

Reduction Kinetics in Heteropoly Blue Species of Organically Modified Polyoxotungstates

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Introduction

Investigation into the electrochemical properties of POMs has been diverse. Cyclic Voltammetry for Dawson POMs have been reported. Cyclic Voltammograms investigate the unique redox behavior of these species, specifically their electron processes. Depending on which family of POM is being studied, reductions occur as either one, two, or more electron processes.

A heteropoly blue species appears in POMs when held at certain reduction potentials during Electrolysis. Electrolysis is a method of using a direct electric current to drive a reaction to occur, in this case, a reduction. This held voltage at a reduction potential gives rise to the heteropoly blue species. This unique property yields their electrochromic properties. Characterization of these heteropoly blue species using Ultraviolet Visible Spectrometry has not been well investigated.

The focus of this research was to investigate the spectroscopic states of the Dawson-Wells POMs ($P_2W_{16}O_{62}$). Reported are the experimental parameters of these investigations, and data concerning the kinetics of the reduction.

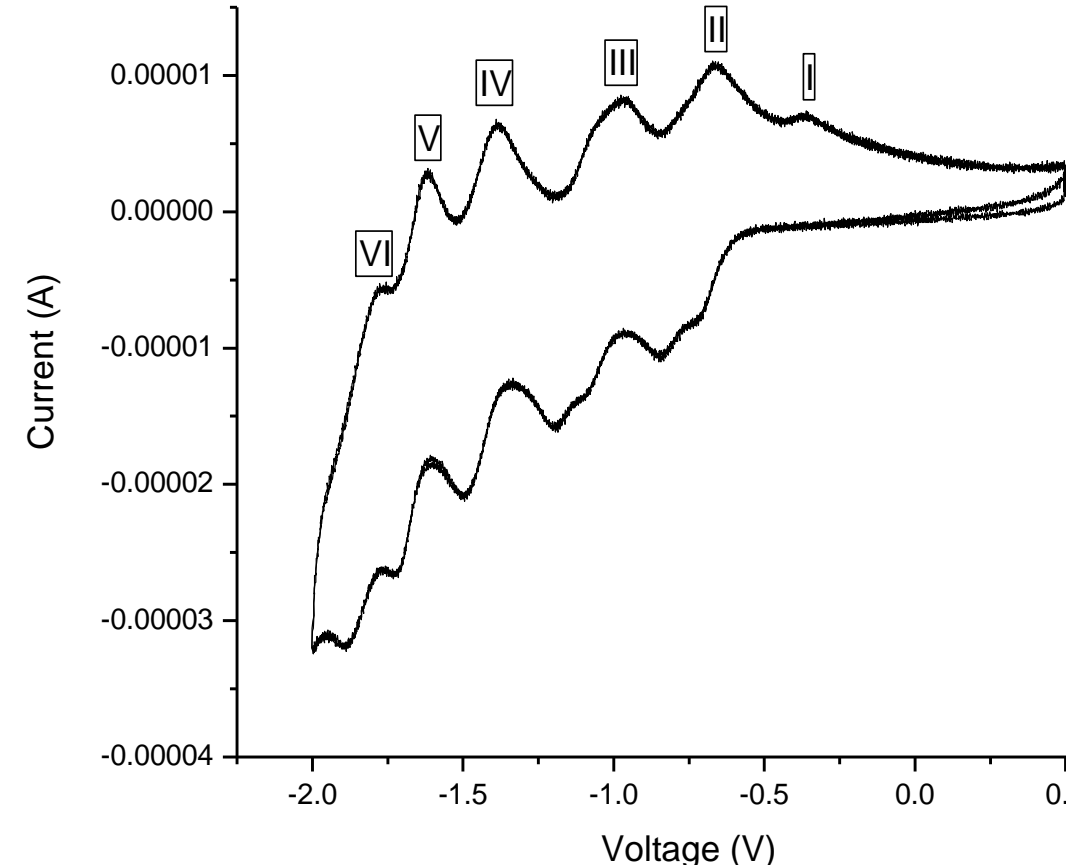


Figure 1. A Cyclic Voltammogram of the C12 Molecule, indicating where reduction and oxidation peaks are located.

