Experiment 3: Cyclic Voltammetry
(Dated: October 29, 2009)

I. INTRODUCTION

Redox reactions of quinone compounds have found application in many areas of chemistry and biology, such as photosynthesis [1], anthracycline cytostatic drugs [2], and wood and paper chemistry [3]. In this exercise cyclic voltammetry is used to study the redox processes and solvent hydrogen bonding effects in 2,3,5,6-tetramethyl-1,4-benzoquinone (duroquinone; see Fig. 1) [4–6]. The importance of hydrogen bonding in physico-chemical processes is enormous. For example, the liquid state of water and the helical structure of DNA are attributed to hydrogen bonding.

![Figure 1: Structure and reduction scheme of duroquinone.](image)

FIG. 1: Structure and reduction scheme of duroquinone. The structure shown for the anion radical is one of the two possible resonance structures, where the unpaired electron and the negative charge may exchange. Note that the neutral species is not aromatic.

Voltammetry is a collection of electro-analytical techniques in which information about the analyte or a physical process is derived from the measurement of current as a function of applied potential. It is widely used by chemists for non-analytical purposes including fundamental studies on redox processes, adsorption processes on surfaces, electron transfer mechanisms, and electrode kinetics.

II. CYCLIC VOL TAMMETRY

Voltammetric measurements are carried out using an electrochemical cell made up of three electrodes immersed in a solution containing the analyte and an excess of a non-reactive electrolyte called the supporting electrolyte. One of the three electrodes is the working electrode, which is typically made of platinum, gold, silver, glassy carbon, nickel, or palladium. The redox process occurs at this electrode. Its dimensions are kept small in order to enhance its tendency to become polarized. The second electrode is the reference electrode, which provides calibration for the applied potential. Examples of commonly used references are the normal hydrogen electrode, Ag/AgCl electrode, and calomel electrode (e.g. Hg/HgCl$_2$). The third electrode is the counter electrode, which is often a platinum wire that simply serves to conduct electricity from the signal source through the solution to the other electrodes. An example of a voltammetric setup is shown in Fig. 2. Note that in absence of any redox processes, the electrodes behave like capacitor plates, which polarize the ions in the solution. This results in a small, but measurable, capacitive current in the system.

Fig. 3 shows the nature of the triangular voltage waveform that is applied to the working electrode. After applying a linear voltage ramp between $t_0$ and $t_1$, the ramp is reversed to bring the potential back to its initial value at time $t_2$. Fig. 4 illustrates a typical cyclic voltammogram. In the parts of the wave labeled 'A', 'B', and 'C', the potential is applied and an increasing amount of current is observed. This is the cathodic part of the wave, where reduction of the quinone molecules is occurring. Maximum flow of electrons is observed at point 'C'. After point 'C', potential is still applied, but the current associated with the reduction decreases due to a depletion of quinone molecules at the electrode. Quinone diffusion toward the electrode must occur before reduction. Here diffusion is slower than reduction and therefore there is a reduction in the current flow between the parts 'C' and 'D'. Parts 'E', 'F', and 'G' describe
FIG. 2: An electrochemical cell. 'V' denotes a high impedance voltmeter (no current flows between the reference and working electrodes) and 'A' measures the current between the working and the counter electrodes. In a cyclic voltammetry experiment, the potential of the reference electrode is varied and the current between the working and reference electrodes is measured.

FIG. 3: A triangular waveform is applied to the working electrode. For description of the symbols, see text.

FIG. 4: A typical cyclic voltammogram. For explanation of the symbols, see text.

The reverse process (e.g. the anodic part). When the voltage is decreased, the reverse oxidation process occurs, and the quinone molecules are returned to their initial state. Fig. 5 demonstrates a typical cyclic voltammogram for a two-electron reduction process, where one peak is observed on both sides for each electron transfer process.

The redox potential can be obtained from a voltammogram by calculating the average value of the anodic and cathodic peaks. For example, for the voltammogram shown in Fig. 5, the one-electron \( E_{1,1/2} \) and two-electron \( E_{2,1/2} \) redox potentials can be calculated as:

\[
E_{1,1/2} = \frac{E_{1}^{-} + E_{1}^{+}}{2} \quad \text{and} \quad E_{2,1/2} = \frac{E_{2}^{-} + E_{2}^{+}}{2}
\]  

The subscript 1/2 indicates that the potential is obtained approximately at the half-height of the cathodic and anodic peaks and hence is sometimes called the half-wave potential. At these points the concentrations of the reduced and
oxidized species are equal. Note that in this context concentration refers to concentration of a given species on the electrode – not in the bulk solution. In cases where only one-electron reduction occurs, only one maximum is observed in the cathodic and one minimum in the anodic waves. When the anodic and cathodic waves are symmetric with respect to each other, the redox process is reversible. If they are not symmetric, the redox species may undergo a chemical reaction and will not be observed on the returning sweep. Remember that the measured values are always expressed relative to the reference electrode and appropriate conversions must be carried out when comparing with data taken with a different type of reference electrode.

