Electrochromism of Methylviologen (Paraquat)

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Abstract   The herbicide paraquat, N, N'-dimethyl-4,4'-bipyridiunium dication (N,N'-methyl viologen), is electrochromic. Experiments are described that investigate its redox chemistry (cyclic voltammetry), its optical properties (photometry and UV/Vis spectrophotometry), and its potential as a system for electrical "photoswitching" and as an accumulator for rechargeable devices. This set of teaching laboratory experiments closely reflects true procedures in commercial research and development endeavors, because the same system is probed with several quite different, but complementary, analytical methods.

Keywords: *third-year undergraduate, analytical, electrochemistry, electrochromism, hands-on learning/manipulatives*

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1. Introduction

Electrochromic substances are redox indicators that change their color when a potential is applied. This is due to the different colors of the reduced and oxidized species. One application of electrochromic materials is in electrically conductive windows ("smart windows", "chemical blinds") that can be darkened and can also function as heat insulation glazing [1,2].

A desired characteristic of electrochromic materials is cyclic stability. That means that the number of color changes should be as high as possible, whereby the color intensity should not be affected. Furthermore, a cyclically stable redox material is a potential candidate for an accumulator in a rechargeable battery.

Some examples of electrochromic materials are tungsten oxide (WO_3) [3,4,5,6,7], polyaniline (PANI) [8,9,10,11], and viologen (Vio) [12-17].

The laboratory comprises a set of cyclic voltammetry (CV) measurements as a function of scan rate, measurement of the total light transmission as a function of applied alternating voltage, measurement of the visible spectrum as a function of applied constant voltage, and finally measuring the voltage decay characteristics of the redox couple to test for the material's suitability for rechargeable devices.

The experiments can be completed by a pair of students within 8 hours of laboratory work. It is obvious that the set of experiments can be splitted into electrochemical and spectrophotometric parts.

2. Experimental

2.1. Photometry/Cyclic Voltammetry Setup [18,19,20]

Initial CV measurements were made with Pt working and counter electrodes and a silver/silver chloride reference electrode (DropSens DS 550). For the simultaneous photometric and CV measurements we made our own reaction cell with conducting transparent walls made of either fluorine-doped tin oxide coated glass (FTO) or indium tin oxide glass (ITO) that served as the working and counter electrodes. The reference electrode is a silver wire [1] fed through a pinhole in a rubber spacer ring (thickness 3 mm, diameter 15 mm) that is clamped between the two glass walls (Figure 1).
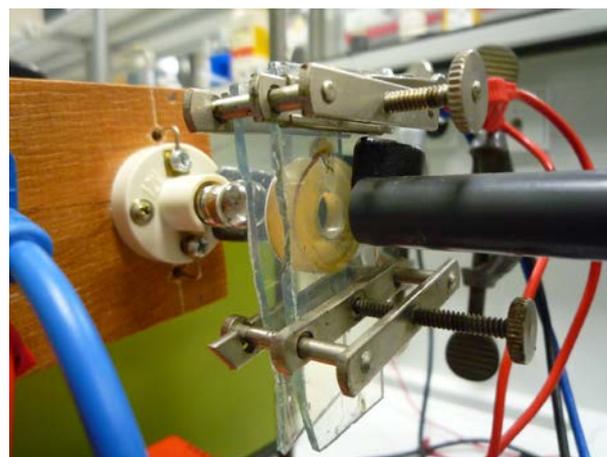

Figure 1. Reaction cell with incandescent lamp (left) and luxmeter (right)

The rubber ring has an opening in the top through which reagents are pipetted in or out. The inner volume of the reaction cell is about 3 mL.

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[1] The silver reference potential is a so-called pseudo-potential. That means that the silver reacts slightly with the aqueous solution to form a low quantity of silver-ions. These ions will react with the supporting electrolyte (here Na_2SO_4) to form insoluble silver sulfate. Therefore, the reference potential is defined. The exactly defined potential is the result of a calibration with the ferrocen / ferrocenium couple.