Materials and methods

Dawson-Wells Polyoxotungstates, (C8)

$\{[C_4H_9]_4N\}_6\{[C_8H_{37}Si]_2OP_2W_{17}O_{61}\}$, (C12)

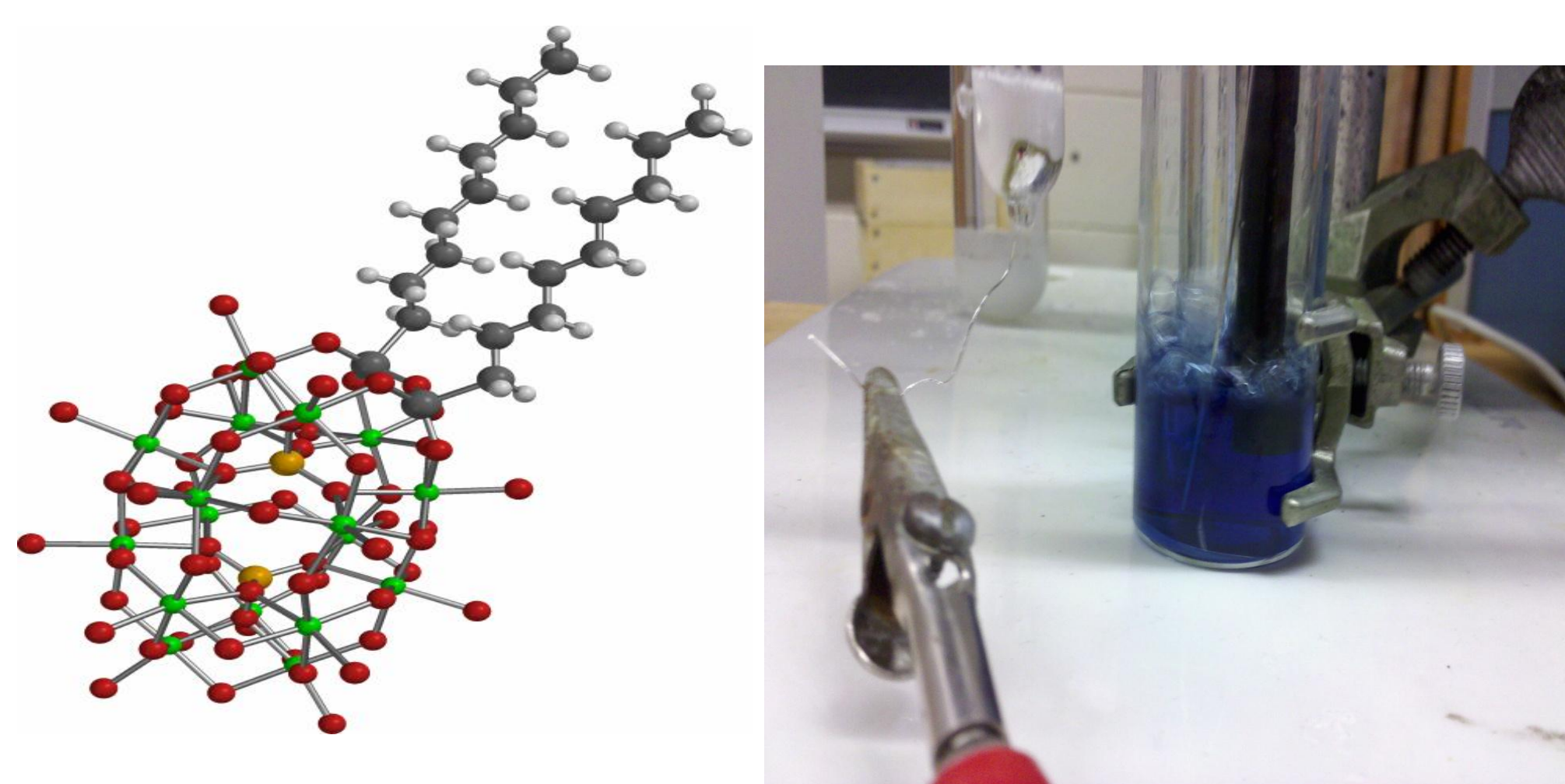
$\{[C_4H_9]_4N\}_6\{[C_{12}H_{37}Si]_2OP_2W_{17}O_{61}\}$, (C18-1)

$\{[C_4H_9]_4N\}_6\{[C_{18}H_{37}Si]_2OP_2W_{17}O_{61}\}$, and (C18-2)

$\{[C_4H_9]_4N\}_6\{[C_{18}H_{37}Si]_2OP_2W_{17}O_{61}\}$ were synthesized and modified by Dr. Carlisle Chambers (George Fox University).

