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Spectroelectrochemical Studies of the Reductive Intermediates of Anthraquinone-2,6-Disulfonate in Aqueous Media

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LOYOLA UNIVERSITY CHICAGO

SPECTROELECTROCHEMICAL STUDIES OF THE REDUCTIVE INTERMEDIATES OF ANTHRAQUINONE-2,6-DISULFONATE IN AQUEOUS MEDIA

A DISSERTATION SUBMITTED TO THE FACULTY OF THE GRADUATE SCHOOL IN CANDIDACY FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

PROGRAM IN CHEMISTRY

BY

ANNA A. WEISS

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For my father
# TABLE OF CONTENTS

ACKNOWLEDGMENTS iii

LIST OF FIGURES ix

LIST OF TABLES xix

LIST OF ABBREVIATIONS xx

ABSTRACT xxii

CHAPTER I: INTRODUCTION 1
    Purpose and Goals 1
    Introduction to Clay Minerals 1
    NAu-2 and AQDS 6
    Anthraquinone-2,6-disulfonate 7

CHAPTER II: EXPERIMENTAL METHODS 11
    Reagents 11
    Methods 12
        Preparation of Clay Suspension 12
        Cyclic Voltammetry 13
        Spectroelectrochemical Cell 22
            Spectroelectrochemical Cell Assembly and Data Acquisition 22
            Calibration of the Spectroelectrochemical Cell and Determination of Cell Path 23
        Cell Path Determination 24
    Preparation of ITO slide 25
    Electrochemical Measurements 26
    Batch Reactor Experiments 26
    FT-IR ATR 29
    OTTLE Cell 30
        Determination of max absorption of OTTLE cell using K₃[Fe(CN)₆] 32
        Nernst Analysis 34
        Determination of OTTLE Cell iR error 36
        The Potential Step Experiment 37
        Sampled current vs. Applied Potential Experiments 38

CHAPTER III: AQDS: REDUCTION BY SODIUM DITHIONITE 43
    The Pourbaix Diagram 43
    Dithionite Batch Reactor Experiments 46
    The Four Stages of AQDS Reduction Reaction 47
APPENDIX D: STATISTICAL VALUES FROM ORIGIN PRO FOR PEAK DECONVOLUTION

REFERENCES

VITA
LIST OF FIGURES

Figure 1. Illustration of layer structure of smectite 2
Figure 2. Illustration of octahedral sheet of smectite 4
Figure 3. Illustration of 2:1 layer structure of smectite 5
Figure 4. 9,10-anthraquinone-2,6-disulfonate, fully oxidized and fully reduced forms 7
Figure 5. AQDS Nine-member square scheme 8
Figure 6. N Au-2 Clay in its raw solid state and in suspension 13
Figure 7. Simulation of applied potential vs. time; Scan rate = 100 mV/s 15
Figure 8. Example of a CV conducted with K\textsubscript{3}Fe(CN)\textsubscript{6}, [K\textsubscript{3}Fe(CN)\textsubscript{6}], 2.0 mM; [KCl], 0.20M 16
Figure 9. Sample CVs at different scan rates: 5, 25, 50 and 100 mV/s, [K\textsubscript{3}Fe(CN)\textsubscript{6}], 2.0 mM; [KCl], 0.20 20
Figure 10. Peak current as a function of square root of scan rate. Demonstrates that CV data shown in Figure 9 obeys Randles-Sevcik equation 21
Figure 11. Photo of Spectroelectrochemical cell used in batch experiments 23
Figure 12. CVs conducted with K\textsubscript{3}Fe(CN)\textsubscript{6} standard in spectroelectrochemical cell at scan rates 1, 20, 50, and 100 mV/s. Inset: Plot of peak current as a function of \nu 24
Figure 13. Determination of spectroelectrochemical path length via titration of K\textsubscript{3}Fe(CN)\textsubscript{6} with ascorbic acid 25
Figure 14. Batch reactor assembly: spectroelectrochemical cell, reaction vessel and peristaltic pump 29
Figure 15. OTTLE cell construction 30

Figure 16. Determination of linear range of OTTLE cell with $K_3Fe(CN)_6$ 32

Figure 17. Determination of OTTLE cell volume with $K_3Fe(CN)_6$ 33

Figure 18. Simulated Nernst plot 35

Figure 19. Determination of OTTLE cell iR error: Nernst plot for potential step experiment conducted with $K_3Fe(CN)_6$ 37

Figure 20. Sample data. Current vs. time plot. NAu-2/AQDS Series, $[AQDS] = 2.4$ mM; unbuffered aqueous media 39

Figure 21. Simulation of current and $[CR]/[CO]$ vs. $E_{applied}$ curve 42

Figure 22. Pourbaix diagram for AQDS with 9-member square scheme 45

Figure 23. The four phases in the reduction of AQDS by $Na_2S_2O_4$ as monitored by the open circuit potential at pH 9.4 47

Figure 24. Simultaneous monitoring of the visible spectrum and OCP. pH 9.4 bicarbonate buffered; $[AQDS] = 2.87$ mM; $[DIT] = 11.5$ mM; $[DIT]/[AQDS] = 4.0$ 48

Figure 25. Illustration of shrinking core model 50

Figure 26. Linear relationship for conversion time as a function of $\frac{1}{[DIT]_{initial}}$ for batch experiments 51

Figure 27. Visible spectrum in the reduction reaction of AQDS. First three minutes in the reaction. Growth of peaks at 410 nm and 479 nm. Peak shift from 479 nm to 481 nm. pH 9.4 bicarbonate buffered; $[AQDS] = 0.62$ mM; $[DIT] = 11.5$ mM 52

Figure 28. Nernst Plot for the 481 nm band for the first three minutes in the AQDS reduction reaction based on data from Figure 27 (pH 9.4; $[AQDS] = 5.63$ mM; $[DIT] = 11.3$ mM) 53

Figure 29. Visible spectrum in the reduction reaction of AQDS. 1st 5 minutes in the reaction of AQDS and dithionite. Very slight growth in spectral peaks is observed until they ultimately merge; pH 9.4 bicarbonate buffered; $[AQDS] = 5.63$ mM; $[DIT] = 11.3$ mM 54
Figure 30. Simultaneous monitoring of the visible spectrum and OCP; 
[DIT]/[AQDS] = 1.3; Lag phase is absent; pH 9.4 bicarbonate buffered; 
[AQDS], 8.6 mM, [DIT], 11.5 mM 56

Figure 31. Simultaneous monitoring of the visible spectrum and OCP 
[DIT]/[AQDS] = 1.92; pH 9.4 bicarbonate buffered; [AQDS], 5.7 mM, 
[DIT], 11.5 mM; Lag phase is present 57

Figure 32. Lag phase of the reaction of AQDS with dithionite. Absorbance at 
727 nm is shown; pH 9.4, bicarbonate buffered; [AQDS], 5.63 mM, 
[DIT], 11.3 mM 59

Figure 33. Absorbance spectra taken during the experiment in Figure 32 from 
6 to 110 minutes; pH 9.4, bicarbonate buffered; [AQDS], 5.63 mM, 
[DIT], 11.3 mM 60

Figure 34. Duration of lag phase is proportional to unreacted mmol DIT. 
Data is plotted for two sets of experiments ([DIT] = 11mM and 
[DIT] = 22 mM) in which AQDS was varied; Data from DIT control 
experiments [AQDS] = 0; pH 9.4, bicarbonate buffered 62

Figure 35. Data exemplifying relationship from Figure 34 for [DIT] = 22mM; 
[AQDS] = 8.6 mM, 5.7 mM, 2.9 mM; pH 9.4, bicarbonate buffered 63

Figure 36. Control experiment with Na$_2$S$_2$O$_4$ at pH 9.4, [DIT], 11.3 mM; 
Absorbance at 727 nm band and OCP plotted against time. pH 9.4, 
bicarbonate buffered solution 64

Figure 37. Deconvoluted spectra for first five minutes in batch reaction for 
AQDS; pH 9.4 bicarbonate buffered; [AQDS], 5.63 mM; 
[DIT], 11.3 mM. [DIT]/[AQDS] = 2.00 65

Figure 38. Emergence of charge transfer bands in 600 – 750 nm region. 
Charge transfer bands appear and begin to grow. Inset: Monitoring the 
727 nm band and OCP over reaction time; pH 9.4 bicarbonate buffered; 
[AQDS], 5.63 mM; [DIT], 11.3 m. [DIT]/[AQDS] = 2.00 66

Figure 39. Charge transfer bands reach a maximum and begin to decrease along 
with CT bands. Inset: Monitoring the 727 nm band and OCP over reaction time; pH 9.4 bicarbonate buffered; [AQDS], 5.63 mM; 
[DIT], 11.3 mM. [DIT]/[AQDS] = 2.00 67
Figure 40. Isobestic point formation during dimer phase; pH 9.4 bicarbonate buffered; [AQDS], 2.873 mM; [DIT], 11.5 mM. [DIT]/[AQDS] = 4.00

Figure 41. Nernst analysis based on data from Figure 38 and Figure 39; pH 9.4 bicarbonate buffered; [AQDS], 5.63 mM; [DIT], 11.3 mM. [DIT]/[AQDS] = 2.00

Figure 42. Nernst Plot to accompany Figure 43. Nernst analysis of 500 nm band based on descent; pH 9.4 bicarbonate buffered; [AQDS], 0.62 mM; [DIT], 11.5 mM. [DIT]/[AQDS] = 18.5

Figure 43. AQDS concentration was decreased in order to maintain 400 and 500 nm peaks within the linear range of the instrument. A small rise and fall in the 500 nm peak is observed around t = 148 minutes (E = -649 mV). pH 9.4 bicarbonate buffered; [AQDS], 0.62 mM; [DIT], 11.5 mM. [DIT]/[AQDS] = 18.5

Figure 44. t = 110 minutes; composite peak after deconvolution superimposed on raw data. pH 9.4 bicarbonate buffered; [AQDS], 0.62 mM; [DIT], 11.5 mM

Figure 45. t = 110 minutes to 141 minutes; Dimer formation: CT bands increase in absorbance intensity. pH 9.4 bicarbonate buffered; [AQDS], 0.62 mM; [DIT], 11.5mM

Figure 46. Deconvoluted spectra; t = 148 minutes to t = 153 minutes (-649 mV to -506 mV). As dimer forms—peak shift occurs from 482 nm to 500 nm. pH 9.4 bicarbonate buffered; [AQDS], 0.62 mM; [DIT], 11.5 mM

Figure 47. Deconvoluted spectra; t = 153 minutes to t = 172 minutes (-506 mV to -430 mV). pH 9.4; [AQDS], 0.62 mM; [DIT], 11.5 mM

Figure 48. Length of dimer phase is proportional to the initial concentration of AQDS

Figure 49. Peak height of 727 nm band within the charge transfer region is linearly related to the initial concentration of AQDS. Experiments for which three different concentrations of DIT were used

Figure 50. Completion of the reaction. OCP reaches its final resting potential; pH 9.4 bicarbonate buffered; [AQDS], 5.63; [DIT], 11.3 mM; [DIT]/[AQDS] = 2.00
Figure 51. FT-IR ATR Difference spectra compared to spectrum at -656 mV; pH 9.4 bicarbonate buffered; [AQDS], 6.30; [DIT], 19.3 mM

Figure 52. FT-IR ATR Difference spectra: Inset of Figure 51; FT-IR ATR Difference spectra compared to spectrum at -656 mV; pH 9.4 bicarbonate buffered; [AQDS], 6.30; [DIT], 19.3 mM

Figure 53. FT-IR data. Change in peak intensity as a function of potential. Log term based on peak intensity; pH 9.4 bicarbonate buffered; [AQDS], 6.30; [DIT], 19.3 mM

Figure 54. Re-reduction of AQDS with a second addition of Na$_2$S$_2$O$_4$; pH 9.4 bicarbonate buffered; [AQDS], 8.60 mM; [DIT], 1st portion, 34.4 mM, 2nd portion, 22.3 mM

Figure 55. Color change of AQDS solution during its reduction reaction with dithionite

Figure 56. Absorbance and potential vs. time plot; pH 11.6 phosphate buffered; [AQDS], 8.60; [DIT], 44.9 mM

Figure 57. Raw data; spectra; t = 675 min to 765 min. Isobestic point occurs between the 544 nm composite peak and the 720 nm peak; pH 11.6 phosphate buffered; [AQDS], 8.60; [DIT], 44.9 mM

Figure 58. t = 745 min. Deconvoluted visible spectrum with cumulative spectrum; composite peak at 544 nm deconvoluted into its constituents: 416 nm, 465 nm, 544 nm, 547 nm and 596 nm; pH 11.6 phosphate buffered; [AQDS], 8.60; [DIT], 44.9 mM

Figure 59. t = 765 to 895 minutes. Visible spectra, raw data; pH 11.6 phosphate buffered; [AQDS], 8.60; [DIT], 44.9 mM

Figure 60. t = 765 to 895 minutes. Deconvolution of peaks. Peak shift occurs from 550 nm to 510 nm; pH 11.6 phosphate buffered; [AQDS], 8.60; [DIT], 44.9 mM

Figure 61. Nernst plot of 560 nm and 727 nm. pH 11 phosphate buffered; [AQDS], 8.60mM; [DIT], 44.9mM

Figure 62. AQDS UV-vis spectra; pH 11.6; (A). Deconvoluted and cumulative spectrum at t = 765 minutes (-510 mV) (B). Deconvoluted and cumulative spectrum at t = 855 minutes (-445mV)
Figure 63. t = 1089 min; Deconvoluted peaks; pH7; [AQDS], 8.60mM; [DIT], 44.9mM; [DIT]/[AQDS] = 5.2; Inset: spectra of raw data from t = 1080 to 1099 minutes

Figure 64. Absorbance and potential vs. time plot; pH7; [AQDS], 8.60mM; [DIT], 44.9mM. [DIT]/[AQDS] = 5.2

Figure 65. Visible spectra, deconvoluted spectra; t = 1099 minutes to 1349 minutes; pH7; [AQDS], 8.60mM; [DIT], 44.9mM. [DIT]/[AQDS] = 5.2

Figure 66. Visible spectrum, raw data t = 1349 minutes to 1624 minutes; pH7; [AQDS], 8.60mM; [DIT], 44.9mM. [DIT]/[AQDS] = 5.2

Figure 67. The Pourbaix diagram including experimental data

Figure 68. CPE experiment of AQDS at pH 9.4 bicarbonate buffered; [AQDS], 3.15 mM; [KCl], 0.2 M; Spectra shown is for E = -350 mV to -600 mV. Inset: Spectra for -60 mV to -340 mV

Figure 69. Absorbance vs. cell potential data at 411 nm, 500 nm, and 727 nm. Reduction and oxidation are shown; pH 9.4 bicarbonate buffered; [AQDS], 3.15 mM; [KCl], 0.2 M

Figure 70. Nernst analysis for 411 nm of raw data shown in Figure 69; pH 9.4 bicarbonate buffered; [AQDS], 3.15 mM; [KCl], 0.2 M

Figure 71. Nernst analysis for 500 nm of raw data shown in Figure 69; pH 9.4 bicarbonate buffered; [AQDS], 3.15 mM; [KCl], 0.2 M

Figure 72. Nernst analysis for 727 nm of raw data shown in Figure 69; pH 9.4 bicarbonate buffered; [AQDS], 3.15 mM; [KCl], 0.2 M

Figure 73. Potential step experiment: AQDS at pH 9.4. [AQDS], 17.2 mM; [KCl], 0.2 M; Visible spectra showing growth of 406 and 511 nm bands and charge transfer bands as potential is stepped from -400 mV to -480 mV

Figure 74. Decrease in CT bands as potential is stepped from -490 mV to -600 mV; pH 9.4. bicarbonate buffered; [AQDS], 17.2 mM; [KCl], 0.2 M
Figure 75. Plot of absorbance at three wavelengths vs. potential; pH 9.4. bicarbonate buffered; [AQDS], 17.2 mM; [KCl], 0.2 M

Figure 76. Plot of absorbance at 727 nm vs. potential; pH 9.4. bicarbonate buffered; [AQDS], 17.2 mM; [KCl], 0.2 M

Figure 77. pH 11.6; Spectral changes as the potential is stepped from -340 mV to -620 mV; pH 11.6 phosphate buffered; [AQDS], 3.15 mM; [KCl], 0.2 M

Figure 78. Difference spectrum produced by subtracting spectrum at -520 mV from spectrum at -610 mV. pH 11.6 phosphate buffered [AQDS], 3.15 mM; KCl], 0.2 M

Figure 79. Plot of absorbance at three wavelengths vs. potential. pH 11.6, phosphate buffer; [AQDS], 3.15 mM; KCl], 0.2 M

Figure 80. Spectral change as potential is stepped from + 280 mV to -900 mV; [AQDS], 3.15 mM; KCl], 0.2 M; pH 7, phosphate buffer

Figure 81. Absorbance vs. applied potential from 340 mV to -520 mV. [AQDS], 3.15 mM; KCl], 0.2M; pH 7; phosphate buffer

Figure 82. Change in spectra as a function of applied potential from+50 mV to -470 mV; [AQDS], 3.15 mM; KCl], 0.2 M; pH 5. acetate buffer

Figure 83. Spectra at -320 mV and -470 mV. 423 nm band increases at a much greater rate than 393 nm band. [AQDS], 3.15mM; KCl], 0.2M; pH 5 acetate buffer

Figure 84. Absorbance vs. applied potential of raw data. +100 mV to -470 mV. [AQDS], 3.15mM; KCl], 0.2M; pH 5, acetate buffer

Figure 85. Spectral change as potential is stepped from + 50 mV to -340 mV; [AQDS], 3.15mM; KCl], 0.2M; pH 3, phosphate buffered

Figure 86. Absorbance at 423 nm as a function of applied potential [AQDS], 3.15mM; KCl], 0.2M; pH 3; phosphate buffer
Figure 87. CVs of AQDS in pH 11.6 phosphate buffer; scan rates 5, 25, 50 and 100 mV/s. [AQDS], 3.15mM; KCl], 0.20 M. Inset: CVs of AQDS at pH 11.6 obeys Randles-Sevcik equation for peak current proportionality to square root of scan rate

Figure 88. CVs of AQDS in pH 9.4 buffer; scan rates 5, 25, 50 and 100 mV/s; [AQDS], 3.15mM; KCl], 0.20 M

Figure 89. CVs of AQDS at pH 7 PIPES buffer; scan rates 5, 25, 50 and 100 mV/s; [AQDS], 3.15mM; KCl], 0.20 M

Figure 90. CVs of AQDS in pH 3 phosphate buffer; scan rates 5, 25, 50 and 100 mV/s; [AQDS], 3.15mM; KCl], 0.20 M

Figure 91. Current vs. time plot. Unbuffered; NAu-2/AQDS Series, [AQDS] 2.4 mM, Eapplied = -150 mV and -550 mV

Figure 92. Sampled current, /i/ vs. Eapplied curve based on data shown in Figure 91; [AQDS] 2.4 mM; unbuffered solution

Figure 93. Simulation of current and [CR]/[CO] vs. Eapplied curve

Figure 94. Sampled current and absorbance vs. Eapplied curve; AQDS in bicarbonate buffered pH 9.4 aqueous solution; [AQDS], 2.37 mM; KCl], 0.20 M

Figure 95. Sampled current vs. Eapplied curve for NAu-2/AQDS series; [AQDS], 2.0 mM, unbuffered; Deconvoluted Eimax peaks

Figure 96. Sampled current, /i/, vs. Eapplied for NAu-2/AQDS series; Resolved Eimax peaks; unbuffered solution

Figure 97. Absorbance (from deconvoluted spectra) and sampled current vs. applied potential; AQDS Series; [AQDS], 2.0 mM, unbuffered solution

Figure 98. Absorbance vs. potential plot based on deconvoluted spectra; AQDS Series; [AQDS], 2.0 mM unbuffered solution

Figure 99. Absorbance vs. potential plot; AQDS Series; [AQDS], 2.4 mM unbuffered solution
Figure 100. Deconvoluted spectra; AQDS Series; [AQDS], 2.0 mM; 
$E_{\text{applied}} = -560$ mV to -780 mV  155

Figure 101. Deconvoluted spectra; AQDS Series; [AQDS], 5.5 mM; 
$E_{\text{applied}} = -570$ mV to -850 mV  156

Figure 102. Deconvoluted spectra; AQDS Series; [AQDS], 2.0 mM; 
$E_{\text{applied}} = -780$ mV to -850 mV  157

Figure 103. Absorbance in the 650 to 800 nm range for both series in 
unbuffered aqueous solutions at -490 mV  158

Figure 104. Absorbance vs. Potential for 702, 730, 402 and 498 nm; based on 
deconvoluted spectra; AQDS Series; [AQDS], 2.0 mM, unbuffered 
solution; $\lambda_{\text{max,700}}$ occurs at -520 mV  159

Figure 105. Sampled current, $i'$, vs. $E_{\text{applied}}$ for NAu-2/AQDS series; 
unbuffered solution  161

Figure 106. Absorbance (from deconvoluted spectra) and sampled current vs. 
applied potential; NAu-2/AQDS Series; [AQDS], 2.0 mM, unbuffered 
solution  162

Figure 107. Absorbance vs. potential plot; NAu-2/AQDS Series; 
[AQDS], 2.4 mM unbuffered solution  163

Figure 108. Absorbance (based on deconvoluted data) vs. potential for 
757 nm band. NAu-2/AQDS Series; [AQDS], 2.4 mM; 
unbuffered solution  164

Figure 109. Deconvoluted spectra; NAu-2/AQDS Series; [AQDS], 5.5 mM 
unbuffered solution; $E_{\text{applied}} = -450$ mV to -590 mV  165

Figure 110. Absorbance vs. potential plot; SWy-1/AQDS experiment; [AQDS], 
2.4 mM unbuffered solution  166

Figure 111. Sampled current vs. Eapplied; AQDS and NAu-2/AQDS 
Experiments at increased concentrations  168

Figure 112. Absorbance (based on raw data) vs. E plots based on raw data for 
AQDS and NAu-2/AQDS series, 5.5 mM AQDS; unbuffered solution  169
Figure 113. UV-Vis spectra, deconvoluted peaks at -590 mV; NAu-2/AQDS Series; [AQDS], 19.6 mM, unbuffered solution

Figure 114. Sampled current $i_{\text{max1}}$ vs. [AQDS]$_{\text{initial}}$, mM for AQDS and NAu-2/AQDS experiments; unbuffered solution

Figure 115. AQDS and NAu-2/AQDS mixture; 2.04 mM AQDS for both CVs. Scan rate 25 mV/s

Figure 116. CVs of K$_3$Fe(CN)$_6$; scan rates 5, 25, 50 and 100 mV/s. [K$_3$Fe(CN)$_6$], 2.0 mM; [KCl], 0.20 M

Figure 117. Sampled current, $i/$ vs. $E_{\text{applied}}$ for AQDS and NAu-2/AQDS series; [AQDS], 1.2 mM; unbuffered solution

Figure 118. Sampled current, $i/$, vs. $E_{\text{applied}}$; for AQDS and NAu-2/AQDS series; [AQDS], 2.0 mM; unbuffered solution

Figure 119. Sampled current, $i/$, vs. $E_{\text{applied}}$; for AQDS and NAu-2/AQDS series; [AQDS], 2.4 mM; unbuffered solution

Figure 120. Sampled current, $i/$ vs. $E_{\text{applied}}$ for AQDS and NAu-2/AQDS series; [AQDS], 5.5 mM; unbuffered solution

Figure 121. Sampled current, $i/$, vs. $E_{\text{applied}}$; SWY1/AQDS, NAU2/AQDS and AQDS; [AQDS], 2.4 mM; unbuffered solution
LIST OF TABLES

Table 1. \( \lambda_{\text{max}} \) corresponding to several of the AQDS forms 8

Table 2. Buffers used in studies 12

Table 3. pH changes for select experiments 140

Table 4. \( i_{\text{max}} \) for the AQDS series and NAu-2/AQDS series. 
\( E_{\text{applied}} \) vs. Ag/AgCl 147

Table 5. Nernst Analysis of select raw and deconvoluted spectral data 149

Table 6. Observed and calculated conversion points of select AQDS and Clay/AQDS experiments. Based on raw data 154

Table 7. List of Experimental \( E^\circ \) values 189

Table 8. Statistical Values from Origin Pro for Peak Deconvolution 193
LIST OF ABBREVIATIONS

Abs  absorbance
ap   apical
AQ   Anthraquinone
AQS  Anthraquinone sulfonate
AQDS Anthraquinone-2,6-disulfonate
CEC  cation exchange capacity
CPE  controlled potential electrolysis
CV   cyclic voltammogram
DIT  dithionite
hmp  hexametaphosphate
i_{pc} cathodic peak current
i_{pa} anodic peak current
MV   methyl viologen
NAu-2 Nontronite Australia
OCP  open circuit potential
oct  octahedral
OTTLE optically transparent thin layer electrochemical
PZNC point of zero net charge
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q</td>
<td>quinone in general; benzoquinone</td>
</tr>
<tr>
<td>SCM</td>
<td>shrinking core model</td>
</tr>
<tr>
<td>SWy-1</td>
<td>Smectite Wyoming Montmorillonite</td>
</tr>
<tr>
<td>TOT</td>
<td>tetra-octa-tetra</td>
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ABSTRACT

Reactive intermediates in the reduction of anthraquinone-2,6-disulfonate (AQDS) by dithionite combine to form a transient dimer which has shown to give rise to a series of charge transfer bands in the visible range (600-750 nm). Additional wavelengths associated with these intermediate species have been observed at wavelengths 402, 444 and 510 nm. These transient intermediates are generated as dithionite decomposition products re-oxidize AQDS. Evidence of the dimer was also found in experiments in which reduction of AQDS was achieved electrochemically by the use of a potentiostat. This implies three things: 1. dithionite is not required for dimerization of reactive intermediates; 2. the dimerization reaction is reversible; 3. the dimer formation reaction involves an intermediate common to both oxidation and reduction.