III. DETERMINATION OF THE REDOX POTENTIAL AND THE DEGREE OF HYDROGEN BONDING IN DUROQUINONE

The purpose of this experiment is to determine the redox potential of duroquinone (e.g. the potential governing the formation of anion radicals and dianions as shown in Fig. 1) and to determine the number of CH$_3$CH$_2$OH (ethanol) molecules hydrogen bonding to the quinone oxygens at positions 1 and 4. The largest partial charges reside on the quinone oxygens and on the alcoholic proton of ethanol. This promotes the formation of hydrogen bond between them. Recall that hydrogen bonding arises from the electrostatic interaction between opposite partial charges as well as possible steric effects for molecular approach.

Benzoquinone and its substituted derivatives (denoted by $Q$) undergo reversible two step-wise one-electron transfer reactions in aprotic (e.g. “non-proton donating”) solvents. Examples of aprotic solvents are acetonitrile (CH$_3$CN), benzonitrile, dimethylsulfoxide (DMSO), dimethylformamide (DMF). The reduction scheme is shown in Fig. 1. In the presence of a protic (e.g. “proton donating”; denoted by $S$) solvent, association of solvent molecules to $Q$ must be considered:

\[
Q^- + S \rightleftharpoons Q^- \cdots S
\]

\[
Q^- + 2S \rightleftharpoons Q^- \cdots S_2
\]

\[
\vdots
\]

\[
Q^- + nS \rightleftharpoons Q^- \cdots S_n
\]

and for the dianion:

\[
Q^{2^-} + S \rightleftharpoons Q^{2^-} \cdots S
\]

\[
Q^{2^-} + 2S \rightleftharpoons Q^{2^-} \cdots S_2
\]

\[
\vdots
\]

\[
Q^{2^-} + mS \rightleftharpoons Q^{2^-} \cdots S_m
\]
where the association of solvent molecules up to \( n \) and \( m \) is shown. In this work, we assume that only one hydrogen bonded form dominates for \( Q^- \) and \( Q^{2-} \): 

\[
\begin{align*}
Q^- + nS & \rightleftharpoons Q^- \cdots S_n \\
Q^{2-} + mS & \rightleftharpoons Q^{2-} \cdots S_m
\end{align*}
\]  

(3)

where symbol \( n \) denotes an average number of protic solvent molecules bound to the anion radical and \( m \) is the corresponding number for the dianion. Note that both (2) and (3) are simplified schemes in a sense that the actual redox processes occur for solvated forms of \( Q^- \) and \( Q^{2-} \) (e.g. for \( Q^- \cdots S_i \) and \( Q^{2-} \cdots S_j \)) and therefore the redox potentials also shift to lower energy (e.g. the redox process occurs more easily). The equilibrium constants for (3) can be written as:

\[
K_1 = \frac{[Q^- \cdots S_n]}{[Q^-] [S]^n} \quad \text{and} \quad K_2 = \frac{[Q^{2-} \cdots S_m]}{[Q^{2-}] [S]^m}
\]  

(4)

Note that the assumption of single solvation form may introduce values for \( n \) and \( m \) that are not integers and thus they should be interpreted as average values for the associated solvent molecules. The effect of solvent molecules on the redox potential can be derived as follows:

1. The anion radical (e.g. the first line in (3)). The total concentration of anion radical is given by:

\[
[Q^-]_{\text{total}} = [Q^-] + [Q^- \cdots S_n]
\]  

(5)

By expressing this in terms of the equilibrium constant \( K_1 \) (see (4)), we get:

\[
[Q^-]_{\text{total}} = [Q^-] \times (1 + K_1 [S]^n)
\]  

(6)

Assuming that the electrochemical reactions are reversible, the Nernst equation for the redox pair \( Q/Q^- \) can be written:

\[
E_1 = E_1^o + \frac{RT}{N F} \ln \left( \frac{[Q]}{[Q^-]} \right)
\]  

