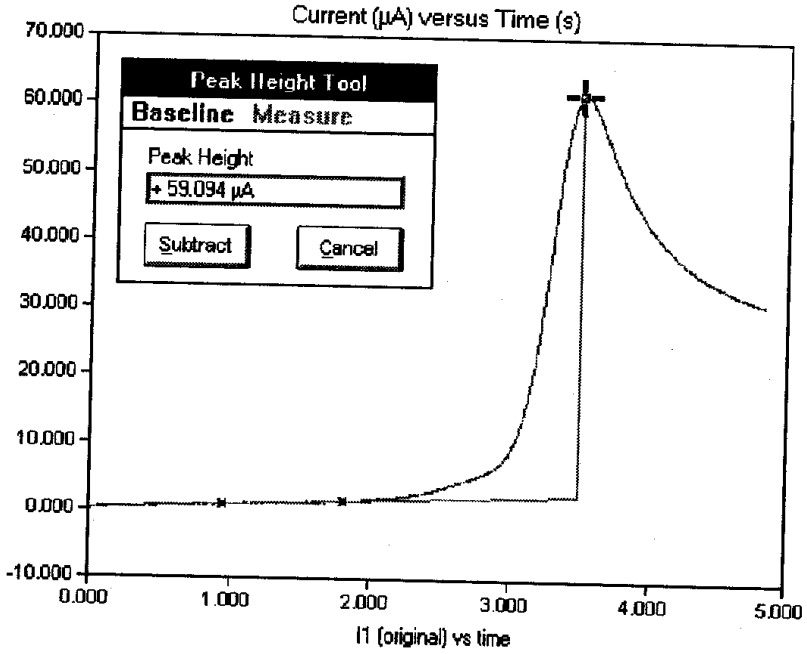


Figure 4: Measuring the Peak Height