In addition our studies have also led to evidence of such a dimer in unbuffered aqueous solution at neutral pH. Dimer formation is enhanced in the presence of clay. Clay appears to stabilize the dimer species via both kinetic and thermodynamic effects.
CHAPTER I

INTRODUCTION

Purpose and Goals

The purpose of these studies is to investigate the spectroelectrochemical properties of the electron carrier, anthraquinone-2,6-disulfonate—a polycyclic quinone derivative well-known for its ability to aid in the redox processes of soils and clays.

Introduction to Clay Minerals

Clay minerals, a class of hydrated layered parallel sheet silicates, make up a larger class of silicate minerals.\(^1,2\) Tetrahedral and octahedral sheets, the building blocks of clays, consist of networks of corner sharing tetrahedra or edge sharing octahedra, respectively.\(^2\) A layer is the smallest repeating unit of combined sheets in which oxygen atoms are shared.\(^2\)

Tetrahedral sheets are composed of individual silica/oxygen tetrahedra.\(^2\) These tetrahedra are linked into a hexagonal pattern with the apical oxygens pointing down into the interior of the clay crystal and the tetrahedral basal oxygens forming the outer layer of the clay crystal.\(^2\) Common tetrahedral cations are Si, Al, and sometimes Fe\(^{3+}\).\(^2\) The clays studied here consist of two tetrahedral sheets sandwiching a central octahedral sheet forming what is known as a TOT for tetra-octa-tetra or 2:1 pattern (Figure 1).
The apical oxygens (Figure 2) of the tetrahedron which point down (or up) are linked to an octahedral sheet composed of a cation (commonly Al, Mg, Fe$^{3+}$, and/or Fe$^{2+}$) with oxygen and hydroxyl ligands. For every two apical oxygens there are two Si$^{4+}$ and 6 basal oxygens. The basal oxygens each bridge between two tetrahedral so the net formula is (2 apical + 3/2 basal) x 2 oxygens = ten O for every two Si.

![Figure 1. Illustration of layer structure of smectite.](image)


Both the octahedral sheet and tetrahedral sheet chemistry affect the electrochemistry of the clay layer. The octahedral sheet can be described as trioctahedral in which every octahedral central cavity is occupied. For example, in an octahedral sheet, the oxygen ligands are linked. Therefore the charge of each oxygen ligand is distributed toward three octahedra so that the oxygens have a formal net negative charge of -1/3. Thus the central cavity experiences (-1)(1/3)(6) for a net negative charge of -2. Consequently, the preferred crystal lattice cation is divalent in charge such as Mg$^{2+}$ or
Fe$^{2+}$ for a trioctahedral sheet. The more common cation in 2:1 clays, however, is trivalent aluminum. In this case the central cavity would end up with a net excess charge of +1. As a result 1 out of every 3 sites must be vacant for charge neutrality. This arrangement of site occupancy is called dioctahedral. Nontronite Australia-2, NAu-2, is an example of a dioctahedral clay and is incidentally the clay studied herein. A net negative charge can arise from the octahedral sheet if a dioctahedral aluminum containing clay has substitution of divalent ions for Al$^{3+}$. The oxygen atoms within clay may be apical, shared with tetrahedral sheet, octahedral, shared only with other octahedral, or basal, on the basal surface. The chemistry of clays also arises from the structure of the tetrahedral layer. The majority of 2:1 dioctahedral clays have isomorphous substitution for Si$^{4+}$ in the tetrahedral sheet (usually by Al$^{3+}$) and for Al$^{3+}$ in the octahedral sheet (by Fe$^{3+}$, Fe$^{2+}$, or Mg$^{2+}$) thereby imparting a net negative charge to the clay layer.
Net neutrality is reestablished by cations or cationic groups that reside in the interlayer space (Figure 3).\textsuperscript{2,7} Species that can occupy the interlayer space include: Group I and II cations such as K\textsuperscript{+}, Na\textsuperscript{+}, Ca\textsuperscript{2+}, Mg\textsuperscript{2+}, cationic organic molecules, non-ionic polar organic molecules and water.\textsuperscript{2}

The clays studied here are part of the class called smectites. Smectites are iron-rich phyllosilicates in which a clustering of iron occurs in the octahedral sheets.\textsuperscript{1,2} The smectite, SWy-1, has the following formula:\textsuperscript{3}

\[ \text{Na}_{0.23} \text{Mg}_{0.11}(\text{Al}_{1.54} \text{Fe}_{0.20}^{3+} \text{Fe}_{0.02}^{2+} \text{Mg}_{0.24})(\text{Si}_{3.80} \text{Al}_{1.20} \text{O}_{10})(\text{OH})_{2} \]

\textbf{Figure 2.} Illustration of octahedral sheet of smectite; \( \text{O}_{\text{ap}} = \) apical oxygen \( \text{O}_{\text{oct}} = \) octahedral oxygens. (Based on a figure found in Brigatti, M. F.; Galan, E.; Theng, B. K. G. (2006) Structures and Mineralogy of Clay Minerals. In Bergaya, F., Theng, B. K. G., & Lagaly, G. (Eds.), Handbook of Clay Sciences: Developments in Clay Science, Vol.1. (pp 19-86). Town, State: Elsevier Ltd.)\textsuperscript{2}
The nontronite, NAu-2 has the formula \( \text{Na}_{0.72} \text{Si}_{7.55} \text{Al}_{0.01} \text{Fe}_{0.42} \) \( \text{Al}_{0.52} \text{Fe}_{3.32} \text{Mg}_{0.7} \) \( \text{O}_{20} \text{(OH)}_4 \) : 

\[
M^+_{0.72} (\text{Si}_{7.55} \text{Al}_{0.01} \text{Fe}_{0.42}) (\text{Al}_{0.52} \text{Fe}_{3.32} \text{Mg}_{0.7}) \text{O}_{20} (\text{OH})_4 
\]

where \( M = \text{Ca, Na, K} \)

**Figure 3.** Illustration of 2:1 layer structure [http://webmineral.com/data/Nontronite.shtml](http://webmineral.com/data/Nontronite.shtml)

Some important properties of clays that make them invaluable to our research are their large surface area-to-mass ratio, the ability of some clays to swell or expand up to twenty times their own volume, their capacity for good intercalation, their high stability, and their large cation exchange capacity (CEC). A cation exchange capacity is a measure of smectites’ ability to adsorb cationic species from solution. Rapid exchange between cations balancing the crystal lattice negative charge and cations in solution shows that it
is reversible and diffusion controlled. A large CEC contributes to a clay’s electrochemical properties as an increase in layer charge is accompanied by an increase in CEC and consequently an increase in the smectite’s ability to fix interlayer cations. Variation of the CEC can influence electrocatalytic oxidation processes.\textsuperscript{8}

Charge transport in aquated clay films depends upon the presence of a mobile charge carrier. Mobility depends upon the strength and extent of interaction of the electroactive complex and other compensation ions with the exchange sites of the clay. For a strongly adsorbed electroactive species adsorbed at values greater than or equal to the CEC, the clay becomes electroactive. If the amount of adsorbed complex is less than the CEC, the clay particle is electroinactive.\textsuperscript{9}

**NAu-2 and AQDS**

Quinone-like substances, anthraquinone derivatives, and their dimers are just some examples of polycyclic compounds found in soils.\textsuperscript{10} This is not entirely surprising. Anthraquinones are known to facilitate electron transfer from an external electron source to the clay surface.\textsuperscript{11} In our research, anthraquinone-2,6-disulfonate, AQDS (Figure 4), was chosen as the electron carrier of interest in part due to its popularity in research regarding microbial reduction on iron-rich nontronites. We demonstrate in our research that AQDS forms a transient dimer as one of many reduction products in buffered moderately alkaline solution. We demonstrate that such a dimer forms in unbuffered aqueous solution and that its occurrence is enhanced when nontronite NAu-2 is present. Unbuffered solution was used to keep clay delaminated in order to make the basal surface accessible to AQDS and to prevent flocculation of the clay. Delamination eliminates the
inner layer space. To aid in delamination, sodium hexametaphosphate, hmp, was added to clay.

**Anthraquinone-2,6-disulfonate**

Anthraquinone-2,6-disulfonate, AQDS (Figure 4), and its derivatives play important roles in dye manufacturing and in electrochemical catalysis. In addition, its solubility in aqueous systems at physiological pH and its redox potentials make it a suitable surrogate for electron carrier in bacterial reduction systems such as microbial fuel cells.

![Figure 4](Image)

**Figure 4.** 9,10-anthraquinone-2,6-disulfonate, fully oxidized and fully reduced forms.

The many forms that AQDS may take in its acceptance of two electrons and two protons may be described by the 9-membered square scheme shown below (Figure 5):
Figure 5. AQDS Nine-member square scheme showing all the forms that AQDS may take. The fully oxidized and the fully reduced structures are shown in the upper left and lower right corners respectively.  

The reduction/oxidation reactions are written horizontally and protonation/deprotonation reactions vertically. The reduction of AQDS may be monitored spectroscopically (Table 1).

Table 1. $\lambda_{\text{max}}$ corresponding to several of the AQDS forms.

<table>
<thead>
<tr>
<th>Species</th>
<th>$\lambda_{\text{max}1}$ [(\varepsilon \times 10^3 \text{ M}^{-1} \text{ cm}^{-1})]</th>
<th>$\lambda_{\text{max}2}$ [(\varepsilon \times 10^3 \text{ M}^{-1} \text{ cm}^{-1})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>AQDS$^{-}$</td>
<td>403$^e$ [5.7]$^c$; (396$^f$ [6.4]$^i$)</td>
<td>515$^e$ [8.3]$^c$; (520$^i$ [7.8]$^i$)</td>
</tr>
<tr>
<td>AH$_2$DS$^{2+}$</td>
<td>385$^g$</td>
<td>420$^g$</td>
</tr>
<tr>
<td>AHDS$^{-}$</td>
<td>406$^g$</td>
<td>481$^g$</td>
</tr>
</tbody>
</table>
The species in the lower left-hand corner of the square scheme are theoretical due to their predicted negative pKa values and are rarely expected to contribute to the electrochemistry of anthraquinone. We therefore focus our attention to the first row and the rightmost portion of the square scheme which has been shaded in Figure 5. In moving from left to right across the first row of the 9-membered square scheme, AQDS accepts an electron to form a radical ion which will be referred to as the semiquinone. The semiquinone is short-lived and dimerizes if the reduction process is temporarily halted at the semiquinone, AQDS⁻.

Quantum mechanical calculations for the dimerization of two radical ions have shown dimerization to be unfavorable in a gas phase environment. Some evidence has shown that dimerization does occur given the proper environment.¹⁸,¹⁹,²⁰,²¹ Solvent effects play a strong role in making dimerization favorable. Polar solvents with large dielectrics aid in dimerization.

The thermodynamics of dimerization may also be explained in another way.²¹ For example, in their work with the electrodimerization of 9-cyanoanthracene, Mazine et. al. found that only the ΔHᵣ of a sigma bond can overcome the energy of strong electrostatic repulsion of the radical ion.¹⁹ Lacroix et. al. also suggest that a sigma bond may stabilize dimer formation.²¹ In their research they studied the dimerization of pyrrole (and oligopyrrole) radicals. Transition state coupling was apparently assisted by sigma bond effects. Transition state coupling distances are those occurring between the carbon atoms (C and C’) of the two reacting radical ions in forming the dimer.
They found a strong correlation between shorter transition state C—C’ coupling distances and lower activation energy. This is an odd finding because longer C—C’ coupling distances are usually associated with faster transition state acquisition and lower activation energies. However, an increase in electrostatic repulsions in the pyrrole dimer with shorter C—C’ distances is more than compensated by the additional stabilization afforded by frontier orbital interactions in the successive transition states.

The argument for π-dimerization has also been made. For dimerization to occur bonding energy, $E_{\text{bond}}$, must be greater than coulombic repulsion, $E_{\text{coul}}$. A metastable π-dimer might form when $E_{\text{bond}} \approx E_{\text{coul}}$. Examples of π-dimers forming between two radical anions have been found in literature. Solid-state calculations for tetracyanoethylene radical (TCNE) indicate that the metastable form is the most likely. Stabilization can be further achieved with shorter bond lengths when cation-mediated C—C occur.
CHAPTER II
EXPERIMENTAL METHODS

Reagents

NAu-2 and SWy-1 clays were purchased from the Clay Minerals Repository of The Clay Minerals Society and were modified by the procedures given below.

All reagents were purchased from suppliers and used without further purification. Sodium dithionite was purchased from J.T. Baker and sodium bicarbonate and sodium carbonate were purchased from Fisher Scientific. 9,10-Anthraquinone-2,6-disulfonate was purchased from Acros Organics. Distilled 18.2 MΩ-cm Millipure water was used in all aqueous solution preparations. A bicarbonate buffer, 0.12 M Na2CO3, 0.27M NaHCO3, ~pH 9.5 was used in the pH 9 experiments. A list of additional buffers used and their respective experiments is given below (Table 2).

Due to the instability of sodium dithionite and to compensate for losses due to its decomposition, a slight excess of dithionite is always required. Sodium hexametaphosphate was purchased from Fisher Chemical and added to clay solution to prevent it from flocculating.
### Table 2. Buffers used in studies.

<table>
<thead>
<tr>
<th>pH</th>
<th>Buffer</th>
<th>Concentration</th>
<th>Actual pH</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>Phosphate</td>
<td>0.020M H₃PO₄; 0.12M KH₂PO₄</td>
<td>3</td>
<td>CPE, CV</td>
</tr>
<tr>
<td>5</td>
<td>Acetate</td>
<td>0.130 M</td>
<td>5</td>
<td>CPE, CV</td>
</tr>
<tr>
<td>7</td>
<td>Phosphate</td>
<td>0.094M KH₂PO₄; 0.091M K₂HPO₄</td>
<td>7.6</td>
<td>Batch, CPE</td>
</tr>
<tr>
<td>7</td>
<td>PIPES</td>
<td></td>
<td>7</td>
<td>CPE, CV</td>
</tr>
<tr>
<td>9.4</td>
<td>Bicarbonate</td>
<td>0.12M Na₂CO₃; 0.27M NaHCO₃</td>
<td>9.4</td>
<td>Batch, CPE, CV</td>
</tr>
<tr>
<td>9</td>
<td>Bicarbonate</td>
<td>0.12M Na₂CO₃; 0.27M NaHCO₃</td>
<td>9.0</td>
<td>Batch/ATR</td>
</tr>
<tr>
<td>11</td>
<td>Phosphate</td>
<td>0.0M NaHPO₄ •7H₂O</td>
<td>11.67</td>
<td>Batch, CPE, CV</td>
</tr>
</tbody>
</table>

### Methods

Preparation of Clay Suspension.

In preparing the clay suspensions, 6g of raw NAu-2 mineral were first ground to a fine powder using a mortar and pestle (Figure 6). The powdered clays were then suspended in 200.0 mL, of 18.2 MΩ-cm Millipure water for 48 hours with minimal stirring. This allows coarse particles to settle. The top portion of the suspension was then decanted and stored. The suspension was then filtered using a 60 mL Buchner filter funnel (Ace Glass, Porosity A, 145-175 μL) to collect particles of less than 200 microns in size. Its concentration, in g/L, was obtained by drying a small measured volume of the suspension and recording its mass. The concentration of NAu-2 clay was determined to be 1.15 g/L.
Figure 6. NAu-2 Clay in its raw solid state and in suspension.

SWy-1 clay was sodium-exchanged by Thomas Nelson of Loyola University Chicago according to the protocol provided in the Master’s Thesis, Electrochemical Studies of Quinone on Clay-Modified Platinum Electrodes. It was further diluted to 1.15 g/L by 18.2 MΩ-cm DI H$_2$O to be equivalent to the concentration of NAu-2 clay suspension. The clays, NAu-2 and SWy-1, were analyzed by ICP-OES (Perkin Elmer ICP-OES Optima 8 x 00 Series) for sodium, calcium and iron content. The [Na]/[Ca] ratio was found to be 3/1 and 30/1 for NAu-2 and SWy-1 respectively.

**Cyclic Voltammetry**

Cyclic voltammetry is one of the trademark tools of the electrochemist. In working with an electroactive species, it proves its usefulness in determining the electrode mechanism, the number of electrons, $n$, transferred in the reaction, and the formal potential, E°, of the species.
In generating a cyclic voltammogram a potentiostat is used to apply a voltage to the working electrode in contact with species in solution. The applied potential is varied linearly with time at what is known as a scan rate, \( \nu \) (Figure 7). After reaching a desired potential, the scan is reversed. Thus the electroactive species undergoes a reduction and an oxidation; the order in which this occurs depends on its initial state. The oxidized and reduced forms of the species, ox and red, are commonly combined in the term, redox couple.

\[ ox + e^- \rightleftharpoons red \quad E^0 \]

The concentrations of the two species relative to each other obey the Nernst Equation when an electrode surface is in thermodynamic equilibrium. The assumption is made that the electrode kinetics are faster than mass transport (Equation [4]).

\[ E = E_{ox/red}^{\circ} - \frac{RT}{nF} \ln \left( \frac{[red]}{[ox]} \right) \]

The term cyclic voltammogram arises from this cyclical nature of reversing the direction of the scan.
Figure 7. Simulation of applied potential vs. time. Scan rate = 100 mV/s.

A cyclic voltammogram, or an i vs. $E_{\text{applied}}$ curve, is a product of measuring the current produced as a function of applied potential. Ferricyanide, a common standard used by electrochemists, is used to generate the sample cyclic voltammogram, CV, shown in Figure 8.
Figure 8. Example of a CV conducted with K$_3$Fe(CN)$_6$; $E_{1/2} = 438$ mV vs. NHE (Literature value 436 mV vs. NHE). [K$_3$Fe(CN)$_6$], 2.0 mM; [KCl], 0.20 M. $i_{pc}$ = cathodic peak current, $i_{pa}$ = anodic peak current.

The variation of current as a function of applied potential provides useful information. In the cathodic sweep, as potential is scanned in the negative direction at potentials sufficiently positive of the formal potential, no current flows. As the potential becomes increasingly negative the oxidized species at the electrode surface are reduced. As a result the concentration of oxidized species at the electrode surface decreases. This establishes a concentration gradient extending from the electrode surface into bulk solution. This results in greater flux to the electrode surface and consequently current will flow. As the formal potential is approached, current values, $i_c$, begin to increase. When
the ratio of the concentrations of reduced species to oxidized species on the electrode surface, \([\text{red}]/[\text{ox}]\) is equal to one, the formal potential is reached and \(E = E^\circ\).

At the cathodic peak current, \(i_{pc}\),

\[
[\text{red}]/[\text{ox}] = e = 2.7183
\]

therefore \(E = E^\circ + \frac{RT}{F}\)

After this point, the current begins its gradual descent to zero where \([\text{red}]/[\text{ox}] \to \infty\) and the concentration of oxidized species at the electrode surface is depleted. The scan is then reversed in the anodic sweep. The previously reduced species is now re-oxidized.

An anodic peak current, \(i_{pa}\) will be generated if the reaction is reversible. The midway point between \(i_{pc}\) and \(i_{pa}\) marks the \(E^\circ\)--the formal potential of the redox couple.

It should be noted that the decision regarding the order of the sweeps, negative vs. positive, cathodic vs. anodic, is dependent on the state of the electroactive species—whether it is in its oxidized or reduced form.

One of the most important defining features of an electrochemical reaction is its reversibility. A reversible electrode reaction is one for which the electrode kinetics are fast relative to mass transport, \(m_T\), (or diffusion) of species from the bulk solution to the electrode surface and vice versa. In superficial terms, if the electron transfer rate constant, \(k^\circ \gg m_T\) the reaction is considered reversible. Conversely, \(k^\circ \ll m_T\) constitutes an irreversible reaction. Early pioneers in electrochemistry, Matsuda and Ayabe, sought to mathematically define reversibility, \(\Lambda\), with certain boundary conditions by taking the ratio of \(k^\circ\) to \(m_T\).
where $D = \text{diffusion coefficient}$, $\nu = \text{scan rate}$, $R = \text{universal gas constant}$, $T = \text{temperature}$, in Kelvin, and $F = \text{Faraday’s constant}$. 

The mass transport term is defined by

$$m = \frac{D}{\delta}$$

where $\delta$ is the diffusion layer thickness which is correlated with time such that $\delta \approx \sqrt{Dt}$. 

The time of the experiment is inversely proportional to the voltage ramp (Figure 7), and

$$t \approx \frac{RT}{F\nu}^{24}$$

As such the mass transport term can also be defined as

$$m \approx \sqrt{\frac{D}{RT/F\nu}}$$

A large diffusion layer thickness renders a small value for mass transport. The parameters that Matsuda and Ayabe give are

$$\Lambda \geq 15 \quad \text{or} \quad \Lambda \geq 0.3 \nu^{1/2} \text{cm s}^{-1} \text{ constitutes a reversible reaction.}$$

$$15 > \Lambda > 10 \quad \text{or} \quad 0.3 \nu^{1/2} \text{cm}^{-1} > k^o > 2 \times 10^{-5} \nu^{1/2} \text{cm s}^{-1} \text{, a quasi-reversible reaction and}$$

$$\Lambda \leq 10^{-3} k^o \leq 2 \times 10^{-5} \nu^{1/2} \text{ an irreversible reaction.}$$

Several hallmarks of a reversible reaction are observed in a CV. One feature is that the ratio of cathodic peak current to anodic peak current, $\frac{i_{pc}}{i_{pa}} = 1$. In other words, the
same amount of current is derived from the cathodic reaction and the anodic reaction.

Figure 8 demonstrates how cathodic peak current and anodic peak current are measured.

A baseline is extrapolated from the linear portion of the scan preceding the peak.

The peak current for a reversible reaction obeys the Randles-Sevcik (Equation [6]).

\[ i_p = 2.72 \times 10^5 n^{3/2} D^{1/2} C^* \nu^{1/2} \]

where \( n \) = the number of mole of electrons transferred per mole of reactive species

\( D \) = the diffusion coefficient of the species

\( A \) = area of the planar working electrode

\( C^* \) = concentration of the species in bulk solution

and \( \nu \) = scan rate.

The Randles-Ševčik equation tells us that a reversible electrode reaction is controlled by diffusion. It also tells us that peak current varies linearly with the square root of the scan rate. This is exemplified in a CV experiment conducted with ferricyanide at scan rates of 5, 25, 50 and 100 mV/s. The CV shown in Figure 9 is consistent with the Randles-Sevcik equation; peak current is a function of scan rate (Figure 10).
Figure 9. Sample CVs at different scan rates: 5, 25, 50 and 100 mV/s (from the same experimental data as Figure 8). \([\text{K}_3\text{Fe(CN)}_6]\), 2.0 mM; [KCl], 0.20 M.
Figure 10. Peak current as a function of square root of scan rate. Demonstrates that CV data shown in Figure 9 obeys Randles-Sevcik equation.