(7)

where \( E_1 \) is the effective redox potential when protic solvent \( S \) is present (V), \( E_1^o \) is the standard redox potential in aprotic solvent (e.g. without \( S \); units in V), \( R \) is the molar gas constant (8.31451 J mol\(^{-1}\) K\(^{-1}\)), \( T \) is the cell temperature (K), \( N \) is the number of electrons transferred (e.g. here \( N = 1 \)) and \( F \) is the Faraday constant (9.648531 \( \times \) 10\(^4\) C mol\(^{-1}\)). Note that only the non-hydrogen bonded form is involved in the reduction process as the hydrogen bonding occurs after the reduction. Inserting Eq. (6) in Eq. (7), we get:

\[
E_1 = E_1^o + \frac{RT}{NF} \ln \left( \frac{[Q]}{[Q^-]} \right) \times (1 + K_1 [S]^n)
\]  

(8)

At the half-wave potential the total concentrations of the oxidant and the reductant are equal (e.g. \([Q] = [Q^-] \)) and \( E_1 \) becomes \( E_{1,1/2} \). Thus Eq. (8) now becomes (with \( N = 1 \)):

\[
E_{1,1/2} = E_{1,1/2}^o + \frac{RT}{F} \ln (1 + K_1 [S]^n)
\]  

(9)

When the hydrogen bonded form dominates (e.g. \( K_1 \times [S]^n \gg 1 \); see Eq. (4)) and the half-wave potential shift is denoted by \( \Delta E_{1,1/2} = E_{1,1/2}^o - E_{1,1/2}^o \), the above equation can be simplified as:
\[ E_{1,1/2} = E^o_{1,1/2} + \frac{RT}{F} \ln (K_1 [S]^n) = E^o_{1,1/2} + \frac{RT}{F} \ln (K_1) + \frac{nRT}{F} \ln ([S]) \] (10)

\[ \Rightarrow \Delta E_{1,1/2} = E_{1,1/2} - E^o_{1,1/2} = \frac{RT}{F} \ln (K_1) + \frac{nRT}{F} \ln ([S]) \]

Thus plotting logarithm of the concentration \([S]\) on the x-axis and \(\Delta E_{1,1/2}\) on the y-axis should yield a straight line ("\(y = b + k \ln(x)\)". Fitting the experimental \(\Delta E_{1,1/2}\) points obtained with various concentrations \([S]\) yields estimates for both the equilibrium constant \(K_1\) and the average number of hydrogen bonded solvent molecules \(n\). The experimental half-wave potentials must be extracted from the voltammograms using Eq. (1).

2. The dianion (see 2nd line in Eq. (3)).

This case proceeds in a similar way as case 1 above. First, we write the total concentration for the dianion:

\[ [Q^{2-}]_{total} = [Q^{2-}] \times (1 + K_2 [S]^m) \] (11)

By writing the Nernst equation for the \(Q^-/Q^{2-}\) redox pair and carrying out similar algebra that we did in deriving Eq. (9), we get \((N = 1)\):

\[ E_{2,1/2} = E^o_{2,1/2} + \frac{RT}{F} \ln \left(\frac{[Q^{-}]}{[Q^{2-}]}\right) = E^o_{2,1/2} + \frac{RT}{F} \ln \left(\frac{1 + K_2 [S]^m}{1 + K_1 [S]^n}\right) \approx E^o_{2,1/2} + \frac{RT}{F} \ln \left(\frac{K_2}{K_1} [S]^{m-n}\right) \] (12)

\[ \Rightarrow \Delta E_{2,1/2} = E_{2,1/2} - E^o_{2,1/2} = \frac{RT}{F} \ln \left(\frac{K_2}{K_1}\right) + \frac{RT(m-n)}{F} \ln ([S]) \]

This is again a straight line when plotted against logarithm of the concentration \([S]\). Fitting would yield estimates for the ratio of \(K_2/K_1\) and the difference \(m-n\). Values for \(K_1\) and \(n\) are known from the anion radical data (previous case) and therefore values for \(m\) and \(K_2\) can be calculated using Eq. (13).

IV. EXPERIMENTAL

**Instrument:** A EG&G Potentiostat / Galvanostat controlled by a computer through Power Suite software ("echem program"). The software has a provision for carrying out Cyclic Voltammetry, storing, overlaying and printing graphs.