For the CV measurements the electrodes are connected to a potentiostat (μStat 400, DropSens). All subsequent measurements, also the photometric ones, were made using the DropSens potentiostat as a power supply. The total light intensity transmitted by the solution is measured by a light-sensitive detector (Lux sensor Leybold Didactic 666243) as a function of the potential and recorded by a data acquisition system (Leybold Didactic CASSY). The light source is a simple incandescent filament lamp.

The viologen solution is 1 mL 0.001 M viologen(aq) (Methyl viologen dichloride hydrate, Aldrich, 856177) in 3 mL 0.1 M Na$_2$SO$_4$(aq).

Hazard: Viologens (registered name "Paraquat") are used as one of the most widely used herbicides. It is toxic by inhalation and ingestion and possible carcinogen if absorbed through skin. Students should practice caution while performing the experiments. Disposal: Waste should be collected by a suitable authority.

The purpose of the sodium sulfate is two-fold: to take up dissolved silver ions from the silver wire reference electrode in order to form insoluble silver sulfate, and to act as a supporting electrolyte to reduce the IR-drop between the working and reference electrode.

2.2. UV/VIS Spectrophotometry Setup

The objective of the spectrophotometry experiment is to measure the transmission of light to assess the stability of the viologen-film on the electrode.

The UV/VIS spectra of the viologen solutions were measured with a Perkin Elmer Lambda XLS+. The only modification to this standard method is that two small FTO panels are inserted into the quartz cuvettes so that the light beam passes through both electrodes which are connected to the potentiostat.

2.3. Cyclic voltammetry: Characterizing the Redox System

The didactical objectives of the cyclic voltammetry experiment are to observe the color changes associated with the scanning potential and to assess the Randles-Sevcik behavior of the redox system.

The novice reader is referred to standard works on CV [21-26] in which the relationship between *I/V* curves, scan rates *v*, and characteristics of the reactive system are described.

Here we only briefly summarize some main aspects of CV:

- According to the IUPAC recommendation anodic peaks appear upward, cathodic downward pointing.
- If the positions of the maximum current peaks with regard to their potential do not change as a function of the scan rate, and the heights of the anodic and cathodic peaks appear to be equal, then the process occurring is reversible.
- If the peaks are about 59 mV apart then the process is a reversible one-electron transfer.
- If the current peaks appear to be sliding apart, the process is quasi-reversible.
- Reversible processes show a $v^{1/2}$-dependence of their current peaks according to the Randles-Sevcik equation:

$$i_p = 0.4463nFAC\sqrt{\frac{nFvD}{RT}} \qquad (1)$$

i_p = current maximum in amps, n = number of electrons transferred in the redox event, A = electrode area in cm^2, F = Faraday Constant in C mol^{-1}, D = diffusion coefficient in cm^2/s , C = concentration in mol/cm^3, v = scan rate in V/s, R = Gas constant in VC K^{-1} mol^{-1}, T = temperature in K.

- The solution is unstirred. This implies that the electroactive species reach the electrode solely under the influence of diffusion i.e. negating migration, adsorption and convective effects.
- If a peak appears or disappears then the process is chemically irreversible.
- The simplest electrochemical process is the reversible electron exchange (E$_r$). In addition, more complicated processes are consecutive electron transfer processes (EE) and / or combinations of electron transfer and chemical reactions (EC or CE).

In the CV of Methylviologen (Figure 2 and Table 1) we see several current peaks:

Table 1. Methylviologen redox reactions (reaction assignments from Ref. [13])

