Cyclic Voltammetry

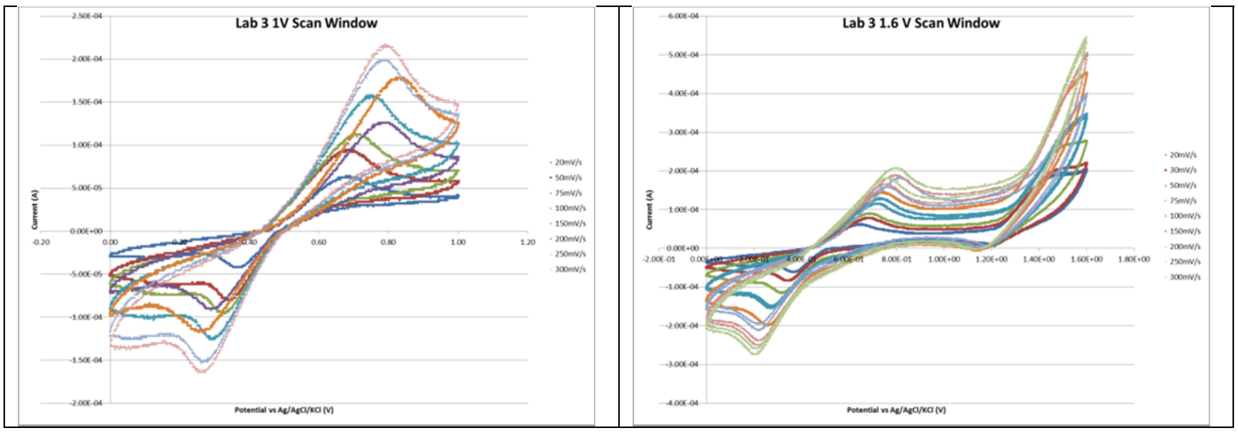
100 pts

Work-Up and Questions

1) Plot your cyclic voltammetry data for each scan rate, including overlays for the baseline scans. To do this neatly you may need a separate plot for each scan-window/scan-rate combination.

10 pts for plots

The figure below shows the CV data for the different scan windows. The baselines were estimated from a foldover of the "beak" of the duck shapes, following B&F Figure 6.5.2.



20 pts - need to do something reasonable to estimate baselines

2) Use your data to make a table including i_{pc}, i_{pa}, E_{pc}, E_{pa}, and $E_{p/2}$(as applicable), similar to the table that accompanied B&F question 6.9.

For the small scan window, peak around 0.5 V vs Ag/AgCl:

scan rate (V/s)	ipa (A)	ipc (A)	Epa (V)	Epc (V)	Ep/2a	ipa/ipc	Epa-Epc (V)
0.02	0.000064	-0.00008	0.678	0.378	0.561	-0.8	0.3
0.05	0.000094	-0.00013	0.685	0.343	0.549	-0.70149	0.342
0.075	0.000112	-0.00016	0.697	0.332	0.565	-0.69136	0.365
0.1	0.000126	-0.00018	0.787	0.29	0.626	-0.71591	0.497
0.15	0.000156	-0.00023	0.751	0.292	0.597	-0.68421	0.459
0.2	0.000178	-0.00024	0.833	0.264	0.663	-0.74167	0.569
0.25	0.000198	-0.00029	0.788	0.269	0.625	-0.6875	0.519
0.3	0.000218	-0.00031	0.789	0.264	0.63	-0.70323	0.525

For the larger window (looking at the second peak) the values for the table couldn't really be determined (gray in table):

scan rate V/s	ipa (A)	Epa (V)	Ep/2	ipc (A)	Epc

0.02	0.000144	1.48	1.34	0.00017	1.2
0.03	0.00016	1.52	1.36	0.000186	1.19
0.05	0.000216	1.54	1.36	0.000248	1.16
0.075	0.000266	1.58	1.43	0.000288	1.15
0.1	0.000252	1.58	1.43	0.00028	1.16
0.15	0.000354	1.6	1.42	0.000396	1.14
0.2	0.000312	1.67	1.52	0.000356	1.16
0.25	?	>1.6	?	?	1.14
0.3	?	>1.6	?	?	1.14

3) From the peak ratios and dependence of peak position on scan rate, comment on whether each wave appears reversible or irreversible.

20 pts

For a reversible wave, E_p is independent of scan rate, and the peak ratios also would be independent of scan rate (and =1).

For the first wave, both E_p and the peak ratio are shifting, so the peak is not reversible. By these criteria, the second peak also does not look reversible.

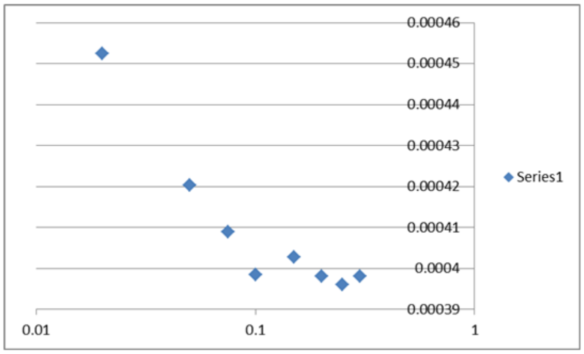
4) Use appropriate plots and fits to analyze the data. Assume n=1. For each reversible wave, determine a diffusion coefficient. For each irreversible wave, determine α and a diffusion coefficient.

20 pts

For an irreversible wave, $\left|E_p - E_{\frac{p}{2}}\right| = \frac{47.7}{\alpha}$mV. However, I don't get a constant value for this for the first wave. The average value I calculate for alpha is 0.33. Fitting a line to the peak current versus square root of scan rate, I can calculate D_R for the molecule. Doing all this, I get a diffusion coefficient of $1.19\text{x}10^{-5}$ cm^2/s, which sounds reasonable.

For the second wave, the E_p-$E_p/2$ looks fairly constant and yields α=0.31. This would yield a diffusion coefficient of 8 $\text{x}10^{-5}$ cm^2/s, which also sounds reasonable, but is different from the first wave. I expected the diffusion coefficients to be approximately the same, but think it makes sense that if one is greater than the other, it is the one from the second wave (because perhaps some product from the first wave hasn't diffused away from the electrode).

5) For each wave, which mechanism from Nicholson & Shain best fits the data?
When I plot the current function versus the log of the scan rate for the first wave, my plot looks like:



20 pts

Comparing this to N&S, I think it looks most like mechanism VII, irreversible catalytic step following a reversible charge transfer. I also tried plotting something like N&S Fig 18, but my plot looks more like a scatter than any of the shapes in the figure.

For the second wave, I can't trust my high-scan-rate data. Just plotting the low-scan-rate data gives me a pretty flat plot, perhaps decreasing as the scan rate increases. I'm not sure which case this best resembles, possibly case II (irreversible), but also possible III or IV.

6) Speculate as to a possible chemical mechanism for the observed behavior.

When the first electron is removed reversibly, a radical cation is formed. This cation can react with water. A second electron can be removed from the radical cation, leaving a dication, again that can react with water, even more so than the first product. (For the cations, the positive charge is on N atoms.)

10 pts