

Affordable Cyclic Voltammetry

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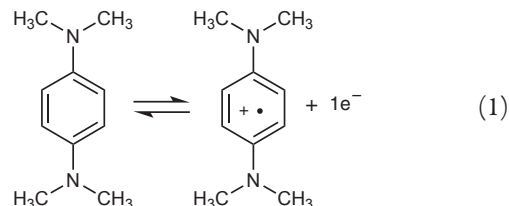
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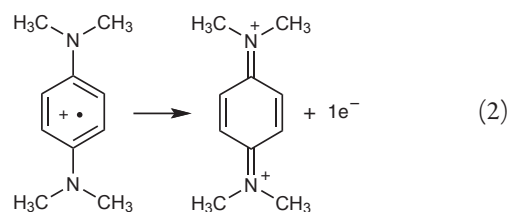
Cyclic voltammetry is a topic that may be incorporated in the analytical (1), inorganic (2), or physical chemistry (3) curriculum. A number of articles in this *Journal* have described both the process of cyclic voltammetry and experiments involving cyclic voltammetry (4, 5). However, experiments in cyclic voltammetry are often excluded from the undergraduate laboratory, probably owing to the prohibitive cost of equipment required. Pine Research Instrumentation (6) has recently released a low-cost voltammetry cell along with inexpensive disposable carbon electrodes designed for student use in the undergraduate laboratory curriculum. The cell may be controlled by a potentiostat and accompanying software that significantly increases the cost of the experiment to over \$6,000.¹ While this is certainly an attractive, economical alternative to the traditional cost of setting up cyclic voltammetric experiments, this price still presents budgetary challenges to small chemistry departments. Therefore, to provide

an even more affordable option for conducting experiments in cyclic voltammetry, we have used a MicroLab (7) model 290 sensor adaptor module and MicroLab FS-522 general purpose laboratory interface² as a potentiostat to control the Pine student electrochemical cell and disposable carbon electrodes; the total cost of this arrangement is under \$1500 per station, less if the chemistry program already uses MicroLab in other areas of the curriculum. Using this Pine–MicroLab interfaced system (Figure 1), we have been able to obtain cyclic voltammograms on a number of chemical compounds.

We present the use of this interfaced system to generate the cyclic voltammogram of tetramethyl-*p*-phenylenediamine (TMPD). TMPD, which is colorless in aqueous solution, undergoes a reversible, one-electron oxidation to a radical cation:



The radical cation is also known as Wurster's blue (TMPD^{•+}), owing to its deep blue color ($\epsilon = 12,000 \text{ M}^{-1} \text{ cm}^{-1}$ at 610 nm) (8). The standard reduction potential for this half-reaction has been reported to be +250 to +284 mV versus NHE (9–14). In addition, Wurster's blue undergoes a one-electron oxidation to a colorless, quinonediiminium dication (TMPD⁺⁺):



The standard reduction potential for this second half-reaction is +900 mV versus NHE (9–13). The colorless dication is unstable in the presence of water and rapidly undergoes chemical decomposition into formaldehyde and other products (9, 10, 15).

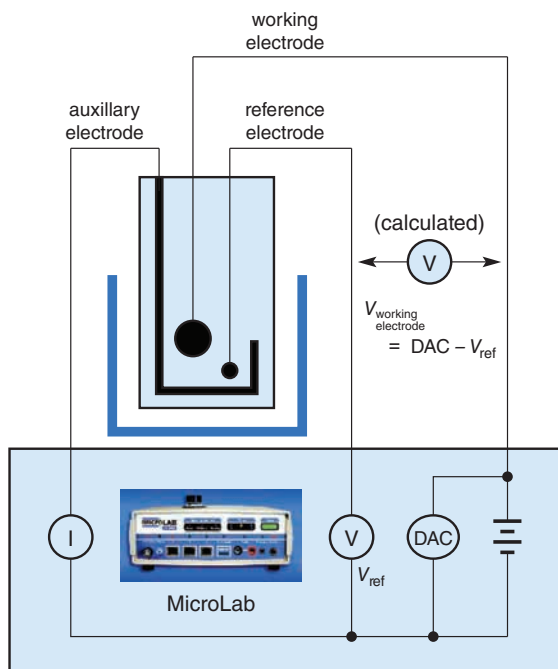


Figure 1. Circuit diagram of MicroLab–Pine interfaced system. The DAC, V, and I leads from the Pine cell plug into the Sensor Adapter Module, which in turn plugs into one of the CAT-5 ports on the MicroLab unit. See the online materials for programming details.