The Glassy Carbon Electrode was rinsed and polished with Micropolish Lumina.

Electrolysis was ran in a UV spectrophotometer, and UV spectras were taken every five minutes.



Figures 2 & 3. The Dawson-Wells POMs with an Organo Silyl Tail Group of 12 carbons long attached (left). This creates an Amphiphilic species, containing hydrophilic and hydrophobic ends. A Dawson-Wells POM displaying the heteropoly blue when undergoing Electrolysis (right).

Results

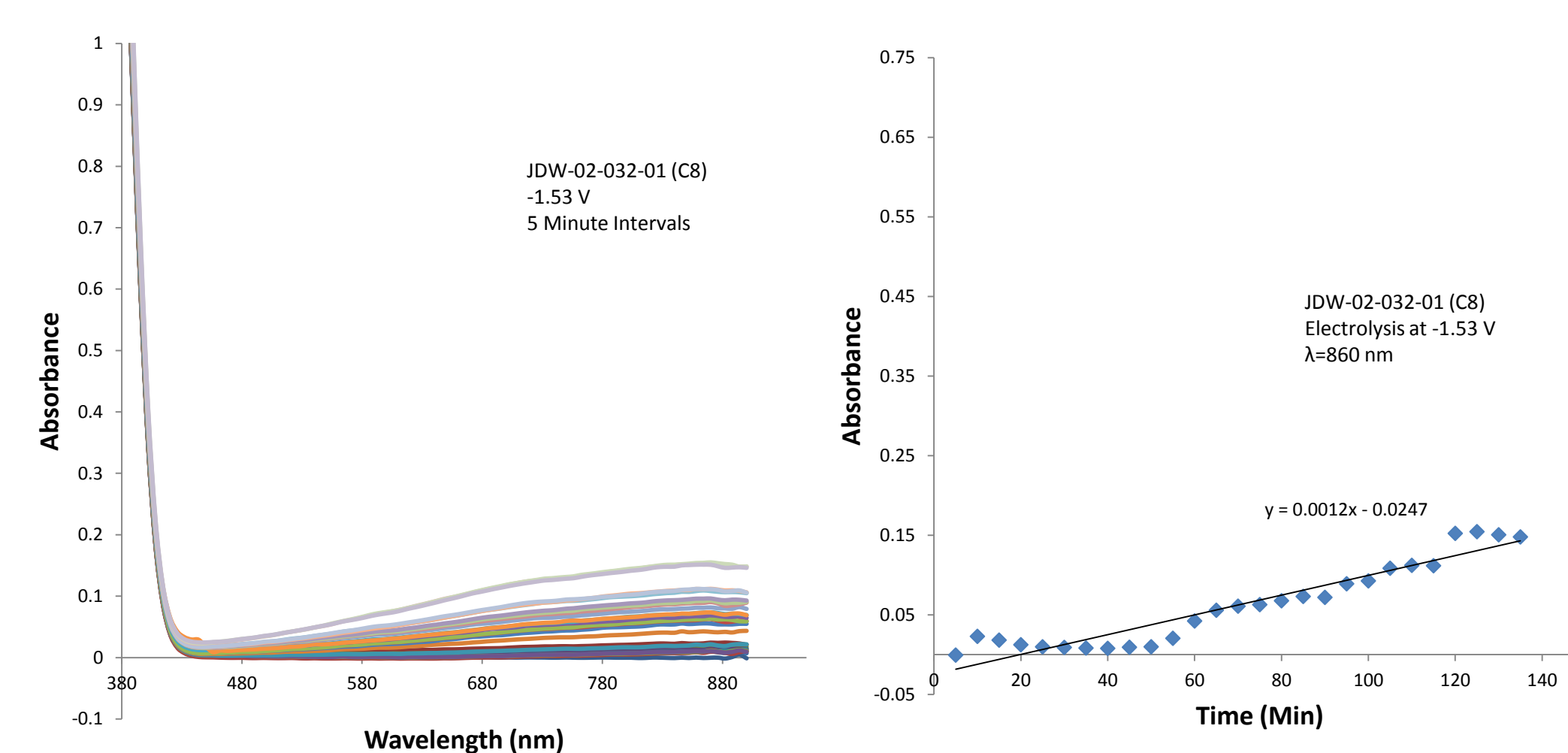


Figure 4. Overlay of various five minute intervals of the C8 molecule's UV spectra's during electrolysis (left), and a time analysis of the absorbance at a wavelength of 860 nm to approximate the rate of reduction (right).

