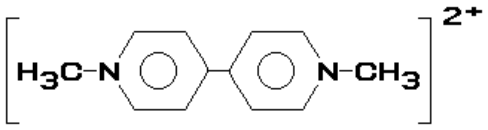
Cyclic Voltammetry

I. Introduction

Cyclic voltammetry will be used to determine the half-wave potential ($E_{½}$), the number of electrons transferred (n) and the reversibility for the first and second reduction processes of methyl viologen (MV^{2+}):

methyl viologen = 1,1′-dimethyl-4,4′-bipyridinium



$$MV^{2+} + ne^- \rightleftharpoons MV^{+\bullet} \quad (1)$$

$$MV^{+\bullet} + ne^- \rightleftharpoons MV^{0} \quad (2)$$

The effect of scan rate on the peak current and the effect of solvent on $E_{½}$ and peak current will be evaluated.

II. Equipment

A. PAR Model 273 Potentiostat with Model 270 computer interface.
B. Voltammetry cell with glassy carbon working electrode, Ag/AgCl reference electrode and a platinum auxiliary electrode.
C. Four 10-mL volumetric flasks.
D. 1000-µL adjustable autopipet and disposable tips (obtain from instructor).
E. 5.00-mL adjustable autopipet and disposable tips (obtain from instructor).
F. Rubber gloves (obtained from instructor).

III. Reagents

A. Lithium chloride
B. 5.00×10^{-3} M methyl viologen standard solution in deionized water.
C. 5.00×10^{-3} M methyl viologen standard solution in methanol.
D. 5.00×10^{-3} M methyl viologen standard solution in ethanol.
E. Nitrogen gas

IV. Procedure

You will work with solutions of methyl viologen in water, ethanol and methanol. Prepare the aqueous solutions first according to the procedure below.

II Weigh out the necessary mass of LiCl to prepare 10 mL of a 0.10 M blank electrolyte solution. Transfer it to a clean 10-mL volumetric flask and dilute with deionized water to the mark.

II Carefully pipet 5.00 mL of the blank solution into the voltammetry cell and slowly bubble N_2 through the solution for 15-20 min.

II Your instructor will demonstrate the software that controls the potentiostat. Select the setup conditions under filename "422LMV.set".

II When deoxygenation is complete, initiate a potential scan at a rate of 20 mV/s. When the scan is finished, save the voltammogram data file on a floppy disk.

E. Weigh out the necessary mass of LiCl to prepare 10 mL of a 0.10 M solution and transfer it to a clean 10-mL volumetric flask. Use a small volume of deionized water to transfer the LiCl quantitatively.

F. Carefully pipet 1.00 mL of the aqueous methyl viologen standard solution into the flask containing the LiCl and dilute with deionized water to the mark.

WARNING: Although only dilute solutions are being used in this experiment, small amounts of methyl viologen can be toxic. Wear rubber gloves when handling any methyl viologen solution. Make all transfers at the assigned work space in the fume hood. Dispose of all waste methyl viologen, contaminated pipet tips and rinses of glassware in the appropriate waste containers. All spills must be cleaned up immediately. READ THE METHYL VIOLOGEN MATERIAL SAFETY DATA SHEET BEFORE YOU BEGIN THIS EXPERIMENT.

G. Carefully pipet 5.00 mL of the diluted aqueous methyl viologen solution into the voltammetry cell and slowly bubble N_2 through the solution for 15-20 min.

H. Meanwhile, prepare the alcoholic methyl viologen solutions as described in steps IV.E-F, **except use the appropriate alcohol to transfer and dissolve the LiCl and to dilute each of the alcoholic methyl viologen standard solutions**.

I. When de-oxygenation of the aqueous methyl viologen solution is complete, initiate a potential scan at a rate of 20 mV/s. When the scan is finished, save the voltammogram data file on a floppy disk. Repeat the potential scan at 50, 100, 250 and 400 mV/s and save each data file.

J. Remove the aqueous methyl viologen solution, carefully clean the voltammetry electrodes and prepare a 5.00-mL sample with an alcohol solution of methyl viologen. De-oxygenate as before and run a potential scan only at 20 mV/s.

K. Repeat step IV.J for the remaining alcohol solution.

V. Treatment of Data

A. Check for the reversibility of each reduction process by comparing the cathodic peak current (i_{pc}) with the anodic peak current (i_{pa}). Recall that for a reversible process

$$\frac{i_{pc}}{i_{pa}} \approx 1$$

For each redox process, i_{pc} and i_{pa} should be measured from the peak current value to the appropriately extrapolated current baseline. Report your ratios.

B. Print out representative voltammograms for each solvent used. Determine $E_{½}$ and n for each reduction process in aqueous and nonaqueous solutions. Report the values obtained. Recall that for a reversible process

$$E_{1/2} = \frac{E_{pa} + E_{pc}}{2}$$

and

$$E_{pa} - E_{pc} \approx \frac{0.057}{n}$$

C. Determine the effect of scan rate (v) on peak current by determining i_{pc} for each reduction process for the various scan rates used in the experiment with the aqueous methyl viologen. Plot i_{pc} vs. $v^{½}$ for each process. Summarize all of your results.

VI. Questions

1. In terms of events at the electrode surface, briefly explain why the peak current should increase as the scan rate increases.

2. Describe the effect of solvent on $E_{½}$ and suggest a chemical reason for this effect.

3. What would be the effect on your methyl viologen voltammogram if you did not thoroughly purge each solution with N_2 prior to running the scan? Explain.

Lab Cautions for Cyclic Voltammetry

1. **Contamination of reagents, glassware or electrodes can be a serious problem in this experiment. Make sure that only the pure reagents identified for this experiment are used and that all glassware and electrode surfaces are thoroughly cleaned before proceeding.**

2. **When you are finished using the electrode assembly, thoroughly rinse the cell and electrodes with deionized water, fill the cell with dilute aqueous LiCl solution and replace the cell.**

3. **Before you leave, turn off the power to the Model 273A potentiostat.**

4. **The last person in the lab using the nitrogen gas for purging should close the valve to the tank before leaving.**