Not evident from the equation but worth noting is that in a reversible electrochemical reaction, $E_p$, the potential associated with peak current, is not a function of scan rate. Consequently, one feature of a reversible electrode reaction is that the peak to peak separation for a one electron transfer is $\sim 60 \text{ mV}$—or $2.302RT/F$ if the diffusion coefficients of the reduced species and oxidized species are equal. In contrast an irreversible reaction has such relatively slow electron transfer kinetics that $E_p$ has been found to change with varying scan rate.
Spectroelectrochemical Cell

Spectroelectrochemical Cell Assembly and Data Acquisition

UV-visible spectra were recorded using an Ocean Optics I Base software. The spectroelectrochemical cell assembly (Delrin plastic by the Abbott Development Shop) is an integrated system which allows for simultaneous acquisition of spectral and electrochemical data (Figure 11). The spectroelectrochemical cell which incorporates a three-electrode system contains an 11 mL cell chamber which allows for light to pass through it. Spectral data were obtained with an Ocean Optics (USP2000 miniature fiber optic) spectrometer with a 75 W Xe-Hg lamp light source (Oriel Model no. 62551), equipped with OOIBASE 32 software. Light was delivered via a fiber optic cable and passed through the cell contents and the ITO slide where it was met by another fiber optic cable which terminated at the detector. The current setup allows for minimal light loss due to scattering as the distance between the accepting cable and the ITO slide is minimized at 2.5 mm.
Figure 11. Spectroelectrochemical cell used in batch experiments.

Calibration of the Spectroelectrochemical Cell and Determination of Cell Path

Cyclic voltammetry was one method used to calibrate the spectrochemical cell. K$_3$Fe(CN)$_6$ was used as the standard. Figure 12 shows CVs at scan rates 1, 20, 50 and 100 mV/s. The inset plot in Figure 12 shows that the Randles-Sevcik equation is obeyed for both cathodic and anodic peak currents. An ipc/ipa $\sim$ 1 was noted for all scan rates. An electron transfer of $n = 1.3$ is given for the lowest scan rate of 1 mV/s. The peak to peak separation increases as scan rates increase indicating either a greater than 1-electron transfer at higher scan rates or increased cell resistance. Therefore, truly reversible conditions are indicated only for the lowest scan rate of 1 mV/s. The lowest possible scan
rate allowed by the potentiostat, 1 mV/s, should be the standard used for all CVs conducted using the spectroelectrochemical cell.

Figure 12. CVs conducted with K$_3$Fe(CN)$_6$ standard in spectroelectrochemical cell at scan rates 1, 20, 50, and 100 mV/s. Inset: Plot of peak current as a function of $v^{1/2}$.

Cell Path Determination

The cell path length of the spectroelectrochemical cell was determined by titrating 50.0 mL of 0.50 mM K$_3$Fe(CN)$_6$ in 0.10 M pH 7 phosphate buffer with 0.060 M ascorbic acid. The amount of Fe(CN)$_6^{2-}$ present is calculated from the titration and is plotted against measured absorbance at 423 nm (Figure 13). Setting absorbance equal to $\epsilon b C$, the
slope, $\varepsilon_b$, may be determined. The literature value of $\varepsilon = 1.02 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$ was used.\textsuperscript{26,27,28}

The titration curve given below was generated and a value of 3.48 mm was calculated for $b$, the path length (Figure 13).

![Graph showing absorbance at 423 nm vs. [Fe$^{3+}$] mM with regression line and equation: $A = 3558 \times C$, $\varepsilon = 1.02 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$, $b = 0.348 \text{ cm}$]

**Figure 13.** Determination of spectroelectrochemical path length via titration of Fe(CN)$_6^{3-}$ with ascorbic acid.

**Preparation of ITO slide**

An Indium Tin Oxide, ITO coated, glass slide (Thin Film Devices; Substrate: TFD Supplied Eagle XG, Dimensions: 90 mm x 19.9 mm +/- 0.05 mm; thickness 1.1 mm; RI = 1.95) was used as the working electrode. The ITO glass slide was washed with 10 g Alconox per 1000 mL deionized water, dried and then left for 1 to 2 minutes to
equilibrate with air. The conductive side was determined by using a voltammeter to select the side with low resistance.

**Electrochemical Measurements**

A conventional three-electrode set-up was used. The ITO glass slide served as the working electrode. A miniature, HPLC grade BASi MW-2030 Ag/AgCl (saturated KCl) reference electrode was used for all measurements. The spectroelectrochemical cell assembly contains two fixed distance platinum wire counter electrodes which project into the 11 mL cell chamber where the sample solution is held.

Spectroelectrochemical studies allow one to simultaneously monitor optical changes and changes in the open circuit potential (OCP) as a reduction/oxidation reaction occurs. The OCP is the potential recorded by a high impedance voltmeter or potentiostat. High impedance implies that the instrument has such high internal resistance that negligible current passes through it such that the current measured can be attributed solely to the reaction being analyzed. Electrochemical measurements were made with Mastech MS-8218 Multimeter.

**Batch Reactor Experiments**

The buffer was purged with O$_2$-free inert gas such as N$_2$(g) or Ar(g) for one hour. The ITO glass slide was first equilibrated with 20 mL buffer solution for ~20 minutes. Equilibration was found to be necessary for stable optical and potential measurements as the ITO surface adsorbs some electrolytes. The reductant, Na$_2$S$_2$O$_4$, was added to the
buffer solution first. The sample to be reduced was added in solid form to the solution after the reductant was well dissolved.

The experimental design involves the above mentioned spectroelectrochemical cell consisting of a small chamber which serves as a 3.48 mm path length optical chamber, a glass slide with a conductive ITO coating which acts as the working electrode, a miniature Ag/AgCl reference electrode and a platinum counter electrode. Solution is allowed to circulate between the cell and a glass batch reactor vessel (the reaction chamber) by way of a peristaltic pump (VWR Variable Flow 0.4 to 85 mL/min Medium Flow) at a flow rate of 47 mL/min. Reagents are added to the system only through the batch reactor vessel at which time all the solution is circulated back to the batch reactor vessel. This is the only time that the system is made open to the atmosphere. All experiments are conducted under constant purging with an inert gas to maintain an oxygen-free system. All permanent joints between the vessel and tubing were sealed with a silicone-based sealant. The closed system batch reactor vessel assembly is shown in Figure 14.

Upon addition of reagents into the reaction vessel and circulation back to the spectro-electrochemical cell, the visible spectrum was acquired and the open circuit potential of the reaction occurring in the cell chamber was monitored every five minutes. The inlet port was then sealed with a 14/20 TS joint ground glass stopper for the remainder of the experiment to ensure a closed system.
pH measurements were made prior to and at the end of the experiment as a check. Dissolved oxygen levels were monitored continuously with the dissolved oxygen sensor (Pasco Pasport [sic]) and data was recorded with accompanying software (Data Studio Version 14.0.0.16).

Acquired spectral data was exported to Microsoft Office Excel where it was converted from intensity measurements to absorbance measurements. Fast Fourier Transform using Microsoft Office Excel software was performed on the absorbance data for smoothing. Data was then plotted as absorbance at various wavelengths for example, 411 nm, 500 nm, and 730 nm, as a function of time.

Additional spectral deconvolution was attained when necessary and able via Origin Pro Data Analysis and Graphing Software, Version 8.5, a data filtering program. In these instances, Origin Pro was capable of baseline correcting and of deconvoluting composite peaks into their constituents. A Gaussian peak type was chosen and all data analyzed by Origin Pro was tested for peak convergence. Limits were set for coefficients of determination and reduced Chi square. A table of the statistical values obtained is found in the Appendix D. Nernst analysis to determine potential and the number of electrons transferred was additionally performed.
Figure 14. Batch reactor assembly: spectroelectrochemical cell on the left, reaction vessel on right. The peristaltic pump (back, middle) circulates the sample solution between the cell and the vessel.

FT-IR ATR

In addition to OCP and UV-Vis spectroscopy, the course of one of the batch reactor experiments at pH 9.04 was monitored by FT-IR ATR. In experiments for which FT-IR data was collected, the O$_2$ sensor port was replaced with a rubber septum which tightly fits the 14/20 TS joint. 2 mL aliquots were transferred to a Thermo Nicolet Nexus 470 TR-IR E.S.P. fitted with Smart Ark accessory for ATR with Omnic Version 6.0a (Thermo Nicolet Corp.) software. The accessory uses a Zn/Se 45º crystal. The aqueous Tris base buffer was used as the blank. A total of five samples were taken reducing the batch reactor to 35 mL. The course of the reaction as monitored by OCP and UV-Vis was unaffected by the removal. A compromise needed to be reached between the amount of time a sample sits on the ATR crystal and the number of scans taken. 64 scans were found to be optimum correlating to 53.5 seconds.
**OTTLE Cell**

The optically-transparent thin layer electrochemical (OTTLE) cell is a small volume spectroelectrochemical cell. The OTTLE cell used for our experiments was constructed using designs belonging to Dr. Simona Dragan (Figure 15). The quartz glass was purchased from Quartz Plus, Inc. (NH, USA). The holes for the cell were drilled with a diamond drill by Northwestern University Instrument shop. The cell was ultimately assembled by Michael Phelan, Loyola University.

*Figure 15. OTTLE cell construction*
A miniature Ag/AgCl reference electrode is placed in a salt bridge containing 1M KCl solution. A glass frit exists between the salt bridge and the cell. A platinum mesh sheet within the cell serves as the working electrode. Internally two counter electrodes are composed of thin Pt threads which are welded to external wires at the top cell edge.

Nitrogen-purged solution was pumped into the OTTLE cell using a peristaltic pump. Two Teflon capillary tubes at each side of the cell anterior serve as inlet and outlet for solution. After it had been determined that no air bubbles existed in the cell the two tubes were clamped shut to prevent any oxygen from entering the cell.

Two types of experiments were conducted with the use of the OTTLE cell: controlled potential electrolysis (CPE) and chronoamperometry. Such experiments implemented a potentiostat (BASi) controlled by a computer using BASi-Epsilon electrochemical software package. Simultaneous UV-visible spectrum acquisition was recorded using an Ocean Optics I Base software. Spectral data were obtained with an Ocean Optics (USP2000 miniature fiber optic) spectrometer with a 75 W Xe-Hg lamp light source (Oriel Model no. 62551), equipped with OOIBASE 32 software.
The spectral linear range for the OTTLE cell was determined by controlled potential electrolysis using $\text{K}_3\text{[Fe(CN)]}_6$ as a standard. Absorbance maximum is achieved at 0.7 at which point absorbance plateaus (Figure 16). The linear portion of the graph gives corresponds to the equation

$$[7] \quad \text{Absorbance} = \varepsilon b C = 62.6672 \times [\text{Fe(CN)}_6]^{3-}$$

The molar absorptivity of ferricyanide at 420 nm is $1.02 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$ and thus the path length as calculated from Beer’s Law is 0.061 cm (0.61 mm).
The OTTLE cell volume was determined via cyclic voltammetry to be 18.3μL (Figure 17). The second smaller and inconsequential cathodic peak may be attributed to Prussian blue. Prussian blue, KFe$^{III}$[Fe$^{II}$(CN)$_6$], a mixed valence compound, has been known to form and adsorb onto platinum working electrodes.$^{30}$ Integration of the area under the main cathodic curve yields 3.5 mC which can be converted to total moles, N, from $Q = nCN$. The initial concentration of Fe(CN)$_6^{3-}$, $5.2 \times 10^{-3}$M, yields a cell volume of 18 μL.

![Graph](image)

**Figure 17.** Determination of OTTLE cell volume with K$_3$Fe(CN)$_6$; standard for OTTLE CVs; scan rate 1 mV/s. [K$_3$[Fe(CN)$_6$], 2.0mM; [KCl], 0.2M.
Nernst Analysis

Spectral analysis allows us to observe changes in the visible spectrum as a result of changing the electrode potential. From resultant absorbance vs. potential plots and Nernst plots we can obtain valuable information such as $\Delta E_{\text{rxn}}$, the potential associated with a certain reaction, and the number of electrons transferred in the reaction. Nernst analysis is based on the Nernst equation (Equation [8a]):

$$E = E^\circ - \frac{0.0592V}{n} \log \frac{[\text{red}]}{[\text{ox}]}$$

where $[\text{red}]$ and $[\text{ox}]$ are the concentrations of the reduced and oxidized species respectively and “$n$” is the number of electrons transferred in the reaction. Simulated Nernst plots illustrating the effect of $n$ for a reaction with an $E^\circ$ of 500 mV are shown in Figure 18. In Figure 18 the ratio of $[\text{red}]/[\text{ox}]$ is calculated from absorbance (Equation [8b]).

Let $[A]$, the absorbance value at any given potential during the reaction progress, be equal to the concentration of reduced species. $[A_{\text{max}}]$ is the absorbance obtained for a fully reduced solution. Then $[A_{\text{max}}]$-$A$ will be equal to the total concentration of oxidized species. Plotting the log of $[A]/[A_{\text{max}}]-A$ against $E_{\text{applied}}$ or $E_{\text{measured}}$ should produce a straight line within the -1 to +1 log range for the reaction (Equation [8b]). A one electron transfer redox reaction yields the equation $y = (-59.1/n)x - 500$ on the Nernst plot. In this case $E^\circ = -500$ mV and the negative slope implies a reduction reaction.

$$E = E^\circ - \frac{0.0592V}{n} \log \left( \frac{[A]}{[A_{\text{max}}]-A} \right)$$
In the simulated Nernst plot only the slope changes while the $E^\circ \approx -500$ mV remains the same. The magnitude of the slope $59.1/n$ mV. Therefore an $n = 2$ value would give a 29.7 mV slope and an $n = 3$ value, a -19.6 mV slope. A -39 mV slope gives an $n = 1.5$ value which suggests concurrent and independent 1- and 2- electron transfers.

In Figure 19 we demonstrate the results of a potential step experiment performed on a known standard $K_3Fe(CN)_6$ which absorbs at 420 nm with a molar absorptivity of $1.02 \times 10^3 Lmol^{-1} cm^{-1}$. The slope for the Nernst equation for ferricyanide is measured as 48 and 50 mV, or $n = 1.2$, consistent with the known one electron transfer of the complex.
In our studies potential step experiments with AQDS were performed in buffered aqueous solutions at five different pHs: 3, 5, 7, 9.4, and 11.6. Additional experiments were conducted in unbuffered solutions in the absence and presence of NAu-2 clay.

Determination of OTTLE Cell iR error

Electrochemical cells can oftentimes display evidence of Ohmic polarization (iR error)—a result of resistance along the current path in the cell. iR error along the current path is often a function of ion movement within the electrolyte. It may be a property of the electrolyte as well as the result of a systematic error introduced by the distance between the working electrode and reference electrode within the cell. The iR error of the OTTLE cell used in our studies was determined from the preceding potential step experiment with the standard K$_3$Fe(CN)$_6$ (Figure 19). The difference between the midpoint potential and the $E_{\text{red}}$ (or $E_{\text{ox}}$) indicates the magnitude of the iR error. In the case of our OTTLE cell that value was determined to be equal to 1.36 mV—a negligible error.
The Potential Step Experiment

The controlled potential step experiment or controlled potential electrolysis, CPE, was used in our studies. CPE is implemented by an optically transparent thin layer electrochemical (OTTLE) cell. This system allows one to simultaneously deliver a known potential and acquire spectral data.

The potential step experiment is related to the potential scan experiment that gives rise to cyclic voltammograms. Instead of a linear scan in which a change in potential is applied at a given rate, this experiment applies a potential over a period of time and then
steps to the next potential. In the experiments performed here, the potential does not return to the initial potential but continues on its course in either positive or negative direction.

A potentiostat (BASi) controlled by a computer using BASi-Epsilon electrochemical software package was used to deliver a known potential to the cell contents. Simultaneous UV-visible spectra were recorded using an Ocean Optics I Base software. Spectral data were obtained with an Ocean Optics (USP2000 miniature fiber optic) spectrometer with a 75 W Xe-Hg lamp light source (Oriel Model no. 62551), equipped with OOIBASE 32 software.

**Sampled current vs. Applied Potential Experiments**

The reduction of AQDS and the effect of NAu-2 clay in unbuffered aqueous environment was studied. Two series of potential step experiments were conducted: one series with AQDS and a second series with a NAu-2/AQDS mixture. Seven different concentrations of AQDS were used. Two control experiments were conducted: a clay control and a sodium hexametaphosphate control. For comparison between clays the smectite, SWy-1, was used in one experiment. All measurements were made against a silver/silver chloride reference electrode. Spectroscopic data and chronoamperometric data were acquired at each five minute interval. The concentrations of AQDS were 1.2 mM, 1.6 mM, 2.0 mM, 2.4 mM, 5.5 mM, 15.7 mM and 19.6 mM. Sodium hexametaphosphate, hmp, 3.81 mM, was added to all samples to give a final concentration of 0.095 mM. This was done to help prevent flocculation and settling of
clay. Hexametaphosphate delaminates the clay thereby providing access to AQDS and a surface on which to properly adsorb.

For each experiment, the initial potential was set at +300 mV and was stepped negative in 10 mV increments to a final potential of -850 mV. Each potential step was five minutes in duration. It was determined from such curves that a steady state current was reached by 300 seconds. Sample data is shown in Figure 20. A current vs. time curve was generated for each potential step.

![Current vs. Time Curve](image)

**Figure 20.** Sample data. Current vs. time plot. NAu-2/AQDS Series, [AQDS] = 2.4 mM, $E_{\text{applied}} = -150$ mV and -550 mV.
Each potential step experiment generated a current vs. time curve. Sampled \(i_i\) (current, \(\mu\)A) values were obtained by subtracting \(i_{\text{initial}}\) from \(i_{\text{final}}\) from data from each 10 mV potential step (Figure 20). The absolute value of \(i_i\) as a function of \(E\) (mV) was plotted and analyzed. For each \(i_i\) vs. \(E_{\text{applied}}\) graph a peak was observed. This peak was noted as \(i_{\text{max}}\). A simulated current vs. time curve is shown in Figure 21.

Equation [9]\(^{31}\) relates current to concentration of the oxidized species as a function of time.

\[i(t) = \frac{nFAD_O^{1/2}C_O^*}{\pi^{1/2}t^{1/2}}\]

where \(n\) = number of electrons transferred

\(A\) = area of the planar electrode

\(D_O\) = diffusion coefficient

\(C_O\) = concentration of the oxidized species

Consider a potential step experiment in which the potential is incremented in \(j\) steps from an initial or starting potential where the compound is completely oxidized to a final potential where the compound is completely reduced.

Assuming currents are diffusion limited, the current sampled at time, \(t\), after a reductive potential step, \(j\), can be solved as (Bard, 2\(^{\text{nd}}\) Ed. equation 5.4.16)\(^{31}\)

\[i_{j,t} = \frac{nFAD_O^{1/2}C_O^*}{\pi^{1/2}t^{1/2} \left(1 + \left(\frac{D_O}{D_R}\right)^{1/2}\right) \exp \left[\frac{nF}{RT} \left(E_j - E'\right)\right]}\]

Concentration in each step is controlled by the Nernst equation.
\[ E = E^o' - \frac{RT}{nF} \ln \left( \frac{C_R^*}{C_O^*} \right) \]

which is rearranged to

\[ [11] \quad C_O^* \exp \left( -\frac{nF}{RT} (E - E^o') \right) = C_R^* \]

Using the mass relationship

\[ [12] \quad C_{O, \text{init}}^* = C_O^* + C_R^* \]

The new concentration with each step to \( E_{\text{consecutive step}} \)

should depend on the potential of the previous step, \( E_{\text{last step}} \)

\[ [13] \quad C_{O, \text{init}}^* = C_O^* \exp \left( -\frac{nF}{RT} (E_{\text{last step}} - E^o') \right) + C_O^* \left( 1 + \exp \left( -\frac{nF}{RT} (E_{\text{last step}} - E^o') \right) \right) \]

\[ [14] \quad C_{O,E}^* = \frac{C_{O, \text{init}}^*}{\left( 1 + \exp \left( -\frac{nF}{RT} (E_{\text{last step}} - E^o') \right) \right)} \]


\[ k = \frac{nFAD_O^{1/2}}{\pi^{1/2}} \]

\[ [15] \quad i_{t,E} = \frac{k C_O^*}{t^{1/2} \left( 1 + \exp \left[ -\frac{nF}{RT} (E - E^o') \right] \right)} \]
\[ i_{t,E} = \frac{kC_{O,init}^*}{t^{1/2}} \frac{1}{\left( 1 + \exp \left[ -\frac{nF}{RT} \left( E_{last \ step} - E^o' \right) \right] \right) \left( 1 + \exp \left[ \frac{nF}{RT} \left( E - E^o' \right) \right] \right)} \]

Figure 21. Simulation of current and \([C_R]/[C_O]\) vs. \(E_{applied}\) curve.

A simulation using equation [16] for some random values of \(A\), \(t_{1/2}\), \(C_{o\text{init}}\) is shown in Figure 21. The plot is of current vs. \(E_{applied}\). Here we let \(E^o = -540 \text{ mV}\). \(E_{\text{imax}}(E^o)\) occurs when \([C_R]/[C_O] = 1\). \(i_{\text{max}}\) is a function of concentration and therefore for a system at equilibrium increases as the sample concentration increases.
CHAPTER III

AQDS: REDUCTION BY SODIUM DITHIONITE

AQDS is a tricyclic organic compound and known chromophore. In the oxidized state, the primary chromophores are the benzene rings which absorb at short wavelengths (328 nm)\(^{17}\). On reduction, better conjugation of the three rings occurs and λ shifts to the red. As AQDS gains each electron the negatively charged oxygens on the center ring may each in turn accept a proton. Several of the reduced intermediates and fully reduced species may be observed optically. The chemical reduction of AQDS by sodium dithionite was followed by UV-Vis and by OCP (open circuit potential). Reduction experiments were conducted at pH values 7, 9.4 and 11.6.

The Pourbaix Diagram

A Pourbaix diagram is a phase diagram relating formal potential to pH which gives information of the possible species found at a given pH and potential. Pourbaix diagrams are constructed from Gibbs free energy values. Gibbs free energy may be expressed by two different equations:

\[ \Delta G = -nFE \]

\[ \Delta G = -RT \ln K_a \]
If the ΔG of a reaction is known then the potential values and K_a values calculated may be used to generate the Pourbaix.

The pH-dependent potential for experiments conducted at pH 9.4 and pH 11.6 is represented by the dotted diagonal line in Figure 22 and is calculated by

\[
E_{ox/red}^{\circ} = E_{Q/Q^2-}^{\circ} - \frac{RT}{nF} \ln \left[ \frac{1}{1 + \frac{[H^+]}{K_{a,HQ^-/Q^2-}} + \frac{[H^+]^2}{K_{a,H_2Q/HQ^-}K_{a,HQ^-/Q^2-}}} \right]
\]

where \( H_2Q = AH_2DS \)

\( HQ^- = AHDS^- \)

\( Q^{2-} = AQDS^{2-} \)

The operative process for the reductions at pH 9.4 and pH 11 describes a reduction reaction that gives three protonated species; the principal species for this pH range is \( AHDS^- \). The equation is given by:

\[
AQDS + 2e^- + xH^+ \leftrightarrow [AQDS^{2-} \leftrightarrow AHDS^- \leftrightarrow AH_2DS]
\]

At pHs 3, 5, and 7 the reaction is best described by

\[
AQDS + 2e^- + 2H^+ \rightleftharpoons AH_2DS
\]

and results in the pH-dependent solid diagonal line shown in both Figure 22 and 67.
**Figure 22.** Pourbaix diagram for AQDS with 9-member square scheme based on $E^\circ$ values and pKa values from references 12-15.
Dithionite Batch Reactor Experiments

The chemical reduction of AQDS by Na$_2$S$_2$O$_4$ in mildly alkaline aqueous solution (pH 9) is governed in part by the complex kinetics associated with dithionite decomposition. The reaction begins with oxidized form of AQDS. The open circuit potential, OCP, as defined in Chapter II, was observed during the reduction of AQDS with Na$_2$S$_2$O$_4$ moves through four distinct stages: OCP$_I$, the initial phase; OCP$_L$, the lag phase; OCP$_D$, the midway potential associated with the dimer phase; and the OCP$_F$, the resting potential of the cell in the final phase (Figure 23). During these phases it is believed that AQDS becomes reduced by Na$_2$S$_2$O$_4$ and then re-oxidized by the dithionite decomposition products. During this process reactive AQDS intermediates combine to form a transient dimer complex.
The Four Stages of AQDS Reduction Reaction

Figure 23. The four phases in the reduction of AQDS by Na₂S₂O₄ as monitored by the open circuit potential. pH 9.4 bicarbonate buffered; [AQDS], 2.87 mM; [DIT], 11.5 mM. [DIT]/[AQDS] = 4.0.