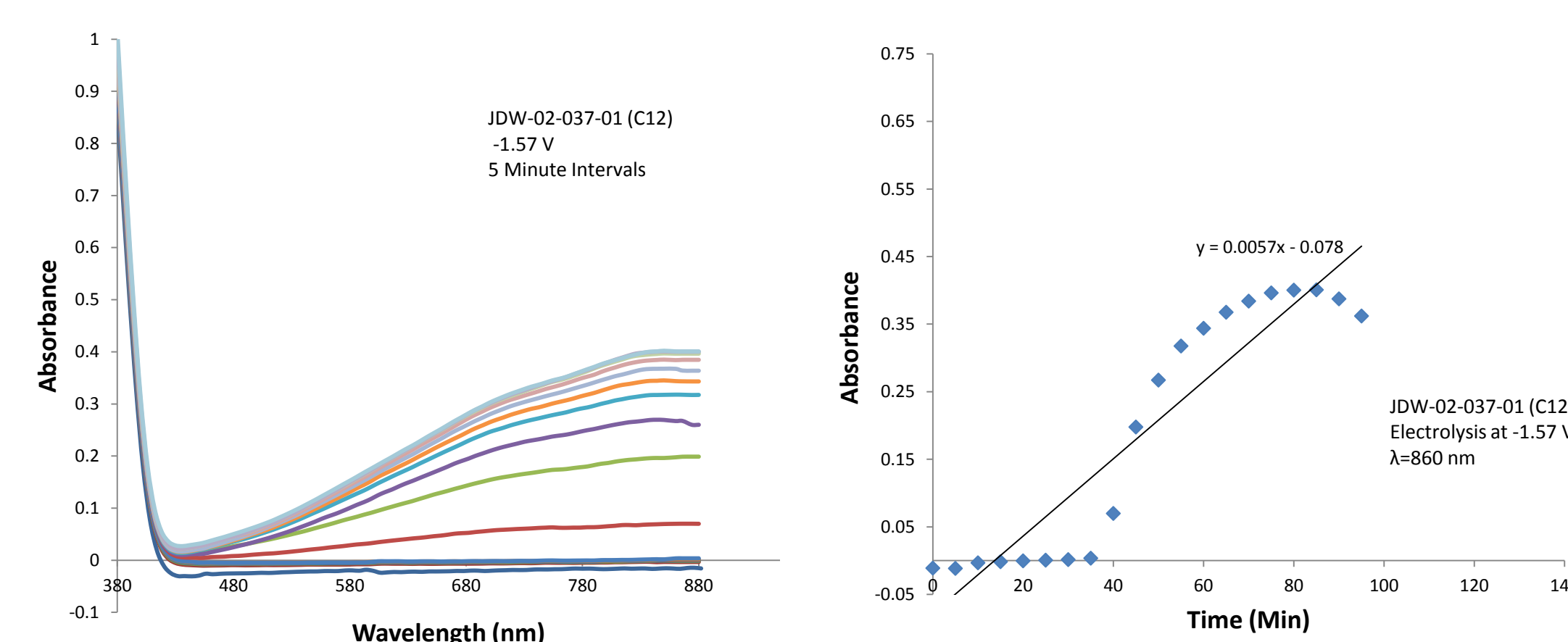


Figure 5. Overlay of various five minute intervals of the C12 molecule's UV spectra's during electrolysis (left), and a time analysis of the absorbance at a wavelength of 860 nm to approximate the rate of reduction (right).