**Electrodes:** Working electrode: glassy carbon (Bioanalytical systems, 6 mm diameter); Counter electrode: Pt electrode; Reference electrode: Ag wire ("quasi electrode"). For the latter, a standard Ag/AgCl, SCE or Ag/AgNO₃ electrode can also be used.

**Chemicals:** Quinone (duroquinone; M.W. 164.21 g mol⁻¹), Tetra-n-butylammonium hexafluorophosphate (TBAHFP; M.W. 387.44 g mol⁻¹), acetonitrile (aprotic solvent; dried over drierite), dry ethanol (Fisher reagent grade dried over molecular sieves; "protic solvent"; denoted by \(S\) previously).

**Task overview:** You will record cyclic voltammograms (CVs) of a 2 mM solution of quinone in dry acetonitrile (25 mL; do not shake!). You will add successive amounts of dry ethanol to the solution in the cell to make 0.05 M, 0.1 M, 0.2 M, 0.5 M and 1.0 M in ethanol. In order to get the correct ethanol concentrations, you will need to use the molecular weight of ethanol (46.0634 g mol⁻¹) and density of ethanol (0.789 g mL⁻¹). The initial amount of solution in the CV cell will be 10 mL. Be sure to make the required calculations in advance (e.g. how much ethanol will need to be added at each step). The amount for the first addition is some tens of \(\mu\)L. Finally, the solution in the CV cell will have to be purged (e.g. remove oxygen) by bubbling nitrogen gas after each successive addition of EtOH.

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

2. When you are finished using the electrode assembly, thoroughly rinse the cell and electrodes, clean the working electrode by rubbing it very gently with a very fine emery paper, washing it with deionized water and then with acetonitrile or ethanol. Clean the jacket of the reference electrode by throwing out the contents of the jacket and rinsing with acetonitrile. Also wash the silver wire and counter electrode with acetonitrile.

3. The last person in the lab using the nitrogen gas for purging must close the valve to the tank before leaving.

The experimental procedure:

1. Prepare 25.0 mL of a 2.0 mM solution of quinone (< 10 mg needed) with 0.1 M TBAHFP (< 1 g needed) as the supporting electrolyte in acetonitrile using a 25 mL volumetric flask. Do not wash anything with water. Make sure the solution is mixed well and that all solids have been dissolved.

2. Prepare the sample and install the electrodes:

   (a) Assemble the reference electrode ("R"). Insert the jacket of reference electrode in one of the holes of the stopper. If the silver wire is not shiny use a fine emery paper to clean the surface and then wipe it with kimwipe.

   (b) Take a look at the working electrode surface ("W"). If the surface is not mirror shiny, notify the instructor. In this case the electrode needs polishing: put a drop of distilled water on a 1500 grade emery paper and gently rub the electrode surface on the emery paper rotating it in clock and then counter-clock directions 5 - 6 times. Wash the surface of the electrode and dry with kimwipe. The electrode should be as shiny as a mirror. If not, the electrode needs more polishing.

   (c) Deliver 10.0 mL of the 2.0 mM solution to the voltammetric cell.

   (d) Insert the counter ("C") and working electrodes in the two holes of the stopper and stopper the cell. Insert the reference electrode in the jacket of the reference electrode.

   (e) Bubble the solution with \( \text{N}_2 \) for 5 - 10 min.

3. Make the following settings in the CV program: Double click on the "echem" icon to start the program. Click on SETUP and NEW TECHNIQUE and select IMMEDIATE MODE. Click on GET SETUP and write pchem.set. The parameter values should be: PURGE TIME = 0.0, SCAN RATE = 50.0, INITIAL PLOT = -0.1, VORTEX 1 POT = -2.0, and FILTER = 5.3 Hz. Press the "Cell enable" button on the potentiostat and click on RUN. After the run has finished, press the "Cell enable" button again to turn it off. After scanning save and print a copy of the resulting voltammogram. Locate the peaks (two on both cathodic and anodic waves) by clicking on GRAPH, CURVE, and FREE CURSOR. These values are required to use Eq. (1). Bring the cursor to the two peak positions and read the \( x \)-axis values. Write your values on the printed curve. Remember also to write down the file name, what sample the file corresponds to, concentrations, etc.

4. Using a microsyringe, add the proper amount of dry ethanol to the solution in the cell to make it 0.05 M in ethanol and bubble the solution for 5 - 10 min with \( \text{N}_2 \) gas. Measure the sample, record the peak maxima, and save and print a copy of the voltammogram.