Initial Phase (OCPᵢ)

We may follow the reaction progress using a spectroelectrochemical cell which allows us to simultaneously monitor the visible spectrum and the OCP of the system. The plot in Figure 23 is in essence a titration curve. The shape of the two “end” points vary because the equivalence point is $E_{eq} = \frac{E_A^* + E_B^*}{n_A + n_B} - f[H^+]$. The first end point of the reaction is not 1:1.
In the initial reduction of AQDS the OCP drops to a negative potential of ~ -550 mV (OCP\textsubscript{i}) (Figures 23 and 24) which we can attribute to the formal potential of the following reaction (see also Pourbaix diagram, Figure 22):

\[
\text{[22]} \quad \text{AQDS}^+ + e^- \rightleftharpoons \text{AQDS}^2^- \quad E^\circ = -0.548 \text{ mV vs. Ag/AgCl}^{13}
\]

\textbf{Figure 24.} Simultaneous monitoring of the visible spectrum and OCP; pH 9.4 bicarbonate buffered; [AQDS], 2.87 mM; [DIT], 11.5 mM. [DIT]/[AQDS] = 4.0 Absorbance at 727 nm is a wavelength associated with the charge transfer region.

It is assumed that all of the AQDS will be consumed by dithionite at this stage.

The product of the reaction can be either the semiquinone, AQDS\textsuperscript{+}, or the dianion (AQDS\textsuperscript{2-}, AHDS\textsuperscript{-}, AH\textsubscript{2}DS). At pH of 9.4, the predominant species is the singly
protonated form, AHDS, the product of a two electron reduction (see Pourbaix Figure 22).

The shrinking core model, SCM, has been used to describe the kinetics in the redox reaction of the slightly soluble anthraquinone, AQ, with Na₂S₂O₄ in alkaline aqueous medium. In the shrinking core model the reaction products are all in solution and the chemical reaction occurs at the solid surface of the slightly soluble reactant. A similar model is proposed for our AQDS. A pseudo-steady state approximation is applied and the solid AQDS is treated as a spherical solid particle. The solid particle, AQDS, is decreasing in size over time. As AQDS is reduced and the reaction progresses the reaction products enter into solution. In each case if dithionite is present in excess with respect to AQDS, the rate-determining step is the surface chemical reduction of AQDS. Reaction time is obtained as a function of solid fractional conversion, X_B:

\[ \frac{t}{\tau_s} = 1 - (1 - X_B)^{1/3} \]

where \( X_B = \frac{[\text{AQDS}^2-]}{[\text{AQDS}]_{tot}} \) and

where the complete conversion time of the particle, \( \tau_s \), is given by

\[ \tau_s = \frac{\rho_B R_0}{b k_c C_D} \]

where

\( \rho_B = \) solid molar density, mol/cm³
\( R_0 = \) solid particle initial radius
\( b = \) stoichiometric concentration
\[k_s = \text{surface chemical reaction rate constant, cm/s}\]

\[C_D = \text{liquid phase concentration of dithionite, mol/cm}^3 \text{ which reacts with stoichiometric concentrations of AQDS.}\]

**Figure 25.** Illustration of shrinking core model.

In the SCM, \( C_D, [S_2O_4^{2-}] \) was found to be inversely proportional to \( \tau_s \).\(^{33}\) We may take the segment of time during which OCP\(_1\) is present to be the complete conversion time. If we plot conversion time against \( 1/ [S_2O_4^{2-}] \) we find that this linear relationship holds true for anthraquinone-2,6-disulphonate (Figure 26).
Figure 26. Linear relationship found for conversion time as a function of \( \frac{1}{[DIT]_{\text{initial}}} \) for batch experiments. pH 9.4, bicarbonate buffer; [AQDS] = 2.87 mM.

The products of the reduction of the shrinking core of AQDS depend on pH. For experiments shown in Figure 24 a pH of 9.4 was used. At this pH the predicted product (Pourbaix diagram, Figure 22) is AHDS\(^-\). This species can be obtained directly in a two electron reaction

\[
AQDS + 2e^- + H^+ \rightleftharpoons AHDS
\]

or via a one electron transfer producing the semiquinone, AQDS\(^-\). The semiquinone has limited thermodynamic stability at pH < 10 and undergoes a rapid disproportionation reaction (Equation [24]).
The dianion formed in Equation [24] can be protonated to the doubly reduced singly protonated species, AHDS\(^{-}\). Optical evidence for AHDS\(^{-}\) (pH 9.4) is given by peaks at 410 nm and 479 nm (Figure 27). The literature values of 406 and 481 nm for these peaks indicate reasonable agreement.\(^{17}\)

**Figure 27.** Visible spectrum in the reduction reaction of AQDS. First three minutes in the reaction. Growth of peaks at 410 nm and 479 nm. Peak shift from 479 nm to 481 nm. pH 9.4; [AQDS], 0.62 mM; [DIT], 11.5 mM. [DIT]/[AQDS] = 18.5

During the first three minutes of one experiment, the 479 nm peak was observed to shift as it develops from 479 nm to 481 nm. 481 nm was used for Nernst analysis.
Setting $A_{\text{max,481nm}}$ equal to $[\text{AQDS}]_{\text{tot}}$ and $A_{481nm} = [\text{AQDS}_{\text{red}}]$ and plotting cell potential, $E^\circ$, against $\log ([A_{481nm}]/[A_{\text{max,481nm}} - A_{481nm}])$ we find a Nernstian relationship in which $n = 1.62$ and $E^\circ = -500.15$ mV (Figure 28). The cell potential of -500.15 mV is relatively close in value to the predicted two electron reduction potential of -495 mV. $^{13}$

\[ \text{[25]} \quad \text{AQDS} + 2e^- \rightleftharpoons \text{AQDS}^{2-} \quad E^\circ = -0.495 \text{ V vs. Ag/AgCl}^{13} \]

The number of electrons, $n$, intermediate between 1 and 2, suggests two separate reduction mechanisms occurring concurrently—Equations [25] and [26].

\[ \text{[26]} \quad \text{AQDS} + e^- \rightleftharpoons \text{AQDS}^- \quad E^\circ = -0.441 \text{ V vs. Ag/AgCl}^{13} \]

![Nernst Plot for the 481 nm band for the first three minutes in the AQDS reduction reaction based on data from Figure 27. pH 9.4; [AQDS], 0.62 mM; [DIT], 11.5 mM. [DIT]/[AQDS] = 18.5. The first phase of the reaction thus can be adequately described by simultaneous one and two electron reductions of AQDS by dithionite to products, AQDS$^-$ and](image-url)

**Figure 28.** Nernst Plot for the 481 nm band for the first three minutes in the AQDS reduction reaction based on data from Figure 27. pH 9.4; [AQDS], 0.62 mM; [DIT], 11.5 mM. [DIT]/[AQDS] = 18.5. The first phase of the reaction thus can be adequately described by simultaneous one and two electron reductions of AQDS by dithionite to products, AQDS$^-$ and
AQDS$^{2-}$ as shown by optical analysis of multiple experiments. Data from another batch experiment is shown in Figure 29. Similar results are observed when concentrations are varied (Figure 29). Additional support for this argument is obtained from Burillo et. al. They studied the reduction of anthraquinone, AQ, in alkaline media and offered the following half reactions for a net two electron reduction$^{33}$:

\[
\begin{align*}
\text{S}_2\text{O}_4^{2-} + 4\text{OH}^- & \rightleftharpoons 2\text{SO}_3^{2-} + 2\text{H}_2\text{O} + 2\text{e}^- \\
\text{AQ} + 2\text{e}^- & \rightleftharpoons \text{AQ}^{2-}
\end{align*}
\]

**Figure 29.** Visible spectrum in the reduction reaction of AQDS. 1st 5 minutes in the reaction of AQDS and dithionite. Very slight growth in spectral peaks is observed until they ultimately merge. pH 9.4; [DIT]/[AQDS] = 2.0; [AQDS], 5.63 mM; [DIT], 11.3 mM.

Experiments in the chemical reduction of electron carriers have traditionally indicated that the principal reductive species of dithionite is the radical anion, $\text{SO}_2^-\text{e}^-$ rather
than the dianion, $S_2O_4^{2-}$. The $SO_2^{-}$ species undergoes a one-electron oxidation delivering one electron to the acceptor, in this case, AQDS. However, in their work with methyl viologen, MV, Mayhew et. al. found that when $[\text{DIT}]/[\text{MV}]$ increased, $[\text{MV}^{-}\cdot]$ decreased indicating that under conditions in which DIT was in great excess, MV was reduced beyond the semiquinone. In our chemical reduction experiments the presence of OCP$_1$ was observed only when DIT was added in great excess relative to AQDS. When $[\text{DIT}]/[\text{AQDS}]$ was relatively small (~1.3), OCP$_1$ and OCP$_L$ were both absent and the open circuit potential went directly to OCP$_D$ values (Figure 30, Figure 31). A slight initial dip in OCP was observed prior to the dimer phase but the rapid kinetics prevented detection of the initial more negative OCP values observed at higher $[\text{DIT}]/[\text{AQDS}]$ values (Figure 24).
Figure 30. Simultaneous monitoring of visible spectrum and open circuit potential (OCP); Lag phase is absent; [DIT]/[AQDS] = 1.3. pH 9.4 bicarbonate buffered; [AQDS] 8.6mM, [DIT], 11.5mM.
Figure 31. Simultaneous monitoring of the visible spectrum and open circuit potential (OCP); Lag phase is absent; [DIT]/[AQDS] = 1.92; pH 9.4; [AQDS], 5.7 mM; [DIT], 11.5 mM.

The data suggests that [DIT]/[AQDS] ≤ 2 produces a 1-electron transfer, while high [DIT]/[AQDS] ≥ 4 produces a 2-electron transfer involving the reaction with S$_2$O$_4^{2-}$.

Dithionite has a relatively large association equilibrium constant indicating that the dimer state is favored.$^{35}$

\[ \text{S}_2\text{O}_4^{2-} \rightleftharpoons K_a \text{S}_2\text{O}_4^{2-} \]

In order for S$_2$O$_4^{2-}$ proportional concentrations to be significant initial dithionite concentrations must drop below 10 nM.$^{37}$
SO$_2^*$ and S$_2$O$_4^{2-}$ have different formal potentials, where the formal potential, $E^\circ$, of SO$_2^*$ is more positive than that of S$_2$O$_4^{2-}$.

\[ \text{[28]} \quad \text{SO}_2^{*} + H_2O \rightleftharpoons HSO_3^- + H^+ + e^- \]

The midpoint between the two potentials is defined by Mayhew as $E' (\text{pH}) =$ formal potential for 2 SO$_2^{*}$ (as compared to S$_2$O$_4^{2-}$).

$E' = -614$ mV vs. Ag/AgCl.$^{37}$

The midway potential has been labeled in Figure 24.

Equation [29] predicts that the effective midpoint potential, $E_m$, will become more positive with increasing [DIT].

\[ \text{[29]} \quad E_h = E_m = E' + 0.029 \log 4K_{a} \ [\text{S}_2\text{O}_4^{2-}] \]

where $E'$ is the potential for the oxidation of the two monomers, 2SO$_2^{*}$.

An increasingly more positive $E_m$ indicates that the reaction in Equation [28] becomes more favorable in the direction written. Equation [29] also indicates that the effective midpoint potential for monomer oxidation varies with log [S$_2$O$_4^{2-}$]. The slope of such a relationship, $\Delta E_m/\Delta \log[S_2O_4^{2-}]$, should be equal to 0.029 V—an indication of a two electron reduction.$^{37}$

In summary, intermediate values of [S$_2$O$_4^{2-}$]/[AQDS] OCP$_1$ varies as a function of the initial concentration of S$_2$O$_4^{2-}$, yet still with a two electron reaction (Equation [29]). At very low values of unreacted S$_2$O$_4^{2-}$, the primary reductant is SO$_2^{*}$ (Equation [27]) and a one electron process is predicted, as well as the loss of the OCP$_1$ phase.
Lag Phase (OCP<sub>L</sub>)

At the end of the initial phase, the OCP has a steep drop to a more negative potential, OCP<sub>L</sub>, where it sits for a period of time termed the lag phase (Figure 24). As just discussed OCP<sub>I</sub> is followed by OCP<sub>L</sub> when dithionite is in excess.

During the lag phase, no appreciable changes are observed in the OCP nor in the visible spectrum (Figures 32 and 33).

**Figure 32.** Lag phase of the reaction of AQDS with dithionite. Absorbance at 727 nm is also shown. pH 9.4; [AQDS], 5.63 mM; [DIT], 11.3 mM; [DIT]/[AQDS] = 2.00.
Figure 33. Absorbance spectra taken during the experiment in Figure 32 from 6 to 110 minutes. pH 9.4; [AQDS], 5.63 mM; [DIT], 11.3 mM; [DIT]/[AQDS] = 2.00.

The cell potential, OCP$_L$, is ascribed to the formal potential of the following reaction:

$$30 \quad S_2O_4^{2-} + 4OH^- \leftrightarrow 2SO_3^{2-} + 2H_2O + 2e^- \quad E^o = -613 \text{ mV vs. Ag/AgCl}^{38}$$

$$E^o = -613 \text{ mV vs. Ag/AgCl at pH 7}$$

At pH 9.4 the pH-dependent formal potential, $E_H$, was predicted to be

$$E_H = \sim -700 \text{ mV at pH 9.4}$$

Our experimental value, -704(+/30) mV vs. Ag/AgCl (for 14 experiments) is in excellent agreement.

The correspondence of the OCP$_L$ with the reaction potential of $S_2O_4^{2-}$ (Equation [30]) indicates that the solution potential is no longer controlled by the presence of
AQDS and that the full reduction of AQDS has been achieved. Excess DIT and associated decomposition reactions now dominate the cell potential (system).

Consider a series of experiments at pH 9.4 in which OCP is tracked for solution containing only dithionite (Figure 34). The time lag can be seen to be directly proportional to initial \([S_2O_4^{2-}]\) (Figure 34). These observations are consistent with known routes of dithionite decomposition. During the lag phase, sulfite ion, \(SO_3^{2-}\), accumulates in the system by way of Equation [30] and by Equation [31], a slow, irreversible disproportionation reaction.\(^{35}\)

\[
[31] \quad 2S_2O_4^{2-} + H_2O \rightarrow S_2O_3^{2-} + 2SO_3^{2-} + 2H^+
\]

A large concentration of [DIT] makes this reaction kinetically favorable. The potential will continue to be controlled by dithionite until the dithionite is fully consumed. The rate of consumption of dithionite has been described by Equation [32].\(^{39}\)

\[
[32] \quad \frac{d[S_2O_4^{2-}]}{dt} = -k_1[S_2O_4^{2-}][HSO_3^+] - k_2[S_2O_4^{2-}]^{1/2}[HSO_3^+][SO_3^{2-}]
\]

Equation [32] indicates that the rate is, in part, controlled, by the initial amount of dithionite present.

For experiments involving AQDS the “initial” amount of dithionite decomposing is the excess amount after reaction with AQDS. We thus predict that the time lag should be dependent upon the unreacted dithionite estimated by \([DIT]_{tot} - [AQDS]_{tot}\).

Figure 34 proves the prediction.
Figure 34 shows another interesting feature. The lag time is not only dependent on excess DIT, but on total DIT. This may describe mechanisms during decomposition involving the first and second terms of Equation [32]. The different slopes in Figure 34 may reflect the different mechanisms of decomposition.

**Figure 34.** Duration of lag phase is proportional to unreacted mmol DIT. Data is plotted for two sets of experiments ([DIT] = 11 mM and [DIT] = 22 mM) in which AQDS was varied. Data from DIT control experiments are plotted in green circles. Lag time as a function of initial mmol of sodium dithionite. For DIT control, [AQDS] = 0.
Figure 35. Data exemplifying relationship from Figure 34 for [DIT] = 22 mM. (– 8.6 mM AQDS) (— 5.7 mM AQDS) (— 2.9 mM AQDS)
In the presence of AQDS, lag phase is marked by a composite spectral peak centered at 535 nm (Figure 29). The composite 535 nm peak can be deconvoluted into four peaks. Three peaks are associated with the fully reduced species, 423 nm (420 nm, AH$_2$DS), 490 nm (490 nm, AHDS$^-$), 540 nm (540 nm, AQDS$^{2-}$) and 590 nm (Figure 37). The 540 nm peak increases in absorbance and shifts to slightly longer wavelengths while the 590 nm peak appears to decrease. The 590 nm peak is observed in other experiments (Figure 37) but remains unidentified. Deconvolutions using fewer/more...
spectral peaks resulted in higher residual errors. Statistical data is presented in Appendix D.

![Deconvoluted spectral peaks](image)

**Figure 37.** Deconvoluted spectral peaks for first five minutes in batch reaction for AQDS; pH 9.4 bicarbonate buffered; [AQDS], 5.63 mM; [DIT], 11.3 mM. [DIT]/[AQDS] = 2.00.

**Dimer Phase (OCP\textsubscript{D})**

The lag phase is followed by a rise in OCP to a “dimer” phase, OCP\textsubscript{D} (Figure 23). The value OCP\textsubscript{D}, was reasonably constant, regardless of the starting concentrations of AQDS and dithionite. The value, [-478 (+/- 9) mV], is most consistent with the potential established by Equation [25] (Pourbaix diagram, Figure 22). The association of OCP\textsubscript{D}
with a two electron reaction is somewhat surprising given that the most likely reaction is a one electron donation from $\text{SO}_3^{2-}$ accumulated during the lag phase.

Sulfite ion in large amount has been shown to reoxidize electron carriers such as MV— by the following mechanism.\textsuperscript{37}

\[
[33] \quad \text{SO}_3^{2-} + e^- + \text{H}_2\text{O} \rightleftharpoons 2\text{S}_2\text{O}_3^{2-} + 2\text{H}^+
\]

\[
[34] \quad \text{MV}^{2-} \rightleftharpoons \text{MV}^- + e^-
\]

Figure 38. Emergence of charge transfer bands in $600 - 750$ nm region. Charge transfer bands appear and begin to grow. Inset: Monitoring the 727 nm band and OCP over reaction time. pH 9.4 bicarbonate buffered; [AQDS], 5.63 mM; [DIT], 11.3 mM; [DIT]/[AQDS] = 2.0.
Figure 39. Charge transfer bands reach a maximum and begin to decrease along with CT bands. Inset: Monitoring the 727 nm band and OCP over reaction time. pH 9.4 bicarbonate buffered; [AQDS], 5.63 mM; [DIT], 11.3 mM; [AQDS]/[DIT] = 2.00.

Mayhew showed that the oxidation of the electron carrier could be achieved by titrating methyl viologen semiquinone with bisulfite. Furthermore, the degree of oxidation was a function of the initial ratio of $\text{MV}^*/\text{MV}_{\text{ox}}$ and the concentration of bisulfite added. The OCP$_D$ midpoint value corresponds with the peak absorbance associated with new, long wavelength bands which appear only in the OCP$_D$ phase (Figures 38 and 39). That red band is quantitatively related to the loss of the fully reduced species (see isobestic points in Figures 38 and 40).
It there is a one electron oxidation the mix $[\text{AH}_2\text{DS}, \text{AHDS}^-, \text{AQDS}^2]$ the probable product is AQDS$^+$ (see Pourbaix diagram, Figure 22).

An accumulation of AQDS$^-$ may give rise to a dimer complex:

$$[35] \quad 2\text{AQDS}^+ \leftrightarrow [\text{AQDS}^+\cdots\text{AQDS}^+]$$

An isobestic point forms indicating a conversion in which a loss of semiquinone gives way to a rise in the dimer complex. Though an isobestic point is detected in Figure 38 data from another batch experiment gives a better representation (Figure 40).

**Figure 40.** Isobestic point formation during dimer phase. pH9.4 bicarbonate buffered; [AQDS], 2.87 mM; [DIT], 11.5 mM. [DIT]/[AQDS] = 4.00.

The dimer complex may be the result of a semiquinone pair coming together to form a transient pi-stacked structure. Small et. al have shown evidence of a π-dimer—the
π-bonding interaction between two tricyclic phenalenyl radicals capable of absorbing in the visible region.\textsuperscript{39} Research has also indicated the formation of sigma dimers in the electrodimerization of 9-cyanoanthracene and the dimerization of radical cations of oligopyrroles.\textsuperscript{19,21}

In monitoring changes in the charge transfer (CT) region during the dimer phase, we observe an increase in intensity of the CT bands until they reach an absorbance maximum which occurs at the midpoint potential of the OCP\textsubscript{D} phase. The OCP\textsubscript{D} phase is observed between 115 and 360 minutes. During the latter half of OCP\textsubscript{D}, reagents are consumed until such a point as the control of the OCP shifts to the cell and electrolyte components. The consumption of those reagents can be seen in the simultaneous decrease in intensity of the CT band along with the composite spectral peak associated with AHDS (Figure 39). This is followed by a resolution of the composite spectral peak into two distinct spectral bands at 406 nm and 511 nm.

If we monitor one single wavelength in the CT region, the 727 nm band, and perform Nernst analysis on the rising half (Figure 38) and the falling half (Figure 39) we find an \( n = 3 \) value (Figure 41) for both the formation of the dimer on oxidation of reduced products (Figure 38) and oxidation of the dimer (Figure 39). Multiple replicates of the batch experiments are ambiguous, resulting in \( n \) values between 2 and 3. A two electron oxidation of the dimer reaction could indicate a disproportionation reaction followed by oxidation (Equations [36], [37]).

\[
\text{[36]} \quad [AQDS^- \cdots AQDS^-] \rightarrow AQDS + AQDS^{2-}
\]
\[ AQDS^2 \rightleftharpoons AQDS + 2e^- \]

Some clarity on oxidation of dimer can be obtained by analysis of the resolved spectral bands (406 and 511 nm) (Figure 39). Those peaks could be analyzed when the [AQDS] was within the linear range of our instrument (Figure 43).

In batch experiments for which initial AQDS concentrations were kept low in order to maintain 400 and 500 nm peaks within the linear range Nernst analysis of the 411 nm and 500 nm peaks during the dimer phase gave \( n \) values of 1.5 (Figure 42). Additionally, a small rise and fall in intensity is observed for the 500 nm band in the absorbance vs. time plot (Figure 43). It should be noted that the feature was observed in
four such experiments for which [AQDS] was kept low indicating a reproducible phenomenon. The point at which this small peak rises is coincident with the point at which the 727 nm band is first observed signaling the formation of the dimer.

Figure 42. Nernst Plot to accompany Figure 43. Nernst analysis of 500 nm band based on descent. pH 9.4 bicarbonate buffered; [AQDS], 0.62 mM; [DIT], 11.5 mM. [DIT]/[AQDS] = 18.5.
Figure 43. AQDS concentration was decreased in order to maintain 400 and 500 nm peaks within the linear range of the instrument. A small rise and fall in the 500 nm peak is observed around $t = 148$ minutes ($E = -649$ mV). pH 9.4 bicarbonate buffered; $[\text{AQDS}]$, 0.62 mM; $[\text{DIT}]$, 11.5 mM. $[\text{DIT}]/[\text{AQDS}] = 18.5$.

To summarize results thus far during OCP$_D$ three spectral features are observed:

i) a small rise in the 500 nm band is sometimes observed at the onset of

ii) a 727 nm CT band. The CT band decreases simultaneously with

iii) loss of a peak composed of peaks at 406 and 511 nm.