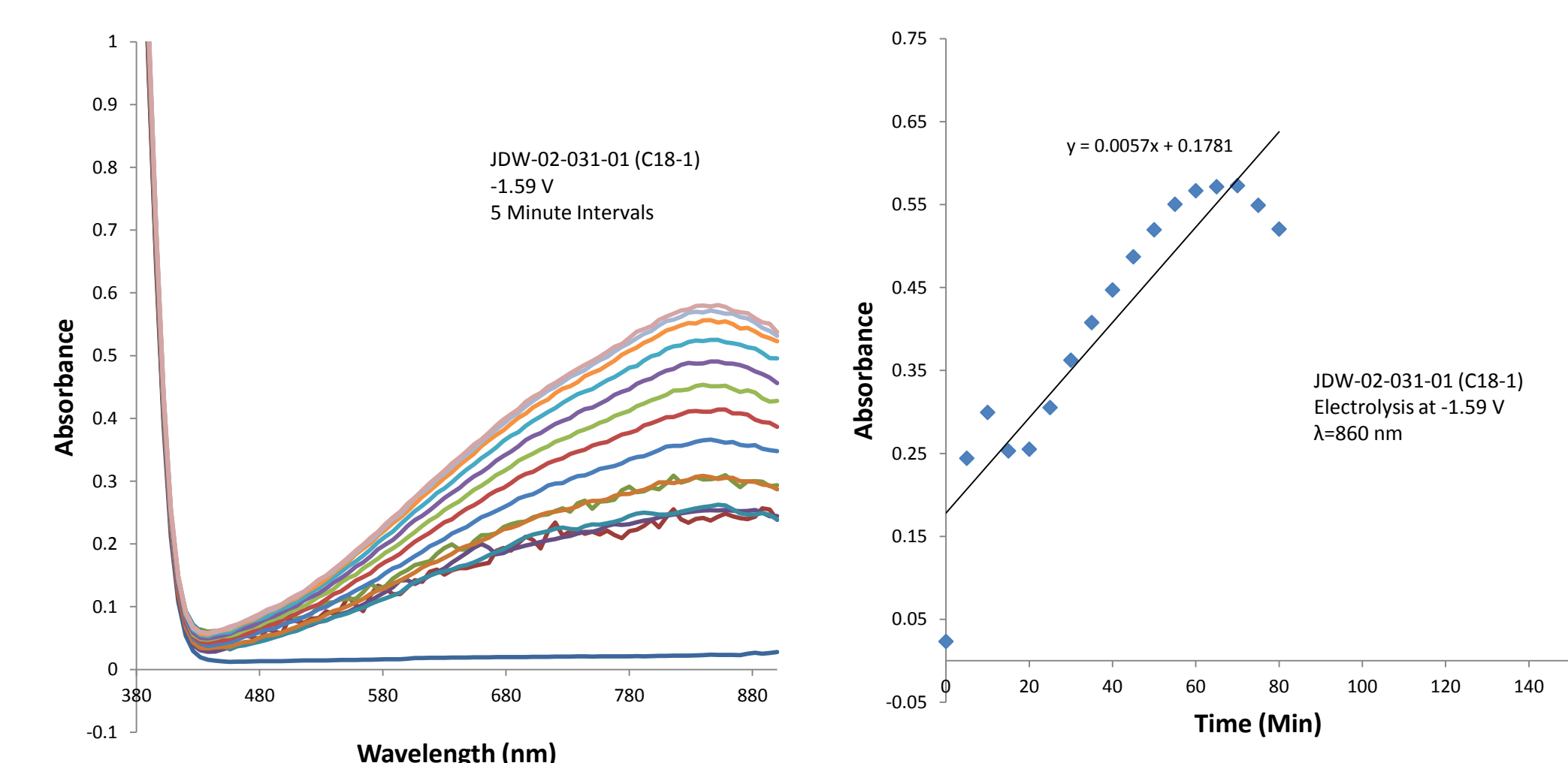


Figure 6. Overlay of various five minute intervals of the C18-1 molecule's UV spectra's during electrolysis (left), and a time analysis of the absorbance at a wavelength of 860 nm to approximate the rate of reduction (right).