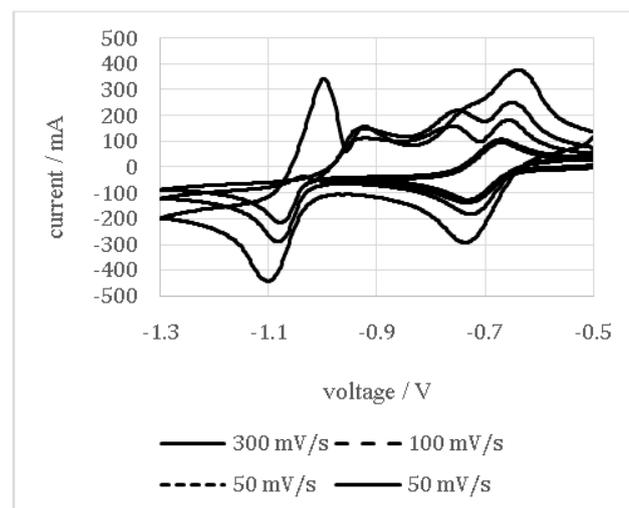|	Pt electrode	FTO electrode	
C Cathodic peaks			
1	-0.73 V	-0.70$_5$ V	Vio^{2+} + e$^-$ → Vio$^{.+}$ colorless → blue
2	-1.08 V	-1.05 V	Vio$^{.+}$ + e$^-$ → Vio blue → yellow
3	-1.03 V	-0.98 V	Vio → Vio$^{.+}$ + e$^-$ yellow → blue
Anodic peaks			
4	-0.93 V	-0.89 V	2Vio → [(Vio)$_2$] → (Vio)$_2$$^{2+}$ + 2e$^-$
5	-0.77 V	-0.77 V	(Vio)$_2$$^{2+}$ → 2 Vio^{2+} + 2e$^-$
6	-0.65 V	-0.65 V	Vio$^{.+}$ → Vio^{2+} + e$^-$ blue → colorless

Figure 2. N-methyl viologen CV at different scan rates (50, 100, 300 mV/s) on Pt electrodes. The arrow shows the direction of scan rate increase. The bold curve shows the CV measured at 50 mV/s but only between -0.5 V and -1.0 V

- **-0.73 / -0.65 V**: The right-most features are the quasi-reversible redox pair at -0.73 / -0.65 V corresponding to a single electron transfer between the double and single cation of viologen: Vio^{2+} ↔ Vio$^{.+}$. (This

assignment is supported by a narrower range scan limited to between -0.5 and -1.0 V, which prevents reactions that require higher/lower potentials from occurring, and is shown by the bold curve in Figure 2).

- **-1.08 / -1.03 V**: The left-most two peaks at about -1.08 V and -1.03 V are again a redox couple: $Vio^{·+}$ ↔ Vio.

  The I_p ~ v dependence indicates an adsorption process of the Vio [28]. At low scan rates the viologen has time to desorb from the electrode at higher scan rates it doesn't have time to escape the electrode and can be ionized to the $Vio^{·+}$.

- **-0.93 V and -0,77 V**: At about -0.93 V and -0.77 V some scan-rate independent oxidation (anodic peak) are happening. This is attributed to a reaction of the viologen dimer cation, dissociating to two dications and two electrons [27,28]. At this potential we see a very interesting process, because it is scan-rate independent – all the peak currents are the same, regardless of scan rate, the formation of the dimer dication from 2 *neutral* viologen molecules at -0.93 V (see process 4 in Table 1) [27].

Repeating the CV with FTO electrodes yields the same results with the potential scale by about 0.08 V, on average, less negative that with platinum (Table 1).

Scanning through these potentials shows viologen to be a three-color system, Vio^{2+} is colorless, $Vio^{·+}$ is blue, Vio is yellow. (The color of $(Vio)_2^{2+}$ has not been defined. It is not easy to determine, since solutions of the dimer dication always contain the neutral and the single cation as well). Scanning from -0.5 V to -1.3 V along the cathodic curve makes the solution go from colorless to blue to yellow, and going back along the anodic curve from yellow to blue to colorless.

2.4. (Spectro) Photometry: Evaluating the Cyclic Stability

The objective of the photometry experiment is to monitor and assess the light transmission as a function of the applied triangular voltage and so to assess the cyclic stability of viologen.

A useful electrochrome will have high cyclic stability. In Figure 3 we show a test of the cyclic stability. The applied triangle shaped potential varies between 0 and -1.5 V, so that potentially all reactions listed in Table 1 and seen in the CV in Figure 2 should be occurring. This can be inferred by looking at the transmission curve for a single cycle, Figure 4. Here one can correlate the color change to applied potential to see the onset of reaction 1 (colorless to blue, transmission drops), reaction 2 (blue to yellow, transmission rises slightly), reaction 3 (yellow to blue, transmission drops again), and reaction 6 (blue to colorless, transmission rises to original value).