Hazards

TMPD is harmful if swallowed, inhaled, or absorbed through the skin. It is an eye, skin, and respiratory irritant.

Results and Discussion

A cyclic voltammogram of 1 mM TMPD in aqueous, anaerobic solution using the Pine–MicroLab interface is displayed in Figure 2. Two waves are clearly discernible. The first wave is quasi-reversible with a cathodic peak at 235 mV and an anodic peak at 5 mV (vs Ag/AgCl). The second wave has a cathodic peak at 835 mV vs Ag/AgCl; no anodic peak is observed. Thus, the cyclic voltammogram qualitatively displays the known chemistry of TMPD: a reversible oxidation of TMPD to $\text{TMPD}^{+\bullet}$, and a second oxidation of $\text{TMPD}^{+\bullet}$ to TMPD^{2+} that is irreversible because of the chemical instability of TMPD^{2+} in the presence of water.

Upon converting the reduction potentials observed versus Ag/AgCl in Figure 2 to NHE (addition of 197 mV to midpoint potentials³), the reduction potentials for half-reactions 1 and 2 are estimated to be +282 and +912 mV, respectively. Thus, the basic quantitative features of the cyclic voltammogram are in good agreement with the reported electrochemical behavior of TMPD. For a perfectly reversible process, the separation (ΔE_{pp}) of the anodic (E_{pa}) and cathodic (E_{pc}) peaks of the first wave should be separated by 57 mV at 298 K (16):

$$E_{pp} = E_{pc} - E_{pa} \quad (3)$$

For the reversible wave in Figure 2, ΔE_{pp} is 230 mV. The observed deviation from perfectly reversible behavior is probably due to sluggish heterogeneous kinetics, a property of screen-printed conductive carbon inks (17).

Conclusion

Cyclic voltammetry is an important component of research in a variety of chemical fields. Certainly, undergraduates should have exposure to this important technique. Recently, commercial packages have been released that offer affordable (\$6,000) options to implementing high quality cyclic voltammetric experiments in undergraduate laboratories. It is our hope that the even more affordable (\$1,500) Pine–MicroLab interface described in this article will allow this technique to be more broadly available to undergraduates.

Acknowledgment

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Notes

1. The prices of the components from Pine Research Instrumentation are student electrochemical cell, #AKSPEKIT, \$375; disposable carbon electrodes, #RRPE1001C, ~\$3 each; potentiostat, #AFCBP1, ~\$4,000; accompanying software, #ASCBP1, ~\$2,000.

2. It should be noted that the older MicroLab 402 units also can be used. In addition, MicroLab has recently added a \$295 Pine cell adapter module that allows the user to bypass the sensor adapter module and plug directly into the CAT-5 connector.

3. Midpoint potentials may be estimated by inspection for the approximate position of the inflection point of each wave. Derivative plots (which we employed in the analysis reported here) allow for a more quantitative determination of midpoint potentials. See refs 1 and 16 for more information.

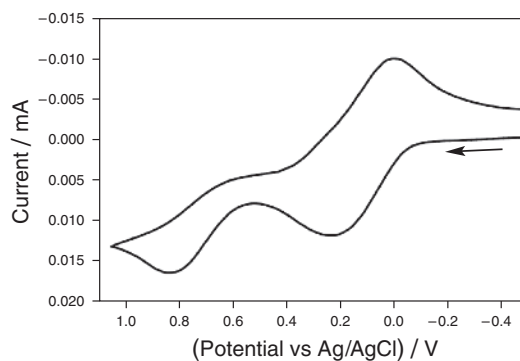


Figure 2. Cyclic voltammogram of 1 mM TMPD (0.1 M NaCl supporting electrolyte) at a disposable, screen-printed carbon electrode (Ag/AgCl reference electrode) in aqueous, unstirred anaerobic solution (bubbled with N_2 gas for 5 minutes prior to scan) using the Pine–MicroLab interface at 298 K and pH 2.5. Anodic potentials are positive, 40 mV/s scan rate, sweep direction is from right to left and back again.

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Supporting JCE Online Material

<http://www.jce.divched.org/Journal/Issues/2009/Sep/abs1080.html>

Abstract and keywords

Full text (PDF) with links to cited URL and JCE articles

Supplement

Specific instructions for assembling the Pine–MicroLab interface and programming instructions for a sample voltammetry program