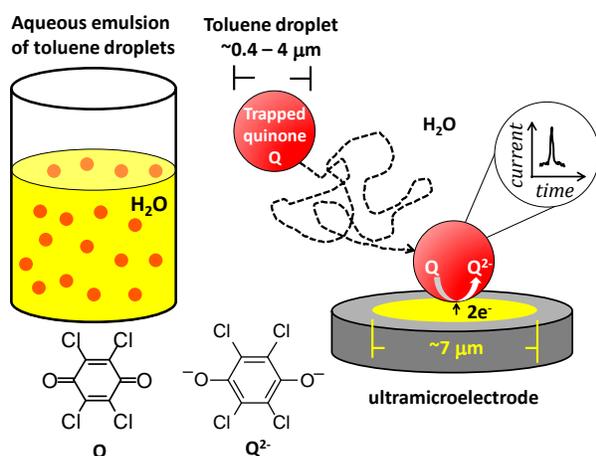


Mechanistic Investigation of the Water-Organic Interface in Aqueous Emulsion Micro-droplets as a Model to Understand “On-Water Catalysis” in Heterogeneous Water-Organic Systems

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Project Overview

The goal of this project is to shed light on the factors that control chemical reactivity at the organic-water interface for reactions that undergo “on-water catalysis”. This phenomenon first reported in 2005,¹ refers to a set of chemical

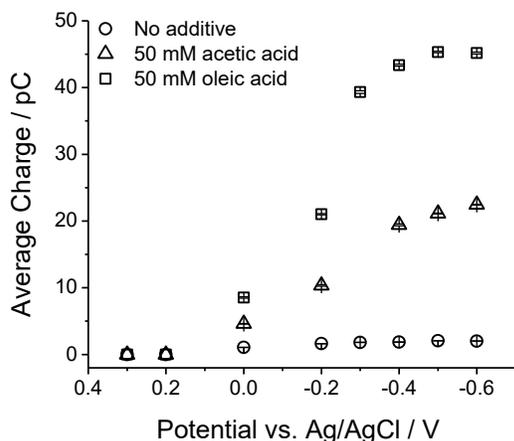


transformations, that when carried out in water by stirring mixtures of insoluble reagents (liquid or solid), exhibit significant increase in reaction rate with respect to the conditions in organic solvents. The source of this effect has been attributed to water but a precise mechanism has defied consensus.² We set out to study micrometer-size droplets of toluene (or other water immiscible solvent) dispersed in water because these systems mimic the conditions in which “on-water catalysis” have been observed. That is, millions of particles with microscopic interfaces of insoluble liquid (emulsion) or solid (suspension), surrounded by water. The first-year specific aims of the project were to examine the effect of the microscopic immiscible interface on electrochemical mechanisms that involve proton transfer and hydrogen bonding. The method for tracking the mechanisms was

Particle Collision Electrochemistry (PCE) by which particles in Brownian motion strike an electrode of comparable dimensions through single detectable collisions.³ Spikes of electrochemical current produced at the moment of impact by individual toluene droplets loaded with a hydrophobic quinone, were used to infer mechanistic features.

Progress July 1 2017 to September 30 2018.

We studied the two-electron reduction of tetrachloro-1,4-benzoquinone (TCBQ) trapped inside the toluene droplets setting the potential of the ultramicroelectrode at increasing negative values to drive the reaction to different levels



of completion inside the droplet.⁴ Current-time profiles for 1000 s were recorded in the presence of additives, oleic and acetic acid, to compare with the pristine emulsion. From current-time curves, we measured the area (charge) under every spike of current induced by droplet collisions and plotted the average as a function of potential. Control experiment in homogeneous toluene were also performed, which showed that upon addition of acids, the half-wave potential of TCBQ shifts positively (easier reduction), thus implying hydrogen bonding and/or protonation of the reduction product TCBQ²⁻. The shift is commensurate to the proton donating capacity of each acid, so that, acetic acid (pK_a=4.8) displayed higher shift than oleic acid (pK_a=9.9). However, when the reduction took place inside the toluene droplets, the trend was completely reversed and the average charge (current) transferred

per droplet was higher in the presence of oleic acid. This result led us to conclude that the reversal of hydrogen bonding/protonation effect in the emulsion appears to be driven by preferential partition of acetic acid in water, given that the hydrophobic oleic acid stays inside the droplet. Additionally, these effects seemed to be competing with the underlying binding between TCBQ²⁻ and the tetraalkyl phosphonium cation of the ionic liquid used to enhance the conductivity of toluene. Overall, this work showed that micro-confinement of immiscible phases renders sizeable consequences in chemical reactions occurring around the interface, in or out of the droplet.

Furthermore, we also illustrate the potential of PCE to extract chemical reactivity information at the organic-water interface. A second system based on thiol redox chemistry undergoing proton-coupled electron transfer was studied in aqueous solution but it will be investigated in emulsion format to compare the effects of the immiscible microscopic interface.⁵

Impact of Research in PI's Career:

During the first year this research produced two research publications in premier journals of physical and electrochemistry. It also generated an invited speaking engagement at the International Electrochemical Society Meeting "AIMES" in Cancun, Mexico, September 30-October 4 2018.

The preliminary results derived from this research are currently being used for application to funding from federal agencies.

Impact of research on the career of students who worked and are currently working in this project:

Two students obtained one first-author publication each, which allowed them to complete requirements for PhD graduation in May 2018. Both students are currently employed one in industry and the other in academia. Two new students have joined the PI's lab in summer 2018 and started to work in this project.

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