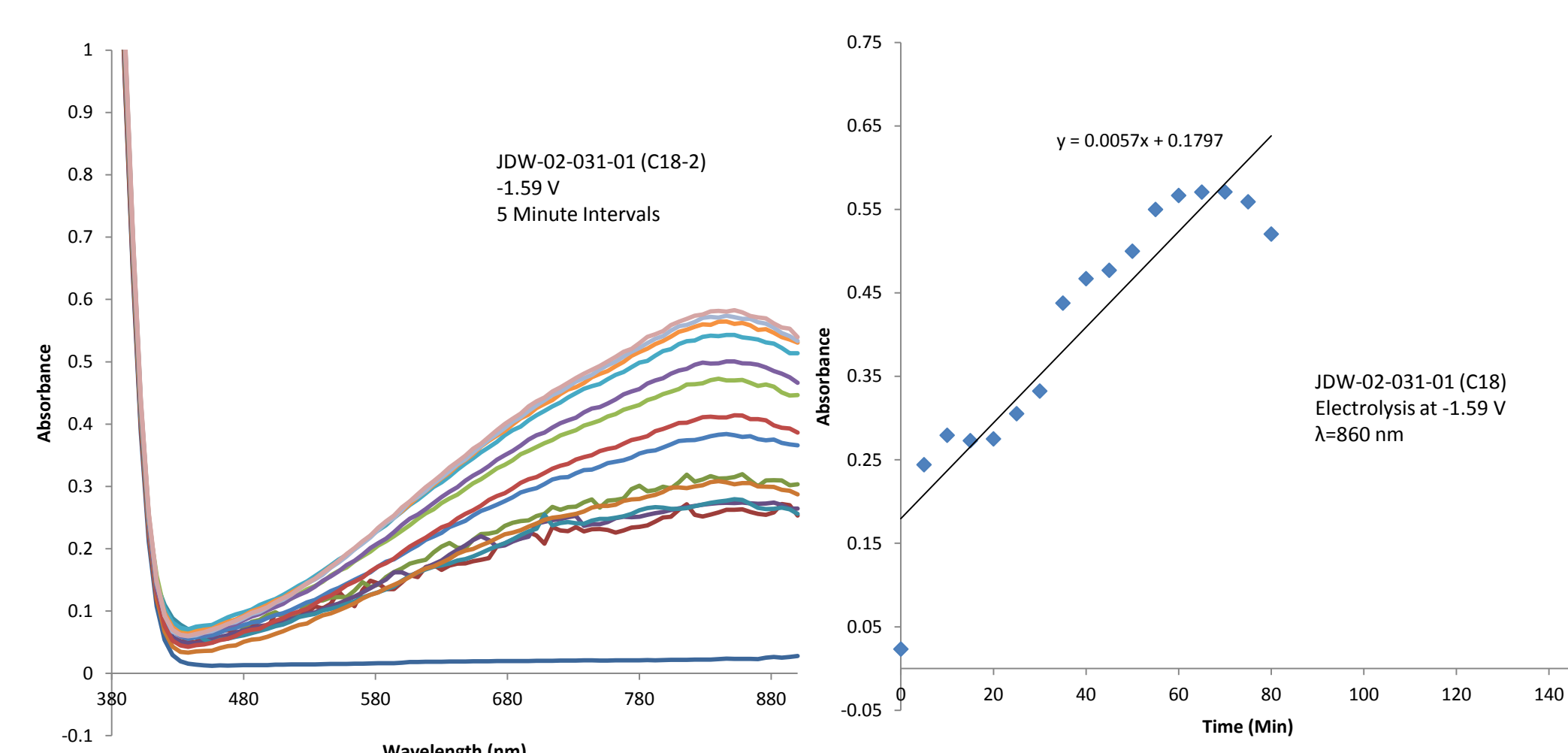


Figure 7. Overlay of various five minute intervals of the C18-2 molecule's UV spectra's during electrolysis (left), and a time analysis of the absorbance at a wavelength of 860 nm to approximate the rate of reduction (right).

- Time to maximum absorbance decreases with increasing length of carbon tail
- Maximum absorbance increases with increasing length of carbon tail
- No difference in reduction between the two C18 molecules