In order to better determine the changes occurring, spectra from $t = 110$ minutes to $t = 173$ minutes for the experiment shown in Figure 43 were deconvoluted using Origin Pro software. An example raw spectrum along with the deconvoluted spectrum is shown in Figure 44 to demonstrate that the integrity of the raw data is not compromised during the
deconvolution process (statistical data given in Appendix D). Figure 45, the spectra of deconvoluted peaks indicates that the spectra does not change significantly between $t = 110$ minutes and $t = 141$ minutes (see marker in Figure 43). Changes in the deconvoluted spectra were not observed to occur until $t = 148$ minutes which coincides with the small rise of the 500 nm peak shown in Figure 43 (see box in Figure 43).

**Figure 44.** $t = 110$ minutes; composite peak after deconvolution superimposed on raw data. pH 9.4 bicarbonate buffered; [AQDS], 0.62 mM; [DIT], 11.5 mM.
Figure 45. t = 110 minutes to 141 minutes; Dimer formation: CT bands increase in absorbance intensity. pH 9.4 bicarbonate buffered; [AQDS], 0.62 mM; [DIT], 11.5 mM.

Deconvolution of visible spectra at the onset of the OCP$_D$ phase (148 to 153 minutes) (Figure 46) suggest the following mechanism.

[38] $AH_2DS \rightleftharpoons AHDS^- + H^+$

[39] $AHDS^- \rightleftharpoons AQDS^- + H^+$

[40] $AQDS^- \rightleftharpoons AQDS^- + e^-$

Rise of the charge transfer band is seen by the broad deconvoluted band centered at ~680 nm.

[41] $2AQDS^- \leftrightarrow [AQDS^-]^2$
AHDS$^-$ increases (406 nm) and also decreases (loss in 482 nm band) when it is deprotonated to AQDS$^{2-}$ (444 nm band increases). This is rapidly followed or consumed by oxidation of the dianion to form the semiquinone, AQDS$^-$ (500 nm peak). The net 402-500 nm peak shift results in the apparent intensity change at 500 nm (Figure 43). Formation of the dimer phase begins (increase in 727 nm band).

**Figure 46.** Deconvoluted spectra; $t = 148$ minutes to $t = 153$ minutes (-649 mV to -506 mV). As dimer forms—peak shift occurs from 482 nm to 500 nm. pH 9.4 bicarbonate buffered; [AQDS], 0.62 mM; [DIT], 11.5 mM.
Figure 47. Deconvoluted spectra $t = 153$ minutes to $t = 172$ minutes (-506 mV to -430 mV). pH 9.4; bicarbonate buffered; [AQDS], 0.62 mM; [DIT], 11.5 mM.

At the end of the OCP$_D$ phase species present are likely to be (based on deconvolution of spectral data, Figure 47 and Pourbaix Figure 22) a mix of various oxidation and protonated species. The spectral peak at 500 nm is assigned to the semiquinone, AQDS$^-$. Peaks at 406 and 444 nm are assigned to the fully reduced compound, AHDS$^-$ and AQDS$^{2-}$, respectively. On decomposition all species disappear concurrently.

The dimer decomposition may be brought about in three ways:

1. heterolytic cleavage— the disproportionation reaction given in Equation [36]:

   $[AQDS^- \cdots AQDS^-] \rightarrow AQDS + AQDS^{2-}$
2. homolytic cleavage

\[ [AQDS^- \cdots AQDS^-] \rightarrow 2AQDS^- \]

followed by oxidation

\[ AQDS^- \rightleftharpoons AQDS + e^- \]

\[ [AQDS^- \cdots AQDS^-] \rightarrow AQDS^- + AQDS + e^- \]

The multiplicity of pathways may explain the 3 electron transfer measured in oxidation of the dimer (Figure 41).

The length of the dimer phase has been found to be proportional to the concentration of AQDS (Figure 48). Additionally, a linear relationship has been found between peak height of a particular charge transfer band, in this case 727 nm, and the initial concentration of AQDS (Figure 49).

Experiments were conducted in which three different amounts of dithionite were used. For each amount of dithionite, the concentration of AQDS was varied. Data as shown in Figure 49 clearly indicates that peak height as determined by maximum absorbance of the 727 nm band is a function of the initial concentration of AQDS and consequently moles of AQDS and not by dithionite concentration. If peak height were dependent on dithionite different linear slopes would be observed for varying amounts of dithionite. Therefore the dimer phase is governed entirely by AQDS. Absorbance maximum occurred at -478 (±9) mV vs. Ag/AgCl.
Figure 48. Length of dimer phase is proportional to the initial concentration of AQDS.
Figure 49. Peak height of 727 nm band within the charge transfer region is linearly related to the initial concentration of AQDS. Experiments for which three different concentrations of DIT were used.

\[ = 0.1118 \text{ g DIT} \quad = 0.2236 \text{ g DIT} \quad = 0.3354 \text{ g DIT} \]

Final Phase

At the end of the dimer phase, the OCP rises to a final potential \([\text{OCP}_F ( -89(\pm 24) \text{ mV vs. Ag/AgCl})]\) for 14 measurements] established by the batch reactor cell, the surface of the ITO electrode and the buffer solution (Figure 50). The large standard deviation is the result of premature termination of the experiment in some cases.
Figure 50. Completion of the reaction. OCP reaches its final resting potential. pH 9.4; bicarbonate buffered; [AQDS], 5.63 mM; [DIT], 11.3 mM. [DIT]/[AQDS] = 2.00.

FT-IR Analysis

Solution was sampled for FT-IR analysis at various points during the reaction progress for select pH 9.0 experiments. At this pH, the singly protonated dianion is the principal reduction product. Sharp absorptions at 1029 cm\(^{-1}\) and 1037 cm\(^{-1}\) were observed for anthraquinone-2,6-disulfonate which we attribute to changes in the electron density at the SO\(_3^-\) group on the semiquinone. Similar results were noted by Babaei et al.\(^{40}\)
The difference spectra (relative to -656 mV) are shown in Figure 51. The difference peak at 1029 cm\(^{-1}\) corresponding to AQDS\(^{-}\) grows in intensity as the potential moves positive (Figure 52). Nernst analysis of the data results in a potential of -495 mV (n = 1.2). The value is perfectly consistent with the two electron transfer in Equation [37].

\[ \text{[37]} \quad \text{AQDS}^{2-} \rightarrow \text{AQDS} + 2e^- \]

This is a surprising result because the UV-Vis data suggested sequential oxidation of AQDS\(^2-\)/AQDS\(^-\)/AQDS. The results of Nernst analysis of FT-IR data suggests a two electron process while recording a 1.2 electron process (Figure 53). The 1.2 electron process suggests the participation of the semiquinone. The presence of the 1029 cm\(^{-1}\) band, which is attributed to the semiquinone is supporting evidence that both 2-electron and 1-electron processes are likely involved.
**Figure 51.** FT-IR ATR Difference spectra compared to -656 mV. pH9 bicarbonate buffer; [AQDS], 6.30mM; [DIT], 19.3mM.

**Figure 52.** FT-IR ATR Difference spectra compared to -656 mV: Inset of Figure 51. pH9 bicarbonate buffer; [AQDS], 6.30mM; [DIT], 19.3mM.
Figure 53. FT-IR data. Change in peak intensity as a function of potential. Log term based on peak intensity. pH9 bicarbonate buffered; [AQDS], 6.30mM; [DIT], 19.3mM.

Re-reduction of AQDS

Additional evidence that the final phase indicates a return to the oxidized AQDS form is given by an experiment in which a second portion of dithionite was added to the solution mixture at the onset of the final phase (Figure 54). Here we see an immediate drop in potential from -145 mV to the potential initially seen in the lag phase (~ -700mV). A second lag phase occurs followed by a second dimer phase which culminates in an ultimate final phase. The second addition of dithionite was of a lesser amount than the first which results in a shorter lag phase.
Figure 54. Re-reduction of AQDS with a second addition of Na$_2$S$_2$O$_4$. pH 9.4 bicarbonated buffered; [AQDS], 8.60 mM; [DIT], 1$^{st}$ portion, 34.4 mM; [DIT], 2$^{nd}$ portion, 22.3 mM.

Visible Reaction Progress

The solution has been observed to undergo a color change which is dependent on reaction progress. The dithionite in buffer solution begins colorless. Upon addition of AQDS the solution becomes dark red but clear. The dimer phase is uniquely marked by an immediate change to a dark brown-red opaque solution and has become one of the hallmarks (indicators) of the dimer phase. Emerging from the dimer phase the solution turns an amber brown followed by orange and ultimately yellow each color with increasing clarity (Figure 55).
Figure 55. Color change of AQDS solution during its reduction reaction with dithionite. [AQDS], 5.63 mM; [DIT], 11.5 mM.
Reduction at Different pH Values

Batch experiments were conducted at three different pH values: 7.6, 9.4 and 11.6. The dimer complex was observed only for pH values 9.4 and 11.6 indicating that the dimerization reaction is pH dependent.

pH 11

Based on the proposed mechanism for the formation of the dimer (Equation [38]-[41]) and the expected species at pH 11 (Pourbaix diagram, Figure 22) the only major difference we expect on raising the pH is potential elimination of reactions [38] and [39].

\[
\begin{align*}
[38] & \quad AH_2DS \rightleftharpoons AHDS^- + H^+ \\
[39] & \quad AHDS^- \rightleftharpoons AQDS^{2-} + H^+ \\
[40] & \quad AQDS^{2-} \rightleftharpoons AQDS^- + e^- \\
[41] & \quad 2AQDS^- \rightleftharpoons [AQDS^-]^2
\end{align*}
\]

Figure 56 shows the OCP time course of a pH 11 replicate. A large composite spectral peak dominates OCP_t (Figure 57). Changes buried with the broad band are noted by the presence of an isobestic point at ~630 nm. An example deconvoluted spectrum from this time frame is given in Figure 58.
**Figure 56.** Absorbance and potential vs. time plot. pH11.6 phosphate buffered; [AQDS], 8.60mM; [DIT], 44.9mM.
Figure 57. Raw data; spectra; t = 675 min to 765 min. Isobestic point occurs between the 544 nm composite peak and the 720 nm peak. pH11.6 phosphate buffered; [AQDS], 8.60 mM; [DIT], 44.9 mM.
Figure 58. $t = 745$ Deconvoluted visible spectrum with cumulative spectrum. Raw data is shown in red; cumulative spectrum in black dotted line. The cumulative peak given by the program tracks the raw data. Composite peak at 544 nm was deconvoluted into its constituents: 416 nm ($\text{AQDS}^-$), 465 nm ($\text{AQDS}^2$), 544 nm ($\text{AQDS}^2$), 547 nm and ($\text{AQDS}^2$), 596 nm (unknown). pH11.6 phosphate buffered; [AQDS], 8.60mM; [DIT], 44.9mM.

The predominant dianion, $\text{AQDS}^2$, predicted from the Pourbaix diagram is observed (465 and 544 nm peaks). The oxidation of the dianion gives rise directly to the CT dimer, as evidenced by the isobestic point (Figure 56).

After the 727 nm CT band reaches maximum absorbance it begins to decline (Figure 59). Analysis of the raw and deconvoluted data (Figure 60) suggests the sequence
[36] \[ AQDS^{*} \cdots AQDS^{*} \rightarrow AQDS + AQDS^{2-} \]

\[ (727 \text{ nm}) \rightarrow \sim 550 \text{ nm, raw data} \]

[40] \[ AQDS^{2-} \rightleftharpoons AQDS^{*} + e^- \]

\[ (560 \text{ nm}) \rightarrow (510 \text{ nm}) \]

[43] \[ AQDS^{*} \rightleftharpoons AQDS + e^- \]

\[ (500 \text{ nm}) \]

Reaction [36] is based on the simultaneous decrease in the 727 nm CT band with an increase in 550 nm (AQDS\(^{2-}\)). Reaction [40] is based on the shift from 550 nm (AQDS\(^{2-}\)) to 510 nm (AQDS\(^*\)). The shift is shown more clearly by deconvolution at -510 mV and -445 mV (Figure 60 and 62). Reaction [43] is based on the final loss of all spectral peaks including 510 nm (AQDS\(^*\)).

Nernst analysis of the raw data (Figures 57, 59) for the formation and decomposition of the CT band (727 nm) gives \( E^0 \) and \( n \) values of -559 mV (\( n = 1.7 \)) and -452 mV (\( n = 1.5 \)) for formation and decomposition of the dimer phase respectively (Figure 61).
Figure 59. t= 765 to 895 minutes; Visible spectra, raw data. pH11.6 phosphate buffered; [AQDS], 8.60 mM; [DIT], 44.9 mM.

Data for 9.4, in comparison (Figure 41) were -515 mV (n = 3) and -448 mV (n = 3). The convergence of the decomposition potentials is expected because the proposed mechanism was pH independent (Equations [36], [42], [43], and [44]).
Figure 60. $t = 765$ to 895 minutes. Deconvolution of peaks. Peak shift occurs from 550 nm to 510 nm. pH 11.6 phosphate buffered; [AQDS], 8.60mM; [DIT], 44.9mM.
Figure 61. Nernst plot of 560 nm and 727 nm. pH11.6 phosphate buffered; [AQDS], 8.60 mM; [DIT], 44.9 mM. Based on raw data.
Figure 62. AQDS UV-vis spectra; pH 11.6 phosphate buffered; (A): Deconvoluted and cumulative spectrum at $t = 765$ minutes ($-510$ mV); (B): Deconvoluted and cumulative spectrum $t = 855$ minutes ($-455$ mV); [AQDS], 8.60 mM; [DIT], 44.9 mM.
pH 7

The Pourbaix diagram (Figure 22) suggests that pH 7.6 sits at the juncture of several different stability domains which vastly complicates interpretation. Expected species are AQDS which is not spectrally visible on our instrument, AH$_2$DS, visible at 420 nm, and AHDS$^-$ visible at 406 and 481 nm. AHDS$^-$ (406, 481 nm) should be the predominant species.

In the lag phase as predicted (Figure 64), the singly protonated and diprotonated dianion, (AHDS$^-$ at 465 nm and AH$_2$DS at 417 nm) are observed. Figure 63 shows spectra just before final decomposition, confirming presence of these species.

**Figure 63.** $t = 1089$ min; Deconvoluted peaks; pH7; [AQDS], 8.60mM; [DIT], 44.9mM; [DIT]/[AQDS] = 5.2; Inset: spectra of raw data from $t = 1080$ to 1099 minutes.
One intriguing feature at this pH is the presence of a 600 nm band (Figure 65, Figure 66). Like the 727 nm band it rises and falls and appears to control the OCP (Figure 64). This feature was not immediately apparent in the raw data at low concentration. In data at pH 9 it appeared as a small shoulder (Figure 37). At this point and time we do not know what to attribute it to though it is tempting to speculate that it is a protonated dimer. That idea is not entirely unrealistic. Spectral shifts to shorter wavelengths with protonation have been observed with anthraquinone derivatives.\textsuperscript{16,17} This is noted with the 444 and 545 nm bands for AQDS\textsuperscript{2}. Upon accepting a proton and becoming AHDS\textsuperscript{+}, a blue shift occurs from 446 nm and 545 nm to 406 nm and 481 nm, respectively.\textsuperscript{16,17} This shift may be explained as a stabilization of the compound by protonation.

**Figure 64.** Absorbance and potential vs. time plot. pH7; [AQDS], 8.60mM; [DIT], 44.9mM. [DIT]/[AQDS] = 5.2.
Figure 65. Visible spectra; deconvoluted spectra; t = 1099 min to 1349 minutes; pH7; [AQDS], 8.60 mM; [DIT], 44.9mM; [DIT]/[AQDS] = 5.2  Inset: raw data.
Figure 66. Visible spectra, raw data t = 1349 minutes to 1624 minutes. pH7; [AQDS], 8.60 mM; [DIT], 44.9 mM. [DIT]/[AQDS] = 5.2.

Evidence of the dimer at pH 9 and 11 at 727 nm but its absence at pH 7 suggests that dimer formation is pH-dependent and possibly the result of a species formed in slightly alkaline solution.

The Pourbaix Diagram Revisited

The Pourbaix plot for AQDS indicates that the stability region for AQDS\(^{-}\) is narrow implying that several oxidized and reduced species overlap (AQDS, AQDS\(^{-}\), AQDS\(^{2-}\)). It is in this region that the dimer is observed (Figure 67). These reactive intermediates may combine to form a dimer capable of giving rise to the several charge transfer bands observed in the 600 to 750 nm range. Experimental data from several experiments were added to the Pourbaix diagram. As indicated in the Pourbaix diagram,
two possible species are the semiquinone and the protonated dianion. The formation of the reactive species is a result of reoxidation of AQDS$^{2-}$ by dithionite decomposition products. Similar, yet less pronounced, “oscillatory” behavior was achieved through electrolytic reduction which will be discussed in the next chapter.

**Figure 67.** The Pourbaix diagram including experimental data.

**Conclusion**

In this chapter we sought to determine the mechanisms by which AQDS is reduced to its final product at several different pH values within moderately alkaline conditions. Reduction of AQDS by dithionite was studied spectrally by UV-vis and electrochemically by OCP. During its course of reduction both dithionite and AQDS take turns in governing select reaction phases. These phases have been associated not only
with AQDS reduction but with a subsequent re-oxidation of the fully reduced AQDS product giving what may be perceived as an oscillatory effect.

In addition we have observed an unsuspected species which we attribute to a dimer. The dimer is only observed when dianion and semiquinone are present in high concentration. To the best of our knowledge no experimental values have been previously given for this dimer. Data obtained from dimer formation and decomposition give realistic with unrealistic n values which suggest simultaneous and independent 1- and 2- electron transfers.

It is unclear whether dimer formation is the result of the dimerization of two semiquinone intermediates or a comproportionation reaction in which dianion and the fully oxidized species come together. Unresolved spectra for pH 9.4 experiments show an isobestic point between 500 nm and 727 nm – an indication of a conversion from semiquinone to dimer. At pH 11.6, however, an isobestic point was observed between 560 nm (dianion) and 727 nm (dimer). The absence of dimer at pH 7 tells us that the dimer must be an unprotonated species; a protonated semiquinone is present at this pH.

Dimerization between two aromatic radicals in the form of a $\pi$–stacked dimer ($\pi$–dimer) has been shown to occur between tricyclic phenalenyl radicals with absorbance in the visible region ($\lambda = 595$ nm, $\varepsilon = 2.0 \times 10^4 \text{mol}^{-1} \text{cm}^{-1}$). Evidence was also given by Small et. al for a radical-cation interaction (dimerization) given the term $\pi$–pimer to indicate the positive charge on the radical. The $\pi$–pimer gave absorbances in the near-IR region and only approached longer wavelengths with temperature reduction. Both dimers were considered stable for countering reasons. According to theoretical calculations the
\( \pi \)-bonding was characterized by its covalent nature in addition to dispersion interactions for the \( \pi \)-dimer. Gas phase calculations for the \( \pi \)-pimer indicated that strong electrostatic interactions were its stabilizing factor.\textsuperscript{40}

Dimer decomposition gives more definitive results. At pH 11.6, the \(~550\) nm band (dianion) initially increases as the dimer CT band decreases. In other words, the dimer decomposes to the dianion suggesting a heterolytic cleavage process. This is followed by the descent in both \(444\) nm (dianion) and \(~550\) nm bands with simultaneous increase in the \(400\) nm band (semiquinone) indicating that the dianion oxidizes via a two step mechanism in which the semiquinone is intermediate. FT-IR data for pH 9 confirm evidence of semiquinone upon dimer decomposition.

Theoretical studies by Novoa et. al. involving tetracyano-ethylene radical anions produced an energy curve relating total interaction energy to its coulombic energy and bonding energy components. They found that the metastable \(\pi\)-dimer exists because the energy of the interaction energy minimum lies above the energy of the two radical anion monomers.\textsuperscript{22} This energy minimum creates a dissociation energy barrier.\textsuperscript{22} In other words, the dimer cannot decompose into its original fragments. Relating this to our work with AQDS dimer gives credence to heterolytic cleavage as the likely mechanism for dimer decomposition.
CHAPTER IV
AQDS: POTENTIAL STEP EXPERIMENTS

The “oscillatory” nature of the reduction reaction may be due to the complex kinetics associated with the reductant, dithionite ion. For comparison potential step experiments or controlled potential electrolysis, CPE, were conducted. In the potential step experiments, the potential is stepped in increments of 10 mV beginning from an initial positive potential to increasingly negative potentials until a final potential is reached. It was established that 300 seconds was necessary to achieve a steady state current.

CPE experiments were conducted at five pH values: 3, 5, 7, 9.4 and 11.6. The data is presented first at pH 9.4 and 11.6 followed by 7, 5 and 3 in order to first draw comparison to the AQDS/dithionite reactions.

From the Pourbaix diagram in Figure 22 we predict that at pH 9.4, the singly protonated dianion, AHDS⁻, will be the predominant product at full reduction. At pH 9.4 moving in the negative direction in potential from AQDS to AHDS⁻, we encounter AQDS⁻. Therefore we expect to observe evidence of the semiquinone, AQDS⁻⁻, as reduction progresses.
Figure 68. CPE experiment of AQDS at pH 9.4 bicarbonate buffered; Spectra shown is for E = -350 mV to -600 mV. A growth in spectral peaks at 405 nm and 510 nm is observed. Inset: Spectra for -60 mV to -340 mV. [AQDS], 3.15mM; [KCl], 0.2M.

At pH 9.4 the first CPE reduction product is the semiquinone, \( AQDS^- \), as indicated by the emergence of spectral peaks at 405 nm and 510 nm at -350 mV (Figure 68). This is followed by peak shifts to 410 nm and 490 nm respectively indicative of the formation of the singly protonated dianion, \( AQDS^{2-} \), until growth in absorbance between the two peaks results in a composite spectral peak at 489 nm (Figure 68).
Figure 69. Absorbance vs. cell potential data at 411 nm, 500 nm, and 727 nm. Reduction and oxidation are shown. pH 9.4, bicarbonate buffered; [AQDS], 3.15mM; KCl], 0.2 M.

Absorbance at three different wavelengths are plotted as a function of applied potential (Figure 69). The first observation made is that the oxidation and reduction are offset from each other. This has been observed elsewhere for thin layer electrochemical cells and is usually attributed to iR error. For this particular cell the measured iR error was negligible (see Figure 19, Chapter II).

Wavelengths 411 and 500 nm was selected to track the net reduction course. Additionally, 727 nm was tracked to see if any dimer was observed. Reduction, which was performed first, occurs at -496, -501 mV (411 and 500 nm, respectively) which nicely matches the literature for two the electron reduction, AQDS/AQDS$^{2-}$. The number
of electrons were, however, measured as 1.4 for both 411 nm and 500 nm suggesting mixed one and two electron process.

On re-oxidation, the potentials were found to be -439 mV and -443 mV, values more consistent with the one electron oxidation from AQDS$^+$ to AQDS. The number of electrons participating in the process were also closer to 1 (1.1 and 1.3 at 411 nm and 500 nm, respectively). This suggests two separate mechanisms operate during the reduction titration as compared to the oxidation titration.

A CT band at 727 nm was observed although of very low intensity (Figure 69). Nernst analysis (Figure 72) suggests a one electron process involved in formation of the band on reduction ($n = 0.71$) and on loss of the band with re-oxidation ($n = 0.85$). The potentials obtained were -489 mV on reduction (dimer formation) and -435 mV on oxidation (dimer decomposition). -489 mV is relatively close to the 2-electron reduction of AQDS, ($E^\circ_{AQDS/AQDS^{2-}}$ , -495 mV vs. Ag/AgCl) and -435 mV is closer to the one electron transfer ($E^\circ_{AQDS/AQDS^-}$, -441 mV).
Figure 70. Nernst analysis for 411 nm of raw data shown in Figure 69. pH 9.4, bicarbonate buffered; [AQDS], 3.15 mM; KCl, 0.2 M.
Figure 71. Nernst analysis for 500 nm of raw data shown in Figure 69. pH 9.4, bicarbonate buffered; [AQDS], 3.15 mM; KCl], 0.2 M.
In order to better observe the 727 nm band the total concentration of AQDS was increased (Figure 73). Increasing the concentration of AQDS causes the peaks in the 600–750 nm range to become more prominent giving better evidence for the dimer. An increase in absorbance for peaks at 406 nm and 511 nm (AQDS•−) is accompanied by an increase in the charge transfer bands (Figure 73). Again peak shifts are observed as the potential is stepped more negative.
Figure 73. Potential step experiment: AQDS at pH 9; Visible spectra showing growth of 406 and 511 nm bands and charge transfer bands as potential is stepped from -400 mV to -480 mV. pH 9.4, bicarbonate buffered; [AQDS], 17.2 mM; KCl, 0.2 M.