5. Using the microsyringe, deliver the proper amount of ethanol to the same solution in the cell to increase the total ethanol concentrations to 0.1 M, 0.2 M, 0.5 M and 1.0 M. Make sure to deoxygenate the solution with nitrogen every time. Make sure to save each voltammogram and record the required values from the voltammogram. Finally, overlay the curves on the screen to see the trend and make a hardcopy.

V. DATA ANALYSIS

Calculate the \( E_{1,1/2} \) and \( E_{2,1/2} \) values using Eq. (1) for each sample (e.g. each ethanol concentration) and present the data (\( \Delta E_{1,1/2} \) vs. \([S]\) and \( \Delta E_{2,1/2} \) vs. \([S]\)) in tabular form. Download the non-linear least square Maxima program from the course web page (file name "experiment3.mac") and open the file with wxMaxima (e.g. File → Load Package). Run the program and input your values as requested. Input the requested data and remember to press shift-return simultaneously at the end of lines. The notebook will then fit Eqs. (9) and (13) on the experimental
data, provide the corresponding graphs for visual verification that the fitting was successful, and print out the values for \( m, n, K_1, \) and \( K_2. \) Note that the program does not make the assumptions: \( K_1 \times [S]^m \gg 1 \) and \( K_2 \times [S]^m \gg 1. \) The program uses a non-linear least squares routine and the function may therefore have any form. The limiting forms (Eqs. (11) and the last part of (13)) were given just to illustrate the behavior of the data sets. You would use them when you don’t have access to a computer, you are using a linear least squares routine or the resulting non-linear fitting experiences convergence problems. Listing of the Maxima program is as follows:

```maxima
/*
* Unconstrained nonlinear least squares fit module for Maxima.
* nlsq(funcs, ydata, xdata, yvars, xvars, params, initvars, errtol, debug)
*
* funcs = list of functions for fitting [fun1, fun2, ...].
* ydata = list of y-data vectors [yvec1, yvec2, ...].
* xdata = list of x-data vectors [xvec1, xvec2, ...].
* yvars = list of y variables for the functions given in funcs [y1, y2, ...].
* xvars = list of x variables for the functions given in funcs [x1, x2, ...].
* params = list of parameters to be fitted [a, b, ...].
* initvars = list of initial values for params [ai, bi, ...].
* errtol = requested error tolerance in BFGS (1E-4).
* debug = optimization output vector for BFGS ([1, 2] = full output, [-1 0] = no output).
*
* Returns: [F, R2, V, C, E].
*
* F = list of optimized functions.
* R2 = list of r^2 values for each function.
* V = list of optimized parameter values.
* C = covariance matrix for the parameters.
* E = list of standard errors for parameters.
*
*/
load("lbfgs");

nlsq([ArgList]):=
block([narg, funcs, ydata, xdata, yvars, xvars, params, initvars, errtol, debug, neqs, i, sq, tmp, lbfgs_nfeval_max:1000, /* BFGS tends to converge somewhat slowly... */
fun, fit, F, ss, sstot, sm, st, R2, C, lp, E, sigma2, Vm, k, np],
narg:length(ArgList),
if narg # 9 then (
  print("nlsq: bad number of function arguments (requires 9 arguments)."),
  return(false)
),

funcs:ArgList[1],
ydata:ArgList[2],
xdata:ArgList[3],
yvars:ArgList[4],
xvars:ArgList[5],
params:ArgList[6],
initvars:ArgList[7],
errtol:ArgList[8],
debug:ArgList[9],

neqs:length(funcs),
lp:length(params),

if neqs # length(ydata) or neqs # length(xdata) or neqs # length(yvars) or neqs # length(xvars) then (}
print("nlsq: Inconsistent lengths for arguments 1 - 5."),
return(false)
),

/* Construct the least squares sum and call lbfgs to optimize */
tmp:0,
for i:1 thru neqs do (  
  if length(xdata[i]) # length(ydata[i]) then (  
    print("nlsq: Inconsistent lengths for X and Y in set ", i),