At the voltage cycling rate used here of -1.5 V per 90 s the solution darkens briefly as the potential is slowly increased back from -1.5 V, so some neutral viologen must be proximate enough to the electrode to get oxidized to the cation $Vio^{·+}$.

Cycling the system between 0 and -0.9 V allows only the colorless Vio^{2+}/blue $Vio^{·+}$ redox reaction to occur, one gets a smooth curve oscillating between the blue and the colorless phases.
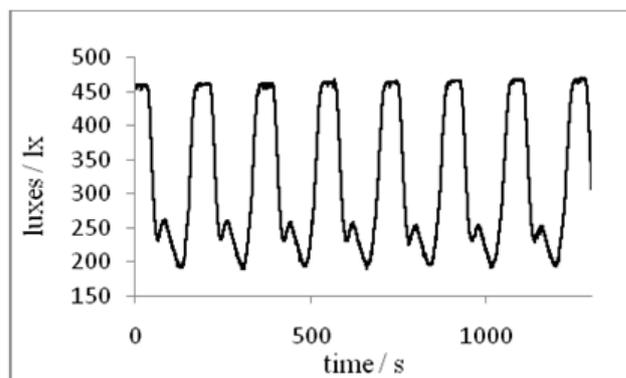

Figure 3. Total light transmission as a function of applied linearly increasing/decreasing voltage between 0 and -1.5 V and back to 0 V.
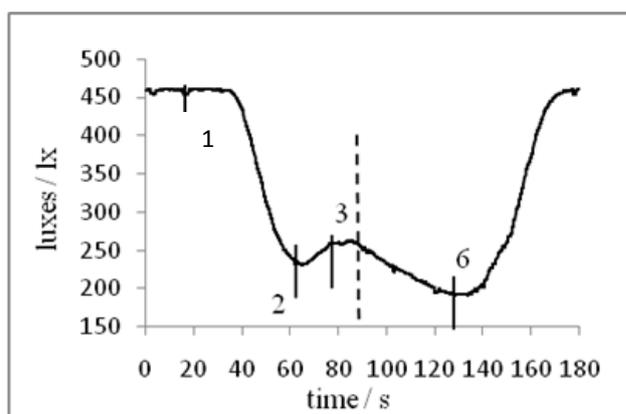

Figure 4. A single cycle taken from Figure 3. The dashed vertical line marks the voltage turning point at -1.5 V (90 s). The solid vertical lines mark the onsets (from left to right) of reactions 1 (colorless to blue), 2 (blue to yellow), 3 (yellow to blue), and 6 (blue to colorless). The novice might need to be alerted to the fact that the potentials at which the color changes start to happen do not correspond to the peak-current potentials in the CV. The CV peak-current potentials show at which potential the reactions are most efficient, not the ones at which they can start to occur
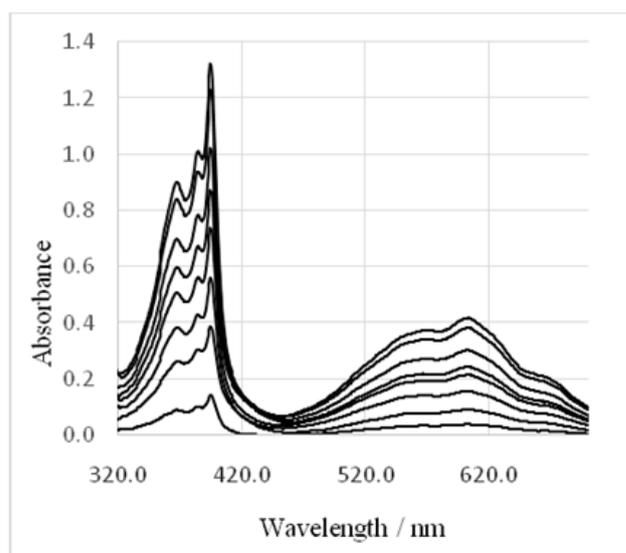