As the potential was moved further negative (-490 to -600 mV) an isobestic point formed between the 511 nm band (AQDS•⁻) and the CT bands (Figure 73) formerly observed in the batch experiments (Figure 74). The quantitative conversion of AQDS⁺ to the CT band was previously observed in the batch reactions (Figure 40). Absorbance vs. applied potential graphs are shown in Figure 75. Increasing the AQDS concentration not only increases the magnitude of the dimer absorption signal but it also alters the oxidation process. This is deduced by the addition of new features at E > -300 mV and by the shift in the main oxidation event from -440 mV (Figure 69) to -356 mV (Figure 75).
A blow-up of the CT bands vs. potential is shown in Figure 76. On reduction the CT band rises at ~450 mV (part a) and falls at ~550 mV (part b). On re-oxidation the dimer is reformed at ~450 mV (part c) and falls at ~350 mV (part d).

**Figure 74.** Decrease in CT bands as potential is stepped from -490 mV to -600 mV. pH 9.4, bicarbonate buffered; [AQDS], 17.2 mM; KCl], 0.2 M.
Figure 75. Plot of absorbance at three wavelengths vs. potential. [AQDS], 17.2mM; [KCl], 0.2 M; pH 9.4 bicarbonated buffered. Labels: a (reduction, dimer formation), b (reduction, dimer decomposition), c (oxidation, dimer formation), d (oxidation, dimer decomposition). Nernst analysis values are also shown.
Figure 76. Plot of absorbance at 727 nm vs. potential. [AQDS], 17.2 mM; KCl, 0.2 M; pH 9.4 bicarbonate buffered. Labels: a (reduction, dimer formation), b (reduction, dimer decomposition), c (oxidation, dimer formation), d (oxidation, dimer decomposition). Values from Nernst analysis are included.

Nernst analysis raw data (Figure 76) results in n values of 2.70 for dimer formation and 1.62 for decomposition on reduction at very negative potentials. With re-oxidation, the number electrons involved are 1.56 and 2.25, on formation and decomposition, respectively. It is interesting to note that a three electron transfer for dimer formation and decomposition was found in previous batch experimental data (Figure 42). The potentials measured in CPE are shown in the experimental Pourbaix diagram (Figure 67).
Dimer formation by reduction noted as part a in Figure 76 occurs at an $E^\circ$ value of -461 mV. The -461 mV regime has multiple possible pathways. There are several candidate reactions for this potential (Equations [25], [26] and [45]).

$[26] \quad AQDS + e^- \rightleftharpoons AQDS^+ \quad E^\circ = -0.441 \text{ V vs. Ag/AgCl}^{13}$

$[25] \quad AQDS + 2e^- \rightleftharpoons AQDS^2 \quad E^\circ = -0.495 \text{ V vs. Ag/AgCl}^{13}$

and

$[45] \quad AQDS^{**} + e^- + H^+ \rightleftharpoons AHDS^- \quad E^\circ = -465 \text{ mV vs. Ag/AgCl at pH 9.0}$

The most probable reaction accounting for this potential in the Pourbaix diagram is Reaction [45]. This indicates that the dimer formed on reduction in the absence of dithionite requires the presence of the monoprotonated dianion. The partner in the dimer must be of a higher oxidation state since the dimer can be reductively decomposed (part b, Figure 76). The potential associated with reduction is -523 mV. This is consistent with the a two electron two proton reaction (Equation [46]).

$[46] \quad AQDS + 2e^- + 2H^+ \rightleftharpoons AHDS \quad E^\circ = -524 \text{ mV vs. Ag/AgCl at pH 9.4}$

This suggests that the dimer formed involves [AHDS$\cdots$ AQDS].

Part c, AQDS re-oxidation and dimer formation gives a potential value consistent with

$[47] \quad AQDS^{**} \rightleftharpoons AQDS + e^- \quad E^\circ = -441 \text{ mV vs. Ag/AgCl}^{13}$

This is surprising because under batch reaction conditions the dimer appeared at the two electron oxidation potential for AQDS$^{2-}$/AQDS. Part d, AQDS re-oxidation and dimer decomposition gives a potential value of $E^\circ = -349 \text{ mV}$ which has not been attributed to any specific reaction at this time.
An interesting feature noted in the absorbance vs. potential plot (Figure 75) are the slight peaks formed by the absorbance of 411 nm and 500 nm bands upon re-oxidation. These features were also observed in replicate CPE experiments so they likely represent a real phenomena. Moving positive, the first maximum occurs at ~ -250 mV and the second at ~ -110 mV. It is difficult to assign the second maximum however the peak at -250 mV may be ascribed to the following reaction given in Equation [48].

\[ \text{AHDS}^- \leftrightarrow \text{AHDS}^+ + e^- \quad E^o = -0.282 \text{ mV vs. Ag/AgCl}\]  

The appearance of either AHDS\(^-\) or AHDS\(^+\) species at this potential is somewhat puzzling. At this point in the re-oxidation reaction the predominant species is the fully oxidized AQDS (Pourbaix diagram, (Figure 22 and 67). At -282 mV, as stated before, the dimer has decomposed, so even if AHDS\(^+\) does occur it cannot be a direct dimer decomposition product.

**Potential Step Experiments at Several Different pH Values**

**pH 11.6**

pH 11.6 is more alkaline than pH 9.4, therefore as indicated by the Pourbaix diagram we would expect to see only the dianion at full reduction. We also expect to observe only the semiquinone, AQDS\(^-\), as a reductive intermediate as we move vertically along the diagram at pH 11.6 to increasingly negative potentials.
At pH 11.6 we have evidence of a two electron process in which the semiquinone, AQDS$^\cdot$ (515 nm peak), is formed along with the dianion, AQDS$^{2-}$ (446 nm peak), (Figure 77). At -530 mV in the reduction we see a small shoulder forming at the longer wavelengths. This is, possibly, further evidence of the dianion, AQDS$^{2-}$. The presence of the dianion was confirmed by taking a difference spectrum (-520 mV; -610 mV) (Figure 78). These peak wavelengths compare well with literature values for the dianion (445 and 545 nm).

An isobestic point occurs at 654 nm indicative of a conversion between an intermediate species giving rise to the dimer which absorbs at longer wavelengths. These
two features suggest that dimer formation does not involve the protonated species at this pH.

**Figure 78.** Difference spectrum produced by subtracting spectrum at -520 mV from spectrum at -610 mV. pH 11.6 phosphate buffered; [AQDS], 3.15 mM; [KCl], 0.2 M.
Figure 79. Plot of absorbance at three wavelengths vs. potential. pH 11.6, phosphate buffered; [AQDS], 3.15 mM; KCl, 0.2 M.

In AQDS/dithionite reactions conducted at pH 11.6 a peak shift from 550 nm to 510 nm was observed along with dimer decomposition. Here, the opposite is observed with dimer formation. The small shoulder that rises along with dimer formation in the 500-600 nm region may be the result of a peak shift as well—from 510 nm to ~550 nm. Evidence for this is apparent in the difference spectrum (Figure 78). The reversal of peak shift is not at all surprising. In the AQDS/dithionite reactions dimer formation is the result of AQDS$^{2-}$ re-oxidation. In the potential step experiments it is the result of AQDS reduction.
pH 7

Controlled potential electrolysis with AQDS was also conducted at pH 7. From the Pourbaix diagram we may predict the principal fully reduced species to be the doubly protonated reduction product, AH$_2$DS.

There are several mechanisms by which AQDS is fully reduced to AH$_2$DS. Electrochemical mechanisms are comprised of two possible events: an electron transfer (E) and a chemical reaction or protonation (C). The three most reasonable mechanisms that AQDS may take considering thermal favorability are EEC, EECC or direct passage from AQDS to AH$_2$DS.

An example of an EC mechanism within the 9-membered square scheme is one in which AQDS$^-$ first accepts an electron before accepting a proton thereby forming AHDS$^-$. A sample EC mechanism:

\[
\begin{align*}
AQDS^{-} + e^- & \rightleftharpoons AQDS^{2-} \\
AQDS^{2-} + H^+ & \rightleftharpoons AHDS^{-}
\end{align*}
\]

E = electron transfer  \hspace{1cm} C = chemical reaction (protonation)

A CE mechanism describes a protonation followed by electron transfer.

A sample CE mechanism:

\[
\begin{align*}
AQDS^{2-} + H^+ & \rightleftharpoons AHDS^{-} \\
AHDS^{-} + e^- & \rightleftharpoons AHDS^{-}
\end{align*}
\]

As reduction progresses from AQDS to AH$_2$DS, moving cathodically along the Pourbaix diagram at pH 7 we cross the diagonal line associated with the following two-electron, two-proton reaction.
Therefore, in relating this to the 9-membered square scheme we expect direct passage from the fully oxidized species in the upper-left hand corner to the fully reduced species in the lower right hand corner. This is the most reasonable mechanism and therefore the one that is expected.

As predicted, only a 423 nm peak, attributed to the diprotonated species, AH$_2$DS, is observed as reduction progresses (Figure 80). Peaks at 444 nm and at 550 nm (AQDS$^{2-}$) are absent supporting our prediction that the mechanism by which AH$_2$DS is formed is indeed by direct passage from fully oxidized to fully reduced. Interesting to note is that the CT band at 727 nm is absent. The semiquinone implicated in dimer formation does not appear to be present in any appreciable amount to form the dimer at this pH.

\[ \text{AQDS} + 2e^- + 2H^+ \rightleftharpoons AH_2DS \]
Figure 80. Spectral change as a function of applied potential from +280 mV to –900 mV. [AQDS], 3.15mM; KCl], 0.2M; pH 7, phosphate buffered.
Moving slightly more acidic along the Pourbaix diagram to pH 5 the principal fully reduced product is AH$_2$DS. At pH 5, as was indicated for pH 7, direct passage from AQDS to AH$_2$DS is the predicted mechanism by which AQDS becomes fully reduced at pH 5.

We first observe a peak at 410 nm (possibly AHDS\(^-\)) which shifts to 423 nm (AH$_2$DS) as we step cathodically (Figure 82). This is counter to our predictions of direct passage. As was explained above for pH 7, we expect AQDS to form AH$_2$DS as we move across the diagonal AQDS/AH$_2$DS line in the Pourbaix diagram. AHDS\(^-\) should not
form at all as no region of stability exists for it at this pH. For this reason we found it necessary to perform a deconvolution of the peak to provide better insight.

Figure 82. Change in spectra as a function of applied potential from +50 mV to -470 mV. pH 5 acetate buffer; [AQDS], 3.15 mM; KCl, 0.2 M.

Raw data (Figure 82) was deconvoluted (Figure 83). Deconvolution indicates that the peak shift that was observed in the raw data is actually a manifestation of 423 nm peak growth. A second peak at the lower wavelength, 393 nm, grows at a significantly slower rate during reduction progress (Figure 83). This may be the reason for the perceived peak shift observed in the raw data shown in Figure 82.

The charge transfer bands associated with the dimer were not observed at pH 5.
Figure 83. Spectra at -320 mV and -470 mV. 423 nm band increases at a much greater rate than 393 nm band. pH 5; [AQDS], 3.15 mM; KCl], 0.2 M.
Nernst analysis was performed on the final observed peak centered at 423 nm and the values reported in Figure 84. Two different values were obtained for $E^\circ$. These values lie exactly along potential values in the Pourbaix diagram for a two electron $\text{AQDS}^+ + \text{H}^+ + 2e^- / \text{AHDS}^-$ reduction and a one electron $\text{AHDS}^- / \text{AQDS}^+ + e^- + \text{H}^+$ oxidation.

The same trend in potential is observed at pH 3 (Figures 84 and 85). In the case of pH 3 the oxidation is clearly incomplete at termination of the experiment, consistent with the net one electron oxidation.
The spectral data suggest a two electron reduction to AHDS- (410 nm) followed by protonation to AH$_2$DS (423 nm) (Figure 85). Deconvolution of the spectral peaks (data not shown) gave similar results as the deconvoluted spectra at pH5.

Figure 85. Spectral changes as a function of applied potential. +50 mV to -340 mV. pH 3, phosphate buffered; [AQDS], 3.15mM; KCl], 0.2M.
Figure 86. Absorbance at 423 nm as a function of applied potential; pH 3; phosphate buffered; [AQDS], 3.15 mM; KCl], 0.2 M.

**Conclusion**

Reduction of AQDS by controlled potential electrolysis results in charge transfer bands in the 600-750 nm region at pHs 9.4 and 11.6. This proves that dimer formation is not a phenomenon peculiar to chemical reduction by dithionite. Furthermore, it shows that dimer formation can be approached by oxidation of the dianion, AQDS$^{2-}$ and by reduction of the fully oxidized species, AQDS. Recall, that the dimer was the result of AQDS$^{2-}$ oxidation by dithionite decomposition products. In CPE, the dimer forms by means of AQDS reduction—we begin at an initial positive potential and step cathodic.

A Pourbaix diagram plotting cell potential as a function of pH serves as a guide for the several forms of AQDS present within these cell parameters. The observation of
dimer formation at pH > 7 indicates that the dimer is comprised of species unique to a certain region of the Pourbaix diagram. The protonated semiquinone, AHDS’ can be excluded as a possible participant in dimer formation because of its low pKa of 3.2\(^{14}\) and its relatively more positive potential at this pH value. At \(E^0 = -0.282\) mV and pH 9.4 AQDS is already in the fully oxidized AQDS region shown in the Pourbaix diagram. Though the protonated semiquinone, AHDS’, may make an appearance at this potential during the re-oxidation step, the dimer has completely decomposed by this point. If AHDS’ is present at this point in the reaction it is merely a product of further re-oxidation and not directly due to dimer decomposition.

No evidence of dimer formation was found at pHs 3, 5 or 7. A two electron reduction to the monoprotonated species followed by further protonation was indicated for pH values < 7.4. Direct two electron passage implies that semiquinone, AQDS\(^{-}\), is not formed as an intermediate. This gives credence to our earlier supposition that the semiquinone is required for dimer formation.

As was demonstrated in the AQDS/dithionite experiments at pH > 7, dimer formation and decomposition may involve different mechanisms. Dimer formation may be the result of dimerization of two semiquinone radicals whereas homolytic cleavage was the likely decomposition mechanism.

Two distinct dimer formation and decomposition mechanisms were also found with the CPE experiments. Different starting products account for the difference in number of electrons transferred. As was observed with batch AQDS/dithionite reactions
at pH 9.4, dimer formation and decomposition do not follow the same mechanism. Batch AQDS/dithionite experiments at pH 9.4 gave evidence of dimer formation being the dimerization of two semiquinone species, AQDS•. Here, again, with CPE reactions we see the possibility of such a mechanism. The reaction

\[ \text{AQDS} + 2e^- + 2H^+ \rightleftharpoons AH_2DS \quad E^o = -524 \text{ mV vs. Ag/AgCl at pH 9.4} \]

implicated in the CPE decomposition reaction gives supporting evidence for the the disproportionation reaction proposed for dimer decomposition in batch AQDS/dithionite experiments.
AQDS: CYCLIC VOLTAMMETRY

Cyclic voltammetry, CV, is a useful tool in determining many redox properties of a compound. It was used here to study AQDS in buffered solutions at several different pHs. CV may help determine the formal potential of the redox reaction, the number of electrons transferred, and any kinetics involved. This, in turn, may help elucidate some of the behaviors previously observed with the spectroelectrochemical data.

Cyclic Voltammetry at Several Different pH Values

In sufficiently alkaline polar solutions anthraquinones have been observed to undergo two sequential 1-electron reductions. Based on the Pourbaix diagram (Figure 22 and 67) we expect to find AQDS\(^{2-}\) as the sole fully reduced species at pH 11.6.

\[
\begin{align*}
[51] \quad AQDS + e^- & \rightleftharpoons AQDS^- & E^\circ = -0.441 \text{ V vs. Ag/AgCl}^{13} \\
[52] \quad AQDS^- + e^- & \rightleftharpoons AQDS^{2-} & E^\circ = -0.548 \text{ mV vs. Ag/AgCl}^{13}
\end{align*}
\]

It is unlikely that a two electron process occurs as there is a small stability region for AQDS\(^{-}\).

\[
\begin{align*}
[53] \quad AQDS + 2e^- & \rightleftharpoons AQDS^{2-} & E^\circ = -0.495 \text{ V vs. Ag/AgCl}^{13}
\end{align*}
\]
At pH 11.6, CVs conducted at four different scan rates show only one cathodic and one anodic peak with an average peak to peak separation of 58 mV—both are indicative of a one electron reduction (Figure 87, Appendix Figure 116). However, the $E_{1/2}$ of -488 mV vs. Ag/AgCl is more in agreement with the literature value associated with a two electron reduction (-495 mV). Other attributes also show that the reaction is reversible. $E_{pc}$ and $E_{pa}$ do not vary with scan rate. The peak ratio, $i_{pc}/i_{pa}$, is equal to one. And most importantly both cathodic peak current and anodic peak current have been found to be proportional to the square root of scan rate. This indicates that the electrode reaction obeys the Randles-Sevcik equation for a reversible diffusion-controlled reaction (Figure 87).
Figure 87. CVs of AQDS in pH 11.6 phosphate buffer; scan rates 5, 25, 50 and 100 mV/s. [AQDS], 3.15mM; KCl, 0.20 M. Inset: CVs of AQDS at pH 11.6 obeys Randles-Sevcik equation for peak current proportionality to square root of scan rate.

The CVs were compared to CVs conducted with standard, K$_3$Fe(CN)$_6$ (Appendix, Figure 116). Assuming that the electrode area, A, scan rate, $\nu$, and concentration, $C^*$, are maintained constant the ratio of $i_{pc,AQDS}$ to $i_{pc,Fe(CN)_6}$ can be calculated from the Randles-Sevcik equation ([6]).

\[
i_p = 2.72 \times 10^5 n^{3/2} AD^{1/2} C^* v^{1/2}
\]
The $i_{pc,AQDS}/i_{pc,Fe(CN)^{3-}_k}$ can be rearranged:

$$
\left[ \frac{D_{Fe(CN)^{3-}_k}}{D_{AQDS}} \right]^{1/2} \left( \frac{i_{pAQDS}}{i_{pFe(CN)^{3-}_k}} \right) = \left[ \frac{n_{AQDS}}{n_{Fe(CN)^{3-}_k}} \right]^{3/2}
$$

[54]

The left hand side represents the diffusion coefficient corrected current ratio.

Ferricyanide undergoes a one electron process so the expected corrected ratio should be either 1 (1-electron reduction, AQDS) or 2.8 (2-electron process). Correcting for differences in diffusion coefficients we find that the ratios obtained at different scan rates give an average value of 0.7 for AQDS in water. Diffusion coefficient for benzoquinone in H$_2$O ($2.7 \times 10^{-5} \text{ cm}^2 \text{s}^{-1}$) was used for AQDS; $7.6 \times 10^{-6} \text{ cm}^2 \text{s}^{-1}$ was used for K$_3$Fe(CN)$_6$. When diffusion coefficients for benzoquinone in DMSO ($D = 6.04 \times 10^{-6} \text{ cm}^2 \text{s}^{1/2}$) or 9,10-anthracenedione in acetonitrile ($D = 2.29 \times 10^{-5} \text{ cm}^2 \text{s}^{-1}$) were used the ratios approached 1.5. Both 0.7 and 1.5 better match a one electron process (corrected ratio = 1) compared to a two electron process (corrected ratio = 2.8). This suggests two concurrent and independent one-electron transfers occur during the reduction of AQDS at pH 11.6 in the CVs shown in Figure 87.
Figure 88. CVs of AQDS in pH 9.4 buffer; scan rates 5, 25, 50 and 100 mV/s. Inset: Experiment at pH 9 also obeys Randles-Sevcik equation. [AQDS], 3.15 mM; KCl, 0.20 M.

At pH 9.4 we expect to see the singly protonated dianion (see Pourbaix diagram, Chapter III, Figure 22). CVs conducted at pH 9.4 give an \( E_{1/2} \) average value of -460 mV vs. Ag/AgCl (Figure 88). This potential was observed in other pH 9.4 experiments and was attributed to Equation [45] at pH 9.0.

\[
[45] \quad AQDS^{2+} + e^- + H^+ \Leftrightarrow AHDS^- \quad E^o = -465 \text{ mV vs. Ag/AgCl at pH 9.0}
\]

The CV does report a one electron process and has peak to peak separation consistent with a one electron transfer. Like pH 11 it also obeys the Randles-Sevcik equation (Figure 88; Inset).
The stability zones in the Pourbaix diagram for pH 7 suggest that a two electron reduction should be concurrent with two proton addition. In other words, reduction will be followed by protonation and thus appear to be irreversible. As predicted, reversibility was not found for pH 7. The cathodic peak current only was found to vary linearly with the square root of scan rate. The peak to peak separation of $0.0592/n$ was only observed when scan rate was 5 mV/s—and in this case described a 1-electron process. The $E_{1/2}$ of -486 mV vs. Ag/AgCl does however agree with $E^\circ$ at pH 11.6 for a two electron transfer (Figure 22).

![Figure 89. CVs of AQDS at pH 7 PIPES buffer; scan rates 5, 25, 50 and 100 mV/s. Inset: Cathodic peak current is proportional to the square root of scan rate. [AQDS], 3.15mM; KCl], 0.20 M.](image)
Figure 90. CVs of AQDS in pH 3 phosphate buffer; scan rates 5, 25, 50 and 100 mV/s. [AQDS], 3.15mM; KCl, 0.20 M.

The CV performed at pH 3 shows a catalytic current effect (Figure 90).

Reduction products are sometimes capable of catalyzing the reduction of a secondary species at the electrode surface which generates a current that is not the direct result of the experimentally applied potential. Closely related anthraquinone-2,7-disulfonate has been shown to catalytically reduce O₂ which may explain the observed behavior here.⁴²

Conclusion

Although literature treats reduction of AQDS at high pH as a single two electron event our data suggests independent and concurrent two 1-electron reductions. These
two events give rise to a single set of voltammetric peaks. These results are not totally unanticipated.

In polar solvents with high dielectric constants such as water the addition of second electron to an already negatively charged species is made possible through polar stabilization.\textsuperscript{43} Stabilization is also possible though hydrogen bonding.\textsuperscript{43} In such cases it was observed that the potential, $E^\circ_{O^2/\text{O}^2}$, at which the second electron is added shifts positive with increasing additions of water to the quinone solution.\textsuperscript{43,44,45} $E^\circ_{\text{Q}/\text{Q}^\ast}$ shifts positive as well but by a much smaller increment. Therefore the gap between the two potentials narrows until the insertion of a second electron is thermodynamically easier than the insertion of the first. The result is a convergence of two sequential CV peaks into a single two electron CV peak. This was demonstrated in the CVs for the three pHs 7, 9.4 and 11.6. Reversibility is indicated for both pH 9.4 and 11.6. The $E_{1/2}$ at pHs 9.4 and 11.6 are consistent with a two electron transfer for AQDS while the peak to peak separation indicates a 1-electron reaction. Though reversibility was not demonstrated for AQDS in buffered pH 7 solution, an $E_{1/2}$ indicative of a 2-electron transfer was found. The principal fully reduced product at pH 9.4 is the singly protonated dianion, AHDS$^+$ and at pH 11.6, the dianion, AQDS$^{2-}$. For pH 7, the diprotonated species AH$_2$DS is predominant fully reduced species.
CHAPTER VI
THE EFFECT OF NAu-2 ON ANTHRAQUINONE REDUCTION AND DIMERIZATION

The novel dimer feature observed in the preceding chapters may affect the rate of electron transfer to clays or it may itself be affected by the presence of clays.