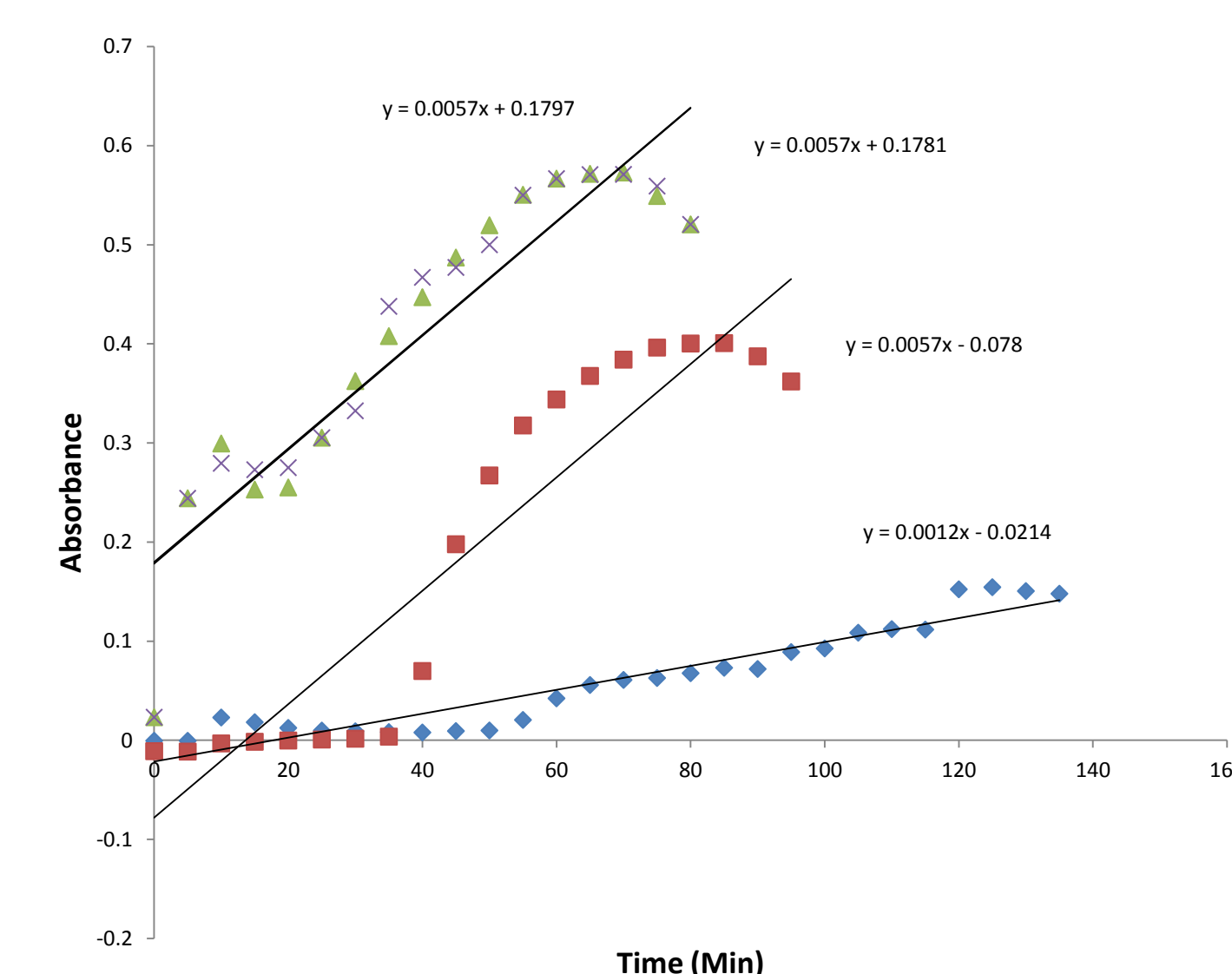


Figure 8. A comparison of the various molecules rates of reductions and maximum absorbances.

When comparing the length of the tails with the maximum absorbance reached, there is a clear correlation indicating the longer carbon tailed molecules reach a higher absorbance. The maximum absorbances of C8, C12, C18-1, and C18-2 were 0.15413, 0.40075, 0.58065, and 0.57847, respectively.

When comparing the length of the tails with the time it took to reach its maximum absorbance, there is a correlation indicating that longer tailed molecules take less time to reach its maximum absorbance. However, when comparing their rates, C12, C18-1, and C18-2 all have the same rate of 0.0057, which is higher than C8 at 0.0012.

Conclusions

The data suggests an interesting phenomenon occurring in these polyoxotungstates. When the kinetics of the experiments are analyzed, there is a correlation with tail length and maximum absorbance attainable. The longer the length of the carbon tails the higher maximum absorbance the molecule has. Also, the longer length of the carbon tails has a shorter time to reach maximum absorbance. And the rate of reduction is constant at 0.0057, except for C8, which is lower at 0.0012.

Further research needs to be performed to understand why this phenomenon is occurring. Also, Keggin type polyoxotungstates should be observed to see if the same data occurs. These Keggin type POMs have a smaller head group, which would put more emphasis on the carbon tails to conclude whether the tails are the sole source of the trend, or whether the head group plays a role in the trend seen.

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For further information

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