Figure 5. UV/vis-spectrum of viologen, measured eight times at 20-second intervals, with an applied potential of -0.9 V

Over the course of 8 cycles (1200 s), no significant changes in the transmission curve are seen despite the quasi-reversible behavior of the Vio^{2+} / $Vio^{·+}$ redox couple (Figure 3), indicating a reasonable cyclic stability at least on this time scale. Should the electrochromic switch stay

"on" or "off" for a significant length of time, however, problems might result, as seen from the spectra in Figure 5. Here the cuvette was held at a constant potential of -0.9 V for the duration of the measurements. Spectra were taken at 20 second intervals; the solution absorption, thus also the concentration of the blue colored single cation, increases. Similar observations have been made in previous experiments. [17] With this experiment one cannot differentiate between a Vio·⁺-coating of the electrode or a simple enhancement of the Vio·⁺ - concentration in the solution.

2.5. Photometry/potentiometry. Viologen as a Redox Couple for a Rechargeable Battery

The objective of the photometry/potentiometry experiment is to monitor and assess the potential of the discharging cell.

Since viologen undergoes quasi-reversible redox processes, it could potentially be used in a rechargeable device (of course a reversible system is a better candidate). Figure 6 shows the measured voltage during discharge (dashed curve) and the total light transmission (solid curve) of an FTO/Vio/FTO cell that was electrolyzed at -0.9 V (top) and at –1.5 V (bottom). The potential of the discharging cell was measured between the working and the reference electrode.
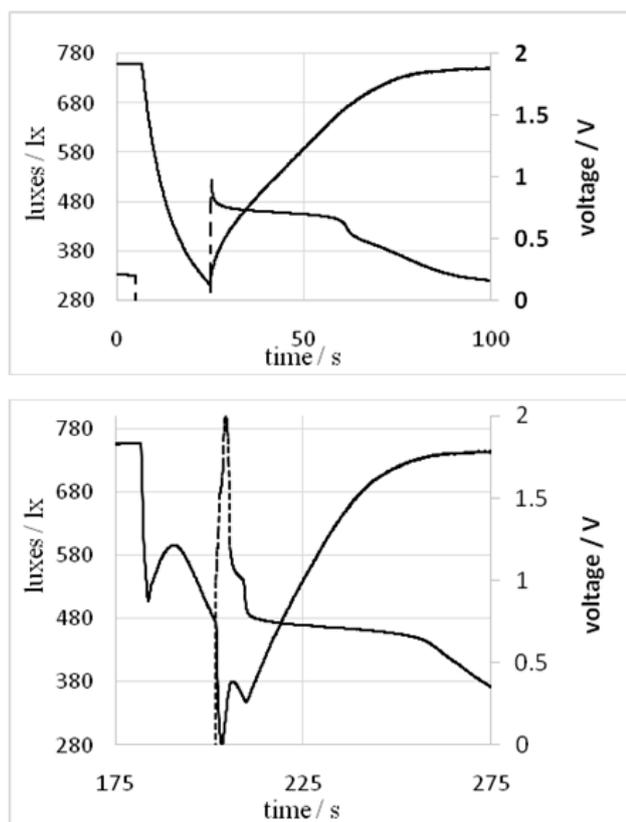

Figure 6. Total light transmission (solid curves) and measured voltage (dashed curves) of an FTO/Vio/FTO cell. *Top*: Applied voltage is -0.9 V starting at 8 s to about 25 s, then switch off of voltage to 0 V. *Bottom*: Applied voltage is 0 V up to 180 s, then electrolysis at -1.5 V between ~180 s and ~200 s, then switch off of electrolysis potential back to 0 V. At the electrolysis voltage of -0.9 V in the top panel viologen neutrals cannot form; but they can in the bottom panel

As the solution is electrolyzed at -0.9 V the colorless Vio²⁺ is reduced to the blue Vio·⁺ (reaction 1). Switching off the voltage allows the Vio·⁺ to re-oxidize (reaction 6). The transmission curve reflects this easily – the high transmission drops during electrolysis and rises steadily when the voltage is turned off. The decay voltage of the cell shows interesting behavior. (We believe the initial spike up to -1.0 V to be an artifact of the measuring system.) The voltage drops rapidly from -0.9 to just below -0.8 V as the viologen cations in the vicinity of the electrode are oxidized immediately. The slow drop off of the voltage between 25 and about 60 s hovering around -0.7 V is the diffusion controlled reoxidation of Vio·⁺. The potential decreases slightly as is typical for discharging behavior in batteries.