In this chapter we explore whether any of the effects just mentioned can be observed by performing experiments in the present of the clay NAu-2. This clay was chosen because its high iron content might allow us to observe electron transfer to clay. NAu-2 is 23% iron by mass and has a cation exchange capacity of 700 mmol/kg. 4

The reduction of AQDS was investigated in unbuffered aqueous solution in the absence and presence of NAu-2 clay; these were noted as the AQDS series and NAu-2/AQDS series, respectively. An additional experiment with AQDS in the presence of the smectite SWy-1 was conducted for comparison against NAu-2. We were forced to accommodate the requirements of clay—that it remain unbuffered at neutral pH. Low pH values and high salt concentrations cause the clay to flocculate—form aggregates. For this reason experiments in this chapter were conducted at neutral pH in unbuffered aqueous media. In order to prevent any flocculation from occurring sodium hexametaphosphate, hmp, was added to solutions. Hexametaphosphate delaminates the clay basal surface.
In an unbuffered solution, the reduction of quinone may cause pH to shift.\footnote{43} Therefore the AQDS reduction products and the reduction mechanisms observed in buffered solution are predicted to differ in unbuffered media. As reduction proceeds in unbuffered solution reduction products and intermediates consume protons near the electrode causing the local pH to increase. An increase in pH places the subsequent reduction reaction in a different region of the Pourbaix diagram. For these experiments the region is predicted to be close to that of the buffered pH 9 experiments.

**Unbuffered Solution**

As discussed above the experiment required unbuffered conditions. This has a positive aspect because in a natural environment pH may be unbuffered or heterogeneous near different mineral surfaces.

Quan et. al. conducted extensive research with quinones in unbuffered solution. In an unbuffered solution in which the proton concentration is less than the quinone concentration they suggest that the completely reduced species, the dianion, is strongly hydrogen-bonded with water and will exist as an equilibrium mixture of protonated and unprotonated species: \( \text{Q}^{2-} \), \( \text{QH}^- \), and \( \text{QH}_2 \). As demonstrated in Chapter III under the discussion on Pourbaix Diagram formation the exact distribution of the AQDS species in solution is dependent on the pKa values and on the total AQDS concentration in solution. In 1 mM concentration solution the principal species will be \( \text{QH}^- \) followed by \( \text{Q}^{2-} \) with \( \text{QH}_2 \) as the minor species.\footnote{44}
If the major species is QH\textsuperscript{−} then it is best to focus our attention on the mechanism leading to its formation. In the reduction of Q to QH\textsuperscript{−} Quan et. al. suggest an EEC mechanism in which quinone accepts two electrons (E)(E) in a stepwise fashion followed by the protonation (C). The reaction mechanism for its AQDS counterpart would be as follows:

\[
AQDS + e^- \rightleftharpoons AQDS^- \quad \text{E}
\]

\[
AQDS^- + e^- \rightleftharpoons AQDS^{2-} \quad \text{E}
\]

\[
AQDS^{2-} + H^+ \rightleftharpoons AHDS^- \quad \text{C}
\]

Quan et. al. observed much slower kinetics in buffered solution as opposed to unbuffered. They attributed the slower kinetics to the different mechanism by which Q is reduced to QH\textsuperscript{−} in buffered solution, ECE.

\[
AQDS + e^- \rightleftharpoons AQDS^- \quad \text{E}
\]

\[
AQDS^- + H^+ \rightleftharpoons AHDS^- \quad \text{C}
\]

\[
AHDS^- + e^- \rightleftharpoons AHDS^- \quad \text{E}
\]

Faster net kinetics are observed in moving horizontally along the nine-membered square scheme as is the case with the EEC mechanism.

Therefore, mechanistically, EEC is expected for AQDS in unbuffered aqueous media at initial neutral pH.

The proposition that effective pH should increase in unbuffered aqueous solution due to reduction progress was indeed found to be the case (Table 3).
Table 3. pH changes for select experiments.

<table>
<thead>
<tr>
<th>Series</th>
<th>AQDS Series</th>
<th>NAu-2/AQDS Series</th>
</tr>
</thead>
<tbody>
<tr>
<td>[AQDS], mM</td>
<td>2.4</td>
<td>5.5</td>
</tr>
<tr>
<td>pH initial</td>
<td>6.843</td>
<td>6.137</td>
</tr>
<tr>
<td>pH final</td>
<td>9.552</td>
<td>10.08</td>
</tr>
<tr>
<td>ΔpH</td>
<td>2.709</td>
<td>3.943</td>
</tr>
</tbody>
</table>

Here we find that pH increased for both series. E° is not concentration-dependent but it is pH-dependent. In unbuffered solution, effective pH, or conversely effective [OH⁻], is a function of quinone concentration. The total [OH⁻] concentration changes as the reaction progresses. The effective potential of the second reduction, E\text{max}_2, becomes increasingly negative as initial [AQDS] increases as shown by Equation [55].

\[ E_H = E_{27}^+ - \frac{0.0591}{2} \log \left( \frac{1}{1 + \frac{K_{b1}}{[OH]_T}} \right) \]

where \( K_{b1} = \frac{[AHDS^-][OH^-_T]}{[AQDS^{2-}]}, \) and [OH⁻] = total hydroxide concentration and a function of [AQDS].

The derivation for Equation [55] is given in the Appendix B.

This equation predicts that E° should shift diagonally and to the right on the Pourbaix diagram during the course of a reaction and that such a shift is pH dependent.

To test our predictions, the potential step experiment (or controlled potential electrolysis) was used. Poor spectral quality necessitated this additional analysis. The potential step data acquired was analyzed a little differently than those for the buffered potential step experiments presented in Chapter IV. In this analysis sampled current is presented as a function of applied potential.
Each potential step experiment generated a current vs. time curve (Figure 91). The current was sampled at $t = 300$ seconds. It was determined from such curves that a steady state current was reached by 300 seconds. Furthermore, Cottrell conditions place certain limitations for measurements longer than 300 seconds.\footnote{Cottrell conditions place limitations on measurements longer than 300 seconds.}

$i_i$ (current, $\mu A$) values were obtained by subtracting $i_{\text{initial}}$ from $i_{\text{final}}$ from data from each 10 mV potential step. The absolute value of $i_i$ as a function of $E$ (mV) was plotted and analyzed (Figure 92). For each $|i_i|$ vs. $E_{\text{applied}}$ graph at least one peak was observed. These peaks were noted as $|i_{\text{max}}|$. The corresponding potential at $i_{\text{max}}$ was noted at $E_{\text{imax}}$. The data in Figure 92 shows sampled current vs. potential of a NAu-2/AQDS experiment. A non-symmetrical peak is observed sitting on a rising background current. For a reversible diffusion controlled reaction the sampled current vs. potential peak should be symmetrically centered on $E^0$ (Figure 93) with a flat baseline.

![Figure 91. Current vs. time plot. NAu-2/AQDS Series; [AQDS] 2.4 mM, $E_{\text{applied}} = -150$ mV and -550 mV.](image)
Theoretically (see Chapter II) we know that the potential associated with $i_{\text{max}}$ should represent $E_{\text{rxn}}$ (Figure 93). Unlike $i_{\text{max}}$, $E_{\text{rxn}}$ or $E_{\text{imx}}$ is not concentration-dependent.

For comparison and as a proof of concept Figure 94 is presented. Here we compare the absorbance vs. potential to the sampled current vs. potential data. The experimental conditions were pH 9.4 bicarbonate buffered 2.4 mM AQDS. The buffered solution was chosen because the reaction mechanism should be simpler in the absence of varying pH.
Figure 93. Simulation of current and $[C_R]/[C_O]$ vs. $E_{\text{applied}}$ curve.

The sampled current potential plot shows the development of a nice sharp peak on a rising background. The peak potential $E_{\text{imax}}$ is -490 mV which matches exactly the reaction potential for pH 9.4 (Equation [55]) (see Pourbaix diagram, Figures 22 and 67). 

$$[55] \quad AQDS^{\ast \ast} + e^- + H^+ \rightleftharpoons AHDS^- \quad E^o = -490 \text{ mV vs. Ag/AgCl at pH 9.4}$$

The absorbance vs. potential data can be seen as offset negative in potential from the sampled current data. The absorbance was tracked at wavelength corresponding to the species AQDS$^-$ (500 nm), AQDS$^{2-}$ (447 nm) and AHDS$^-$ (411 nm). The curves appear to mirror each other, consistent with the unresolved nature of species’ spectra. If the data is considered as an aggregate the average potential obtained is -518 mV which lies midway between the above reaction and a two electron, two proton reaction ($E_H = -524 \text{ mV at pH 9.4}$) (Equation [56]).

$$[56] \quad AQDS + 2e^- + 2H^+ \rightleftharpoons AH_2DS$$
Figure 94. Sampled current and absorbance vs. $E_{\text{applied}}$ (based on raw data); AQDS in bicarbonate buffered pH 9.4 aqueous solution; [AQDS], 2.37 mM; [KCl], 0.2 M.

All such experiments in the unbuffered media demonstrated the presence of at least two reduction steps. Those steps were well resolved at high concentrations of AQDS, but not resolved at low concentrations. When the current decreased to background values, the two reduction events could be deconvoluted via Gaussian statistical methods (Figure 95).

**Results: Unbuffered AQDS**

Sampled current vs. $E_{\text{applied}}$ plots are given in Figure 96 (also Appendix A, Figures 117-120) and the data tabulated in Table 4.
Figure 95. Sampled current vs. $E_{\text{applied}}$ curve for NAu-2/AQDS Series, Resolved $E_{\text{imax}}$ peaks; [AQDS], 2.0 mM; unbuffered.
Figure 96. Sampled current, $i$ vs. $E_{\text{applied}}$ for AQDS series; unbuffered solution.
Table 4. $i_{\text{max}}$ for the AQDS series and NAu-2/AQDS series. $E_{\text{applied}}$ vs. Ag/AgCl. Values are based on raw data. *estimated values; $E_{\text{imax2}}$ values are actual.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>AQDS Series</th>
<th>[AQDS] mM</th>
<th>$E_{\text{imax1}}$ mV</th>
<th>$i_{\text{max1}}$ / (μA)</th>
<th>$E_{\text{imax2}}$ mV</th>
<th>$i_{\text{max2}}$ / (μA)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.2</td>
<td>-490*</td>
<td>3.981</td>
<td>-550</td>
<td>2.660</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.6</td>
<td></td>
<td>3.909</td>
<td>-560</td>
<td>4.683</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td></td>
<td>4.302</td>
<td>-560</td>
<td>5.752</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.4</td>
<td></td>
<td>4.616</td>
<td>-580</td>
<td>6.450</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5.5</td>
<td></td>
<td>6.564</td>
<td>-640</td>
<td>11.775</td>
<td></td>
</tr>
<tr>
<td></td>
<td>15.7</td>
<td></td>
<td>6.859</td>
<td>-650</td>
<td>15.005</td>
<td></td>
</tr>
<tr>
<td></td>
<td>19.6</td>
<td></td>
<td>9.379</td>
<td>-690</td>
<td>22.326</td>
<td></td>
</tr>
<tr>
<td></td>
<td>NAu-2/AQDS Series</td>
<td>[AQDS] mM</td>
<td>$E_{\text{imax1}}$ mV</td>
<td>$i_{\text{max1}}$ / (μA)</td>
<td>$E_{\text{imax2}}$ mV</td>
<td>$i_{\text{max2}}$ / (μA)</td>
</tr>
<tr>
<td></td>
<td>1.2</td>
<td>-490*</td>
<td>4.986</td>
<td>-520</td>
<td>5.588</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.6</td>
<td></td>
<td>5.033</td>
<td>-540</td>
<td>6.188</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td></td>
<td>5.084</td>
<td>-540</td>
<td>6.230</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.4</td>
<td></td>
<td>5.878</td>
<td>-550</td>
<td>7.505</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5.5</td>
<td></td>
<td>7.455</td>
<td>-580</td>
<td>11.455</td>
<td></td>
</tr>
<tr>
<td></td>
<td>15.7</td>
<td></td>
<td>9.515</td>
<td>-610</td>
<td>17.824</td>
<td></td>
</tr>
<tr>
<td></td>
<td>19.6</td>
<td></td>
<td>8.066</td>
<td>-620</td>
<td>18.620</td>
<td></td>
</tr>
</tbody>
</table>

$E_{\text{imax}}$ could be measured experimentally only for the higher concentrations because of significant overlap of two different reduction processes at low concentrations.

The data could not be deconvoluted at the lower concentrations for AQDS because of the lack of a falling baseline, therefore $E_{\text{imax}}$ is estimated from the inflection points. The first reduction process is measured/inferred to occur at a potential consistent with a two electron reduction ($E^\circ_{AQDS/AQDS^{2-}} = -495$ mV).

$$[57] \quad AQDS + 2e \rightleftharpoons AQDS^{2-} \quad \quad E^\circ = -495 \text{ mV vs. Ag/AgCl}$$

The second potential shifts negative with increasing concentration of AQDS—a function of Equation [55].
Nernst analysis was also performed on experiments conducted in unbuffered media. Nernst analysis was conducted on select raw data and deconvoluted spectral data (Table 5).

**Nernst Analysis of Raw Data**

Nernst analysis indicates a one electron process for both the 411 nm (semiquinone) and the 727 nm (dimer) bands (Table 5). This is expected for the 411 nm peak because the band at 411 nm is associated with the presence of semiquinone—the result of a one electron reduction, AQDS/AQDS$^-$ and the dimer is formed from AQDS$^-$ when AQDS is reduced. On the other hand, observed potentials are close to the expected two electron, AQDS/AQDS$^{2-}$ potential, $E = -495$ mV. This discrepancy necessitated a deconvolution of the spectra.

**Nernst Analysis of Deconvoluted Spectra**

Nernst analysis was performed on deconvoluted spectra. Analysis of the 400 nm peak (AQDS$^-$) indicates an intermediate value of 1.3 for the number of electrons transferred (Table 5). This, as mentioned in earlier chapters, is indicative of concurrent and independent 1- and 2- electron transfers. This behavior is observed again for the 500 nm peak (AQDS$^-$) (Table 5). The same data is expected for both 400 and 500 nm wavelengths as they both indicate the same species, the semiquinone. As an internal check, similar analyses were carried out on the second AQDS$^-$ spectral peak, 500 nm.

From Nernst data provided in Table 5 we see that the $E^{\text{o}}$ values associated with the formation of the ~700 nm dimer band is consistently close to the value for a two electron (literature, $E_{\text{AQDS/AQDS}^{2-}}^{\text{o}} = -495$ mV). This is further evidence that the dimer is
formed from the dianion. As expected, spectral deconvolution did result in $n = 1.5$ values supporting the $E^\circ$ values for a two electron transfer.

**Table 5.** Nernst Analysis of select raw and deconvoluted spectral data. $E^\circ$ values given first, $n$ values are presented in parentheses. When necessary exact wavelength analyzed is given in parentheses.

<table>
<thead>
<tr>
<th></th>
<th>[AQDS], mM</th>
<th>400 nm</th>
<th>440 nm</th>
<th>500 nm</th>
<th>700 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$E^\circ$, mV(n)</td>
<td>$E^\circ$, mV(n)</td>
<td>$E^\circ$, mV (n)</td>
<td>$E^\circ$, mV (n)</td>
</tr>
<tr>
<td>Raw Data</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AQDS Series</td>
<td>5.5</td>
<td>-510.4 (n = 1.0) (411 nm)</td>
<td></td>
<td></td>
<td>-498.3 (n = 0.9) (727 nm)</td>
</tr>
<tr>
<td>NAu-2/AQDS Series</td>
<td>5.5</td>
<td>-522.4 (n = 1.1) (411 nm)</td>
<td></td>
<td></td>
<td>-500.5 (n = 0.85) (727 nm)</td>
</tr>
<tr>
<td>Deconvoluted Spectral Data</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AQDS Series</td>
<td>2.0</td>
<td>-467.46 (n = 2.2)</td>
<td>-501.7 (n = 1.4) (ascent)</td>
<td>-505 (n = 1.3)</td>
<td>-499.7 (n = 1.5) (ascent)</td>
</tr>
<tr>
<td></td>
<td>2.4</td>
<td>-501.1 (n = 1.3)</td>
<td>-519 (n = 1.4)</td>
<td>-520 (n = 1.1) (514 nm, ascent)</td>
<td>-499.7 (n = 1.5) (ascent)</td>
</tr>
<tr>
<td></td>
<td>5.5</td>
<td>-491.4 (n = 2.2)</td>
<td>-518 (n = 1.5)</td>
<td>-520 (n = 1.1) (514 nm, ascent)</td>
<td>-499.7 (n = 1.5) (ascent)</td>
</tr>
<tr>
<td>NAu-2/AQDS Series</td>
<td>2.0</td>
<td></td>
<td>-504.3 (n = 1.3)</td>
<td></td>
<td>-476 (n = 2.1)</td>
</tr>
<tr>
<td></td>
<td>2.4</td>
<td>-519.7 (n = 0.88)</td>
<td>-539.4 (n = 1.1)</td>
<td>-533.7 (n = 1.7)</td>
<td>-493.1 (n = 1.6)</td>
</tr>
<tr>
<td></td>
<td>5.5</td>
<td>-519.5 (n = 1.5)</td>
<td>-534 (n = 1.2)</td>
<td>-520.5 (n = 1.2)</td>
<td>-493.1 (n = 1.6)</td>
</tr>
<tr>
<td>SWy-1/AQDS Series</td>
<td>2.4</td>
<td>-488 (n = 1.9)</td>
<td>-504 (n = 2.0)</td>
<td>-504.4 (n = 2.2)</td>
<td></td>
</tr>
</tbody>
</table>
Analysis of Current vs. *E*<sub>applied</sub> plot and Spectral Data

More information regarding AQDS reduction in unbuffered media can be obtained by comparison of the sampled current, \( (i_t) \) with the absorbance of the dianion (444 nm, deconvoluted spectra) as both varying as a function of applied potential.

When sampled current values, were superimposed on absorbance vs. *E*<sub>applied</sub> plots a good correlation between the dianion (445 nm) band and current can be made for the AQDS series (Figure 97).

The relevant potentials are

\[
\begin{align*}
[58] & \quad \text{AQDS} + e^- \rightleftharpoons \text{AQDS}^- \quad E^\circ = -441 \text{ mV vs. Ag/AgCl} \\
[59] & \quad \text{AQDS}^- + e^- \rightleftharpoons \text{AQDS}^{2-} \quad E^\circ = -548 \text{ mV vs. Ag/AgCl} \\
[60] & \quad \text{AQDS} + 2e^- \rightleftharpoons \text{AQDS}^{2-} \quad E^\circ = -495 \text{ mV vs. Ag/AgCl}
\end{align*}
\]

The current rises in advance of the production of dianion consistent with a preceding first reduction of AQDS/ AQDS<sup>-</sup> at \( \sim -440 \) mV. The dianion is produced, as analyzed previously at potentials consistent with the reaction AQDS/ AQDS<sup>2-</sup> (-490 mV).

Recall that two separate *E*<sub>imax</sub> were noted in Figure 96 with the first *E*<sub>imax</sub> occurring at -490 mV.

Current maximizes at *E*<sub>imax2,observed</sub> = -560 mV for the experiment shown in Figure 97. *E*<sub>imax2</sub> does not equal any *E*<sup>o</sup> values found in the Nernst analyses. Rather *E*<sub>imax2</sub> does coincide well with the potential at which absorbance is maximum for the AQDS<sup>2-</sup> (444 nm) band for the AQDS series experiments (Figure 97).
Discussion of Spectroscopic Data

Deconvoluted spectra can also be used to compare the trajectory of two different species relative to each other during the reductive process. Spectral data is reduced into absorbance vs. potential plots for analysis. Two such plots are shown for the unbuffered AQDS experiments (Figures 98 and 99). If the two absorbance vs. potential plots cross each other (conversion point) it is possible, in some cases, to obtain the formal potential of the conversion between the two species.

\[ A_{\text{conv}} = \varepsilon_{402} b [AQDS^{-}] = \varepsilon_{440} b [AQDS^{2-}] \]
\[ \frac{[AQDS^{2-}]}{[AQDS^{*}]} = \frac{c_{AQDS}^{b}}{c_{AQDS}^{*}} \quad \frac{[AQDS^{2-}]}{[AQDS^{*}]} = \frac{c_{AQDS}^{b}}{c_{AQDS}^{*}} \]

Substituting for [red]/[ox] or [AQDS$^{2-}$]/[AQDS$^{*}$] in the Nernst Equation we have

\[ E_{conv} = E^{\circ} - \frac{RT}{nF} \ln \left( \frac{c_{AQDS}^{b}}{c_{AQDS}^{*}} \right) \]

Figure 98. Absorbance vs. potential plot based on deconvoluted spectra; AQDS Series; [AQDS], 2.0 mM unbuffered solution.
The potential at the conversion point, $E_{\text{conv}}$ (Figures 98 and 99) is related to the formal potential (Equation [63]). Given the molar absorptivities the formal potential, $E^\circ$, can be estimated from the conversion potential, $E_{\text{conv}}$. Because our spectroscopic system is incapable for monitoring AQDS we are unable to apply this method to determine the first reduction potential. We are capable, however, of monitoring both AQDS$^-$ (402 nm) and AQDS$^{2-}$ (~440 nm). From Table 1, Chapter I, the molar absorptivities for 402 nm and ~440 nm are estimated as $5.77 \times 10^3 \text{M}^{-1}\text{cm}^{-1}$ and $15 \times 10^3 \text{M}^{-1}\text{cm}^{-1}$, respectively. Values for $E_{\text{conv}}$ and $E^\circ$ are shown in Table 6 for AQDS, NAu-2/AQDS, and SWy-1/AQDS.
Table 6. Observed and calculated conversion points of select AQDS and Clay/AQDS experiments. Based on raw data.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>( E_{\text{conv}1} )</th>
<th>( E' )</th>
<th>( E_{\text{conv}2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 mM AQDS</td>
<td>-0.520</td>
<td>-0.545</td>
<td>-0.700</td>
</tr>
<tr>
<td>SWy-1/AQDS</td>
<td>-0.520</td>
<td>-0.545</td>
<td>-0.720</td>
</tr>
<tr>
<td>2.4 mM AQDS</td>
<td>-0.530</td>
<td>-0.555</td>
<td>-0.690</td>
</tr>
<tr>
<td>NAu-2/AQDS</td>
<td>-0.575</td>
<td>-0.599</td>
<td>-</td>
</tr>
</tbody>
</table>

For AQDS the estimated formal potentials for 2.0 and 2.4 mM AQDS are in agreement with other measurements for AQDS\(^{+}\)/AQDS\(^{2-}\) (-548 mV, literature) (see Pourbaix plots Chapter III).

If the product 400 nm band rising at conversion point 2 was solely due to the semiquinone its rise in absorbance as the 444 nm absorption band descends would indicate that the dianion was re-oxidizing back to the semiquinone which is absurd since we are stepping negative in potential. However a fall in the 444 nm band could also indicate that the dianion is being protonated. A band at 406 nm, evidence of a protonated dianion, could contribute to the 400 nm band. The probable reaction sequence in unbuffered solution is

\[
\text{[22]} \quad \text{AQDS}^{+} + e^- \rightleftharpoons \text{AQDS}^{2-} \quad E^o = -0.548 \text{ mV vs. Ag/AgCl}^{26}
\]

\[
\text{AQDS}^{2-} + H^+ \rightarrow \text{AHDS}^- \]

The reaction mechanism proposed requires the protonated fully reduced species, AHDS\(^{-}\), to be present. To test this spectra associated were deconvoluted for potentials bracketing the second conversion point potential (Figure 98). The deconvolutions for 2mM AQDS are shown in Figures 100 and 102.
Figure 100. Deconvoluted spectra; AQDS Series; [AQDS], 2.0 mM; $E_{\text{applied}} = -560$ mV to -780 mV.

A decrease in the AQDS$^2$-(444 nm) band is observed along with a peak shift in the 500 nm band to 481 nm (Figure 100). The 402 nm band increases and is also observed to shift to slightly longer wavelengths (from $\sim$402 nm to $\sim$407 nm). This is best observed in an experiment in which [AQDS] was increased to 5.5 mM (Figure 101).
**Figure 101.** Deconvoluted spectra; AQDS Series; [AQDS], 5.5 mM; $E_{\text{applied}} = -570$ mV to -850 mV.

These two shifts indicate one of two things: 1. protonation of dianion product; 2. immediate subsequent protonation of the dianion formed as semiquinone product accepts an electron. Both routes have the same end product, AHDS$^\cdot$. Route 2 may be so rapid that any significant spectral changes in the semiquinone peak (~400 nm) may not be detectable.