    return(false)
  ),
  sq:(lhs(funcs[i]) - rhs(funcs[i]))^2,
  sq:subst('xdata[i][j], xvars[i], sq),
  sq:subst('ydata[i][j], yvars[i], sq),
  tmp:tmp + 'sum(sq, j, 1, length(xdata[i]))
),
/* fun:ev(tmp,nouns),*/
fun:tmp,
fit:lbfgs(fun, params, initvars, errtol, debug),
if fit = [] then (  
  print("nlsq: BFGS convergence error. Fit failed.")
),

/* Substitute the optimized values back into the equations */
F:makelist(0,i,1,neqs),
for i:1 thru neqs do (  
  F[i]:float(rhs(funcs[i]))
  for j:1 thru lp do F[i]:subst(rhs(fit[j]), params[j], F[i])
),

/* Calculate r^2 for each data set */
sstot:0,
R2:makelist(0,i,1,neqs),
for i:1 thru neqs do (  
  ss:sum((subst(xdata[i][j], xvars[i], F[i]) - ydata[i][j])^2, j, 1, length(xdata[i])),
  sstot:sstot + ss,
  sm:sum(ydata[i][j], j, 1, length(xdata[i])) / length(xdata[i]),
  st:sum((subst(xdata[i][j], xvars[i], F[i]) - sm)^2, j, 1, length(xdata[i])),
  R2[i]:float(ev(1 - ss / st,nouns))
),

/* Calculate the covariance matrix */
C:ematrix(lp, lp, 0, 1, 1),
for i:1 thru lp do (  
  for j:1 thru lp do (  
    C[i,j]:diff(fun, params[i], 1, params[j], 1),
    for k:1 thru lp do C[i,j]:subst(rhs(fit[k]), params[k], C[i,j])
  )
),
C:float(ev(C,nouns)),
/* watch out when lp = 1, invert returns a number not a matrix */
if lp = 1 then (  
  C[1,1]:1/C[1,1]
) else (  
  C:invert(C)
),
/* Calculate standard errors */
\begin{verbatim}
np: sum(length(xdata[i]), i, 1, neqs),
sigma2: sstot / (np - lp),
E: makelist(0, i, 1, lp),
V: makelist(0, i, 1, lp),
for i: 1 thru lp do (
    E[i]: float(sqrt(sigma2 * C[i, i]))),
    V[i]: float(rhs(fit[i]))
),
return([F, R2, V, C, E])
); /* Experiment 3. Cyclic voltammetry. */
* Given \Delta E_{1,1/2} and \Delta E_{2,1/2} as a function
* of ethanol concentration, the program will fit Eqs. (9) and
* (12) to the experimental data and provide estimates for
* m, n, K_1 and K_2.
* Note that you must download the nlsq.mac subroutine separately.
*/
remvalue(all);

/* The molar gas constant */
R: 8.31451; /* J mol^{-1} K^{-1} */
/* Temperature */
T: 298.0; /* K */
/* Faraday constant */
F: 9.648531E4; /* C mol^{-1} */
/* 5 samples (the pure acetonitrile sample is not given here) */
print("Enter your CV data for 5 samples (only with non-zero EtOH concentration!).");
print("The input must be given in the order of increasing EtOH concentration.");
print("Separate your input with spaces: EtOH DeltaE1 DeltaE2 and press return to proceed.");
print("The input consists of five lines each terminated by return.");
c: makelist(0, i, 1, 2);
c[1]: makelist(0, i, 1, 5);
c[2]: makelist(0, i, 1, 5);
Y: makelist(0, i, 1, 2);
Y[1]: makelist(0, i, 1, 5);
Y[2]: makelist(0, i, 1, 5);
for i: 1 thru 5 do (print("Enter data: "),
    tmp: tokens(readline(?\*standard\*-input\*)),
    c[1][i]: parse_string(tmp[1]),
    c[2][i]: c[1][i],
    Y[1][i]: parse_string(tmp[2]),
    Y[2][i]: parse_string(tmp[3]));
/* Functions to be fitted simultaneously */
/* Note: K2 had to be rescaled by 10^9, otherwise BFGS minimizer gets lost...*/
funs: ['y=(R*T/F)*log(1.0+K1*(s^n)),
'y=(R*T/F)*log((1.0+K2*1E9*(s^m))/(1.0+K1*(s^n)))];
/* Initial guesses for K1, K2, m, and n */
\end{verbatim}
VI. WRITTEN LABORATORY REPORT

Follow the general instructions for written laboratory reports. In addition, include the requested data in the following section:

Results. This section should include the values for $m$, $n$, $K_1$ and $K_2$ and their error estimates. Find the literature values for these quantities [4] (note: different solvent!) and discuss the possible sources of errors. Provide a schematic drawing how the protic molecules might be hydrogen bonded to the quinone molecule.

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VII. REFERENCES


