**Electrochemical Measurement Project: Rough Proposal**

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Goal

Investigate the effect of solvent dielectric on transport and kinetics of reversible redox couples using cyclic voltammetry and electrochemical impedance spectroscopy.

Approach

For the ferrocene/ferrocenium (Fc/Fc+) redox couple, we plan to determine the standard rate constant *k°*, the half-wave potential *E1/2*, and the activation free energy *ΔG‡* as a function of composition of binary solvent mixtures of acetonitrile/acetone and acetonitrile/dichloromethane. These trends will be correlated to the change in the composite dielectric constant of the mixtures.

From a cyclic voltammogram (CV), we will determine the half-wave potential *E1/2*  and the peak separation *ΔEp*. Values of *E1/2* will be compared to literature values of the Fc/Fc+ redox couple.

For each solvent mixture, CVs must be corrected for uncompensated solution resistance (Ru), which will be measured prior to conducting the CV as the *ZRe*-intercept of an EIS spectrum. CVs will then be used to determine the standard exchange rate constants *k°* using Nicholson’s method from Ref. 2. *ΔG‡*can be computed from *k°* using Eqn. 5 in Ref. 1, and the values obtained will be compared to those reported in Ref. 1.

EIS spectra will be further analyzed using the Randles equivalent circuit and the equivalent circuit model described in Fig. 7 of Ref. 1. The relative fits to the EIS spectra and physical meaning of these circuits will be assessed to the extent possible, given the speed of Fc/Fc+ charge transfer.

Required Materials

* Pure, dry solvents: Acetonitrile, Acetone, and Dichloromethane (DCM).
* Analyte and supporting electrolyte: ferrocene, Bu4NPF6 (TBAF)
* 4Å Molecular sieves (activated), to dry solvents
* ~1mm diameter Glassy Carbon (GC) disk electrode
* [Electrode polishing kit](https://safetynet.web.unc.edu/wp-content/uploads/sites/12158/2017/09/ElectrodePolishing_Miller_20160805.pdf) (including polishing pad and alumina slurry, or other polishing powder of 0.3 and 0.5 micron grit)
* Double junction Ag/AgCl/sat. KCl reference electrode
* Pt wire counter electrode
* Balance with sensitivity to ± 0.1 mg, or best offer.
* MyDAQ potentiostat/galvanostat

Week 1 Experiments

* Verify solubility of TBAF, Fc in each of the pure solvents. According to Ref. 1, TBAF and Fc should be soluble in MeCN and MeAc, but we are unsure about solubility in DCM.
* Make solutions of 0.4 mM Fc with 100 mM TBAF in pure solvents and mixtures of solvents.
* Use cyclic voltammetry, measure peak current *ip*, and use them to determine diffusion constants *D* via the Randles-Sevcik equation. Sweep from 0 to +1.0 V versus Ag/AgCl(sat. KCl) by applying scan rates (*v*) ranging from 0.02 to 0.12 V s-1 and applying a least-squares linear regression.
* Verify reproducibility of the electrochemical surface area (ECSA) upon electrode polishing by measuring double layer capacitance *CDL* in solutions of 100 mM TBAF in MeCN. We expect the solution to behave as a series RC circuit. *CDL* can be determined using EIS by fitting -*Zim* vs frequency ω, using the equation -*Zim* = (ω*CDL*)-1
* Verify EIS operating frequencies reported in Ref. 1 (0.1 Hz to limit of DAQ) using the Kramers-Kronig Transform.

Optional Materials

* Commercial Potentiostat to eliminate myDAQ issues with sampling in AC methods and increase the range of operating frequencies.

Primary and Secondary References

1. Tsierkezos, N. G.; Ritter, U. Electrochemical Impedance Spectroscopy and Cyclic Voltammetry of Ferrocene in Acetonitrile/Acetone System. *J. Appl. Electrochem.* **2010**, *40* (2), 409–417. [doi.org/10.1007/s10800-009-0011-3](https://doi.org/10.1007/s10800-009-0011-3).
2. Nicholson, R. S. Theory and Application of Cyclic Voltammetry for Measurement of Electrode Reaction Kinetics. *Anal. Chem.* **1965**, *37* (11), 1351–1355.<https://doi.org/10.1021/ac60230a016>.