**Route 1:**

$$[AQDS^{-} \cdots AQDS^{-}] \rightarrow AQDS + AQDS^{2-}$$

$$AQDS^{2-} + H^+ \rightarrow AHDS^-$$
Route 2:

[42] \[ AQDS^+ \cdots AQDS^+ \rightarrow 2AQDS^* \]

\[ AQDS^+ + e^- \rightarrow AQDS^{2-} \quad \text{rapid} \]

\[ AQDS^{2-} + H^+ \rightarrow AHDS^- \]

The deconvoluted data shown in Figure 102 for 2.0 mM AQDS has been simplified to emphasize the protonation changes. The AHDS' band (481 nm) increases as protonation makes gains as both the 400 nm (AQDS\(^{+}\)) and 444 nm (AQDS\(^{2-}\)) bands decrease.

**Figure 102.** Deconvoluted spectra; AQDS Series; [AQDS], 2.0 mM; \(E_{\text{applied}} = -780 \text{ mV to } -850 \text{ mV}\).
The mechanism presented involves production of AQDS\(^+\) and AQDS\(^2-\) and AHDS\(^-\). The rise in pH during the reaction should allow the dimer to form when those species are produced at -490 mV (Figure 103). Raw spectra over the wavelength range of 650-790 nm obtained at -490 mV are shown in Figure 103. This is the spectral range in which dimerization was observed in buffered AQDS solutions pH ≥ 9.4. The shapes of the peaks from unbuffered AQDS experiments were strikingly similar to that for buffered (Figure 103). This is confirmation that the dimer is formed in unbuffered solution as well as buffered alkaline solutions.

![Figure 103](image.png)

**Figure 103.** Absorbance in the 650 to 800 nm range for both series in unbuffered aqueous solutions at -490 mV.
The deconvoluted spectra absorbances for the 2.0 mM AQDS experiment were plotted as a function of potential to see if any conversion points indicating direct relationship between AQDS$^-$, AQDS$^{2-}$ and the dimer could be observed (Figure 104).

![Graph showing absorbance vs. potential for AQDS](image)

**Figure 104.** Absorbance vs. Potential for 702, 730, 402 and 498 nm; based on deconvoluted spectra; AQDS Series; [AQDS], 2.0 mM, unbuffered solution; $\lambda_{\text{max,700}}$ occurs at -520 mV.

Though no conversion point occurs between the AQDS$^-$ (400 nm) band and the dimer band (~700 nm), a slight dip in absorbance exists for the 400 nm band when the 700 nm dimer band reaches maximum (Figure 104). This reciprocal relationship between dimer and semiquinone provides additional evidence that the semiquinone plays a part in forming the dimer.
The addition of clay to the system could alter the reduction and dimer formation. The primary clay investigated was NAu-2 which is 23% iron by mass and has a CEC of 700 mmol/kg. A second clay was used in a small number of experiments to contrast the NAu-2 clay. Data for NAu-2 clay sampled current vs. \( E_{\text{applied}} \) plots as shown in Figure 105 are overlay with absorbance for AQDS\(^2^-\) as shown in Figure 106. A conversion plot is shown in Figures 107.

A comparison of sampled current, \( i \) vs. \( E_{\text{applied}} \) plots for NAu-2/AQDS to AQDS shows three major differences (Figure 105). In the first case current decays to baseline suggesting a more rapid set of reactions or prevention of slow reactions. This is an interesting point because it may indicate different mechanisms. As discussed in the introduction to this chapter that an EEC reaction mechanism is faster than the ECE mechanism. In the second case sampled current peaks are sharper also consistent with faster kinetics. Finally, the second reduction process is thermodynamically easier in the presence of clay as noted by comparison of \( E_{\text{max2}} \) for 2.0 and 2.4 mM AQDS vs. NAu-2/AQDS (Table 4).
Figure 105. Sampled current, $i'$, vs. $E_{\text{applied}}$ for NAu-2/AQDS series; unbuffered solutions.
In comparison of the sampled current and AQDS\textsuperscript{2-} production vs. $E_{\text{applied}}$ for NAu-2/AQDS (Figure 106) to AQDS (Figure 97) it can be easily seen that AQDS\textsuperscript{2-} remains stable and resistant to further reduction and that, consequently, the current falls. Both AQDS\textsuperscript{-} and AQDS\textsuperscript{2-} are produced up to $\sim$575 mV at which point no further AQDS\textsuperscript{-} is evolved (Figure 107). The dianion, AQDS\textsuperscript{2-}, absorbing at 444 nm, does not decompose in conjunction with the second reduction peak (Figure 106).

The potentials of the second reduction are more positive of those obtained for pure AQDS (Table 4). The production of full reduction for AQDS as discerned from deconvolution does not involve a protonation reaction (Figure 109).
Figure 107. Absorbance vs. potential plot; NAu-2/AQDS Series; [AQDS], 2.4 mM unbuffered solution.
Figure 108. Absorbance (based on deconvoluted data) vs. potential for 757 nm band. NAu-2/AQDS Series; [AQDS], 2.4 mM; unbuffered solution.
Figure 109. Deconvoluted spectra; NAu-2/AQDS Series; [AQDS], 5.5 mM unbuffered solution; $E_{\text{applied}} = -450 \text{ mV to } -590 \text{ mV}$.

In order to ascertain if this behavior was simply due to increased surface area supplied by clay a comparison reaction with SWy-1 was performed (Figure 110, Table 4). Sampled current vs. $E_{\text{applied}}$ and conversion plots for AQDS in the presence of SWy-1 were similar to those for AQDS. The potentials measured via sampled current (Table 4) and the conversion plots (Table 6) were identical. This indicates that the lack of protonation observed for AQDS in the presence of NAu-2 was specific to the qualities of NAu2. The difference in behavior between SWy-1 and NAu-2 clays is intriguing. There are several differences between the clays which may affect stabilization of the dianion. In the first case there is the difference in the net negative charge of the clays, where NAu-
2 has a higher cation exchange capacity (697 mmol/kg) compared to SWy-1 (382 mmol/kg). The change in CEC in nontronite partially arises from the tetrahedral sheet unlike SWy-1 where the change is very near localized in the interior of the crystal in the octahedral sheet. Finally the difference may be the result of cations that had once resided in the interlayer space. ICP analysis gave a 30:1 Na/Ca ratio for SWy-1. Compare this to the 3:1 ratio found for NAu-2. The valency of the cation may play a role in AQDS adsorption to the clay surface.

Figure 110. Absorbance vs. potential plot; SWy-1/AQDS experiment; [AQDS], 2.4 mM unbuffered solution.
To test the role of the CEC of the clay the concentration of AQDS was increased in order to exceed the saturation point for the clay. Data for the concentration dependent sampled current vs. potential was gathered in Figure 111 and Table 4.

The data suggests that the dimer is stabilized by the clay in part by preventing in some fashion of protonation of the dimer decomposition product. Data supporting dimer stabilization is as follows.

Absorbances of the semiquinone (at 402 nm) over the entire concentration range are less for NAu-2/AQDS than for AQDS. A balance is maintained in that loss of absorbance at this wavelength is compensated by a gain in absorbance in the dimer band. This can be seen in Figure 112 which shows the absorbance vs. potential plot. This suggests that a conversion exists between the semiquinone and dimer in solution. Greater absorbance values for the 727 nm peak for the NAu-2/AQDS series vs. AQDS series indicates that more dimer is being formed in the presence of clay.
Figure 111. Sampled current vs. \(E_{\text{applied}}\); AQDS and NAu-2/AQDS Experiments at increased concentrations.
Figure 112. Absorbance (based on raw data) vs. E plots based on raw data for AQDS and NAu-2/AQDS series, 5.5 mM AQDS; unbuffered solution. Dimer (~700 nm), AQDS$^*$ (402 nm).

Similar evidence for dimer stabilization in the presence of clay comes from the absorbance vs. $E_{\text{applied}}$ plots (Figure 113). For the AQDS series the dimer forms, reaches a maximum absorbance value and then decomposes with its absorbance value returning to a value close to its initial value (Figure 104). In contrast the dimer phase appears to plateau in the NAu-2/AQDS series (Figure 108).

Further evidence of stabilization was seen in the sampled current, $i'$, vs. $E_{\text{applied}}$ plots (Figure 105). Current values returned to those consistent with the control experiment—an indication that the reduction process was complete when clay was present. In the absence of clay, the dimer goes on to decompose and current does not readily return to the baseline set by the control.
When the concentration of AQDS exceeds the capacity of the clay evidence suggests that the reaction mechanism is dominated by that observed in the absence of clay. That is, the dimer decomposes and a protonated species is observed.

Decomposition is inferred by failure of the current to return to baseline (Figure 111) and deconvoluted spectra now unambiguously demonstrate the presence of AHDS\(^-\) at 472 nm (Figure 113).

The thermodynamics associated with the second reduction are more favorable in the presence of the clay as observed from the \(E_{\text{imax2}}\) values. The clay stops reduction fully, pre-saturation, suggesting faster kinetics of the shared reaction or alternative mechanisms between clay and no clay in which clay is thermodynamically easier. At very large concentrations of AQDS \(E_{\text{imax2}}\) shifts negative (more so than driven simply by pH change) and the sampled current fails to return to baseline suggesting that AQDS not associated with clay mechanistically reduces in a manner consistent with no clay.
The data proves that the clay alters the thermodynamics of reduction and of dimer formation. Clays provide a surface upon which quinone-like substances can adsorb. Research conducted by Indraratne et. al. have shown that to be the case. Catechols which have OH groups ortho to each other are bidentate and therefore capable of better adsorption. And citrates are better at adsorption because they are better at eliminating the interlayer space. Hydroquinone is not capable of the same degree of adsorption as bidentate catechol however it has been shown to adsorb onto oxides.\textsuperscript{51} Recall that in our studies hexametaphosphate was added to aid in removing the interlayer and exposing the basal surface of clay to AQDS.
In preceding chapters it was suggested that dimerization involves the bonding between two semiquinone intermediates (AQDS⁻). Dimerization of two radical species has long been perceived as being thermodynamically unfavorable due to the repulsive electrostatic interactions between like charged particles. The quantum mechanical studies suggesting unfavorable thermodynamics were based on gas phase calculations. In other words, this assumption does not take into account the effect of reaction media on dimerization. In a solution localization of negative charges on the radical results in an increase in solvation.

**Point of Zero Net Charge**

Clays possess a charged basal surface which may be described in terms of zero net charge. The point of zero net charge is equivalent to the isoelectronic point. For NAu-2 the point of zero net charge has been calculated at pH\text{PZNC} = 7.2. When the pH > pH\text{PZNC} water donates hydroxyl groups to the clay surface. Under these conditions, the clay surface becomes negatively charged and cations are attracted to it. The basal surface sorption site is ionic-strength dependent. Fe²⁺ exhibited a sharp increase in sorption in the pH 7 to pH 9 range when the ionic strength was low.

Cation-stabilization has been shown to play an important role in forming a metastable π-dimer. An implication of this was shown in experiments comparing SWy-1 to NAu-2. The former is deficient in the divalent Ca²⁺. Compare 30:1 Na/Ca for SWy-1 to 3:1 Na/Ca for NAu-2. Recall from Chapter 1 that metastable π-dimers may form when the quasi-covalent bonding energy is equivalent to the electrostatically
The π-dimer formation is made more thermodynamically favorable through the stabilizing factors provided by cations in solution.\textsuperscript{22}

The charged basal surface of clay may also be considered a medium of high polarity. Clays, therefore, may positively affect rate of dimerization between like-charged particles.

**Catalytic Effect**

Clay appears to affect AQDS reduction in yet another way. The reduction reaction indicated by the first $E_{\text{max}}$ occurring at $\sim-490$ mV gives greater $i_{\text{max}}$ values for AQDS in the presence of clay. This suggests that the reaction is kinetically faster for AQDS in clay (or that a catalytic effect is observed) (Figure 114). The faster kinetics associated with AQDS reduction may contribute to the increase in dimer observed in the presence of clay. The basal surface of clay may provide a means of stabilizing the dimer.

At low [AQDS], concurrent 2 e- and 1 e- reactions take place and the dimer formed most probably resides solely along the basal surface. As the concentration of [AQDS] increases and the basal surface becomes increasingly saturated with AQDS, the first $i_{\text{max}}$ peak approach a limit and ceases to increase with increasing [AQDS].
Figure 114. Sampled current $i_{\text{max}}$ vs. $[\text{AQDS}]_{\text{initial}}$, AQDS and NAu-2/AQDS experiments; unbuffered solution.

Calculations performed by Saveant et. al. have shown that the change in enthalpy of repulsion of charged radicals is compensated by increased solvation in the transition state.\textsuperscript{47,48} The activation energy required to achieve a dimer transition state is lowered which should increase the rates of dimerization.

The Debye-Smoluchowski theory of diffusion-controlled reaction between charged species may be used in determining the feasibility of dimerization reactions.\textsuperscript{49} Dimerization of equally-charged radical ions (in our case the semiquinone) is unfavorable due to electrostatic repulsion. The relationship between polar media and kinetics may be given by the Debye-Smoluchowski theory of diffusion-controlled kinetic reactions.
$k_{2d}$, the rate constant of a reaction between two charged particles, A and B, is given by the following equation:

$$k_{2d} = 4\pi \times 10^{-3} N_A^2 (D_A + D_B) R_{AB} \Phi_{AB}$$

where $\Phi_{AB} = \frac{\varphi}{e^\varphi - 1}$ and $\varphi = \frac{Z_A Z_B e^2}{R_{AB} e^k T}$ and $R_{AB} =$ sum of the van der Waals radii of A and B.

The dielectric constant, D, is a unitless ratio that relates the permittivity of a medium to that of a vacuum, $\varepsilon_0$. $D = \frac{\varepsilon}{\varepsilon_0}$. It should be evident that $k_{2d}$ increases as $\varepsilon$ increases.

A large dielectric constant is characteristic of solvents of high polarity. The dielectric constant of water is relatively high—80.37. The repulsive forces of the semiquinone are diminished due to shielding by solvents with high dielectric constants. Heinze et. al. determined that the rate constant of dimerization depends on the dielectric constant of the solvent. Mazine et. al. found that dimerization of radical anion, 9-cyanoanthracene, a tricyclic aromatic compound like anthraquinone, was more favorable in the more polar solvent CH$_3$CN as opposed to CH$_2$Cl$_2$.

Polar solution media aids in dimerization by shielding the repulsive forces felt by like charges. In polar solvents, such as H$_2$O, Lacroix et. al. have shown that the dimerization rate constant approaches or is greater than that of diffusion-controlled process.

It has been shown that clays may function as catalysts. Clays, therefore, may positively affect rate of dimerization between like-charged particles. By providing a surface, like enzymes, clays may act as catalysts in polymerization and humification.
Humification is the oxidation and subsequent decomposition of complex polycyclic organic compounds into simpler organic acids.\textsuperscript{52} The extent to which humification and oxidation occurs is a function of the CEC and specific surface area of the clay. Thompson and Moll (1973) found that the greatest degree of humification with hydroquinone was with the clay montmorillonite for which the interlayer was lacking and for which neither CEC nor specific surface area was compromised.\textsuperscript{53}

**Cyclic Voltammetry**

Cyclic voltammograms of AQDS and NAu-2/AQDS with equal [AQDS] indicate a more positive $E^{\circ}$ for the NAu-2/AQDS (Figure 115). This indicates that it is easier to reduce AQDS in the presence of clay. Recall that $E_{\text{max2}}$ (Table 4) values given in the sampled current vs. $E_{\text{applied}}$ plots were more positive for AQDS in the presence of clay.

![Figure 115](image)

**Figure 115.** AQDS and NAu-2/AQDS mixture; 2.04 mM AQDS for both CVs. Scan rate 25 mV/s.
Conclusion

Evidence for dimerization of semiquinone in moderately alkaline buffered solution was given in Chapter III. In these current studies we also find evidence of such a dimer in unbuffered aqueous solution at neutral pH. This does not, however, go counter the evidence presented in earlier studies. A change in effective pH during reaction progress allows for the production of intermediates necessary for dimerization to occur. Dimer formation is enhanced in the presence of clay. Furthermore, clay appears to stabilize the dimer species. Clay has also demonstrated its catalytic abilities as was seen in the current vs. applied potential plots. Mechanistically, the two series appear to be similar leading up to dimer formation. Post dimer formation, the two series follow two mechanistic paths. The dimer decomposes in the absence of clay which is followed by a series of reactions which ultimately culminate in the formation of AHDS⁻ as the final product.
APPENDIX A

SUPPLEMENTARY FIGURES
Figure 116. CVs of $\text{K}_3\text{Fe(CN)}_6$; scan rates 5, 25, 50 and 100 mV/s. $[\text{K}_3\text{Fe(CN)}_6]$, 2.0 mM; $[\text{KCl}]$, 0.20 M.
Figure 117. Sampled current, $i_v$ vs. $E_{applied}$ for AQDS and NAu-2/AQDS series; [AQDS], 1.2 mM; unbuffered solution.
Figure 118. Sampled current $i_i$ vs. $E_{\text{applied}}$ for AQDS and NAu-2/AQDS series; [AQDS], 2.0 mM; unbuffered solution.
Figure 119. Sampled current $i_i$ vs. $E_{applied}$ for AQDS and NAu-2/AQDS series; [AQDS], 2.4 mM; unbuffered solution.
Figure 120. Sampled current, /i/ vs. E_{applied} for AQDS and NAu-2/AQDS series; [AQDS], 5.5 mM; unbuffered solution.
Figure 121. Sampled current $i_i$ vs. $E_{\text{applied}}$; SWY1/AQDS, NAU2/AQDS and AQDS; [AQDS], 2.4 mM; unbuffered solution.
APPENDIX B:
SUPPLEMENTARY DERIVATIONS
Derivation of Equation [55]

In unbuffered solutions the solution is not held at constant pH.

\[
\text{[64]} \quad AQDS^{2-} + H_2O \rightleftharpoons AHDS^- + OH^{-} \quad K_{b1} = \frac{K_w}{K_{a2}}
\]

\[
\text{[65]} \quad AHDS^- + H_2O \rightleftharpoons AH_2DS + OH^{-}\quad K_{b2} = \frac{K_w}{K_{a1}}
\]

Assume that only the first equation is significant. This increases the hydroxyl concentration at the electrode surface in excess of what is present in the bulk solution.

\[
\text{[66]} \quad C_{OH,T} = C_{OH,B} + C_{OH,Q}
\]

(surface, bulk, anthraquinone)

This then will control the effective pH at the electrode surface

\[
\text{[67]} \quad pH_{eff} = 14 - pOH_{eff} = 14 - pOH_T
\]

Concentrations at equilibrium:

\[
\text{[68]} \quad AQDS^{2-} + H_2O \rightleftharpoons AHDS^- + OH_T^{-}
\]

\[
\text{[69]} \quad (C_{AQDS^{2-}} - C_{OH,Q}) \quad (+C_{OH,Q}) \quad (+C_{OH,Q} + C_{OH,B})
\]

\[
\text{[70]} \quad K_{b1} = \frac{[AHDS^-][OH_T^{-}]}{[AQDS^{2-}]}\quad
\]

Substituting for concentrations at equilibrium:

\[
\text{[71]} \quad K_{b1} = \frac{(C_{OH,Q}) + (C_{OH,Q} + C_{OH,B})}{(C_{AQDS^{2-}} - C_{OH,Q})}
\]

Substituting for \((+C_{OH,Q})\):
[72] \[ C_{OH,Q} = C_{OH,T} - C_{OH,B} \]

[73] \[ K_{b1} = \frac{(C_{OH,T} - C_{OH,Q})(C_{OH,T})}{(C_{AQDS^{2-}} - C_{OH,Q})} \]

Using the quadratic formula to solve to \( C_{OH,T} \):

\[ 0 = C_{OH,T}^2 - (C_{OH,B} - K_{b1})C_{OH,T} - K_{b1}(C_{OH,B} + C_{AQDS}) \]

[74] \[ C_{OH,T} = \frac{C_{OH,B} - K_{b1} \pm \sqrt{(C_{OH,B} - K_{b1})^2 + 4K_{b1}(C_{OH,B} + C_{AQDS})}}{2} \]

[75] \[ AQDS + 2e^- + nH^+ \rightleftharpoons \{AQDS^{2-}, AHDS^-, AH_DS\} \]

[76] \[ \alpha_{AQDS^{2-}} = \frac{[AQDS^{2-}]}{[AQDS^{2-}] + [AHDS^-]} \]

[77] \[ K_{b1} = \frac{[AHDS^-][OH^-]}{[AQDS^{2-}]} \]

Rearranging:

\[ [AHDS^-] = \frac{K_{b1}[AQDS^{2-}]}{[OH^-]} \]

Substituting:

[78] \[ \alpha_{AQDS^{2-}} = \frac{1}{1 + \frac{K_{b1}}{[OH^-]}} \]

The net reduction Nernst Equation is:

[79] \[ E = E^\circ_{27} - \frac{0.0591}{2} \log \alpha_{AQDS^{2-}} \frac{[AQDS_{\text{red},AQDS^{2-}}]}{[AQDS]} \]

[25] \[ AQDS + 2e^- \rightleftharpoons AQDS^{2-} \quad E^\circ_{27} \]
\[ \Delta G_{27} = -2F E_{27}^o \]

Rearranging:

\[-\frac{\Delta G_{27}}{2F} = E_{27}^o \]

\[
E = E_{27}^o - \frac{0.0591}{2} \log \alpha_{AQDS^{2-}} \left[ \frac{AQDS_{red,AQDS^{2-}}}{AQDS} \right]
\]

\[ E = E_{27}^o - \frac{0.0591}{2} \log \alpha_{AQDS^{2-}} + \log \left[ \frac{AQDS_{red,AQDS^{2-}}}{AQDS} \right] \]

The first two terms represent the pH-dependent portion.

\[ E_H = E_{27}^o - \frac{0.0591}{2} \log \alpha_{AQDS^{2-}} \]

Substituting for \( \alpha_{AQDS^{2-}} \):

\[ E_H = E_{27}^o - \frac{0.0591}{2} \log \left[ \frac{1}{1 + \frac{K_{b1}}{[OH_T^-]}} \right] \]

where \([OH_T^-]\) is given by \( C_{OH,T} \)
APPENDIX C

LIST OF EXPERIMENTAL E" VALUES
<table>
<thead>
<tr>
<th>Redox Couple</th>
<th>$E^\circ$, mV. vs. Ag/AgCl (number of electrons)</th>
<th>$E^\circ_{experimental}$ mV. vs. Ag/AgCl (number of electrons)</th>
<th>Experiment (Type of analysis)</th>
<th>Chapter</th>
<th>Figure number</th>
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</thead>
<tbody>
<tr>
<td>AQDS/AQDS$^-$</td>
<td>-441 (1)</td>
<td>-448 (3)</td>
<td>Batch pH 9.4 (Nernst CT band decomp)</td>
<td>III</td>
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<tr>
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<td>Batch pH 11 (Nernst CT band decomp)</td>
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<tr>
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<td>-439 (1.1)</td>
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<td>CPE pH 9.4 (Nernst 411 nm ox)</td>
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</tr>
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<td>AQDS$^+$/AQDS$^2-$</td>
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<td>AQDS/AQDS²</td>
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<td>-500 (1.61)</td>
<td>Batch pH 9.4 (Nernst 481 nm rise)</td>
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<td>Reaction</td>
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<td>pH/CPE</td>
<td>Method/Decomp.</td>
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APPENDIX D

STATISTICAL VALUES FROM ORIGIN PRO FOR PEAK DECONVOLUTION
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<th>Time, (minutes)</th>
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<th>Reduced Chi Square</th>
<th>Time, (minutes)</th>
<th>COD (R^2)</th>
<th>Reduced Chi Square</th>
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Chapter III | Chapter III

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REFERENCES


5 Source Clay Physical/Chemical Data


7 Mineral News: The Mineral Collector’s Newsletter


VITA

Anna Weiss was raised in Chicago, Illinois. Before attending Loyola University Chicago, she earned a Bachelor of Science in Biochemistry from University of Illinois Chicago graduating with college honors and highest distinction in 2002.

In 2007 she entered the Ph.D. program in chemistry at Loyola University Chicago. She was awarded the Advanced Doctoral Fellowship in the academic year of 2010/2011 and the Arthur J. Schmitt Fellowship in the academic year of 2011/2012.

Currently, she lives with her family in the northwest suburbs of Chicago, Illinois.