Effect of Water Concentration on a Proton Coupled Electron Transfer Reaction in Non-Aqueous Solvents

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Webster[1] and coworkers devised a simple method for measuring water content in an electrochemical cell using Vitamin K, a naturally occuring quinone with a long carbon chain. Like all quinones, Vitamin K can undergo a two electron reduction when exposed to increasingly negative potential in a cyclic voltammetry experiment. The first reduction forms a semiquinone radical anion. The second reduction forms the quinone dianion in the absence of a proton source, and the hydroquinone in the presence of a proton source, such as water. Cyclic voltammetry can be used to determine very small concentrations of water in the presence of Vitamin K. This is due to the fact that Hydrogen bonding from water molecules stabilizes the radical anion, allowing the second reduction of the quinone to occur at a slightly less negative potential than it would in the absence of water. Using this theory, Webster was able to correlate the difference in reduction peak potentials (delta-E1/2s) to the water concentration in the cell for various organic solvents.

In this project, Webster's method has been used to determine the water concentration in our "standard" electrochemical cell experiment conditions for various organic solvents. So far, the experiments with solutions of Vitamin K in DMSO, DMF, and acetonitrile have yielded delta-E1/2 values that correspond to less than 5mM water concentrations. In upcoming experiments, known amounts of water will be added to the cell to compare the results with the range of data generated by Webster.

Using a similar method and the information gained from the Vitamin K experiments, the impacts of water content on the oxidation and reduction of an electroactive urea will be investigated. Previous research has shown that this urea undergoes a two electron, one proton oxidation in non-aqueous solvents in which Hydrogen bonding plays a key role.

1. Webster, R. D., 2009, *Hydrogen-Bonding Interactions between Water and the One and Two-Electron-Reduced Forms of Vitamin K1: Applying Quinone Electrochemistry To Determine the Moisture Content of Non-Aqueous Solvents*