Electrolysis at -1.5 V complicates the situation because now also neutral viologen can form (reaction 2). The solid curve shows the colorless solution before electrolysis (high transmission below 180 s), immediate darkening of the solution upon switching on of the electrolysis voltage at 180 s (reaction 1), followed by lightening of the solution (blue to yellow, reaction 2) and, remarkably, subsequent darkening again. Turning off the pulse allows the reduction reaction to cease, the yellow solution oxidizes to the blue immediately (lowest dip at just past 200 s), then starts to lighten, darken (205 - 210 s) and finally lighten again.

Looking at the voltage decay curve first, we see that it is similar to the one in the top part of the figure except for the shoulder between 205 and 209 s. Thus, we can assume that the broad level part of the curve also corresponds to a diffusion controlled oxidation of Vio·⁺ to Vio²⁺ (reaction 6). This also agrees with the behavior of the transmission curve indicating the solution is going from dark (blue) to colorless.

Our interpretation of the transmission curve between 180 and 210 s during the electrolysis and the discharge potential between 200 and 210 s must involve the neutral viologen species. We believe that switching the electrolysis voltage on results in reduction of the colorless Vio²⁺ to Vio·⁺ in the immediate vicinity of the electrode (180 – 185 s). The reduced Vio·⁺ that stays in the vicinity of the electrode gets reduced further to the yellow Vio (the transmission increases, 185 – 190 s). The neutral Vio remains in the vicinity of the electrode since it is unaffected by the electrode potential. More Vio²⁺ can be reduced to blue Vio·⁺ only after it has managed to diffuse through the neutral Vio layer to the electrode; then the transmission decreases again (190 – 200 s). Turning off the electrolysis potential causes immediate oxidation of the electrode-proximate neutral viologen to Vio·⁺, the transmission drops immediately to its minimum (200 – 203 s), the cell potential soars. Because the potential is still lower than -1.1 V, however, the Vio·⁺ can be reduced back to neutral Vio (transmission rises (203 - 205 s; potential drops). Around –1 V the neutral Vio oxidizes to Vio·⁺ (transmission decreases, potential drops slightly (anyway), beyond 205 s the system is close to -0.9 V and thus behaves as in the top panel.

It should be noted that the potential required to electrolyze viologen is within the range supplied by readily available solar cells (e.g. Solarmodul 10 V70, 3 A, LD Didactic, 664 431). We were able to charge up the viologen cell with a conventional incandescent lamp yielding about 3.2 V on the solar cell (depending on the distance between lamp and cell).

3. Conclusion

The conducting of the experiments involves a wide variety of physicochemical principles (cyclic voltammetry, spectrophotometry, charge-discharge measurement). This is a more accurate portrayal of real-world research and development scenarios in which a particular system of interest is examined by as many methods as possible in order to determine its suitability in various applications. In addition, it allows students to see how different analytical methods both supplement and complement each other.

The availability of Methyl viologen for electron transfer has been investigated by cyclic voltammetry. Usually, the main variable of CV is the scan rate to identify the electron transfer process being reversible or not. In this paper, however, the main focus on the one hand refers to the correlation between the electrode processes and the changes of the color of the different redox couples. Otherwise, the discharging curves of the "viologen-battery" as a function of the charging-potentials indicate two different redox-processes, which can be identified by CV.

The viologen double cation that we have chosen for these experiments may also interest students who are familiar with the herbicide, paraquat. The usual prescribed precautions for use and disposal of this hazardous chemical (toxic by inhalation and ingestion; possible carcinogen if absorbed through the skin) must be followed.

Acknowledgement

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