PRF#57846 ND-4

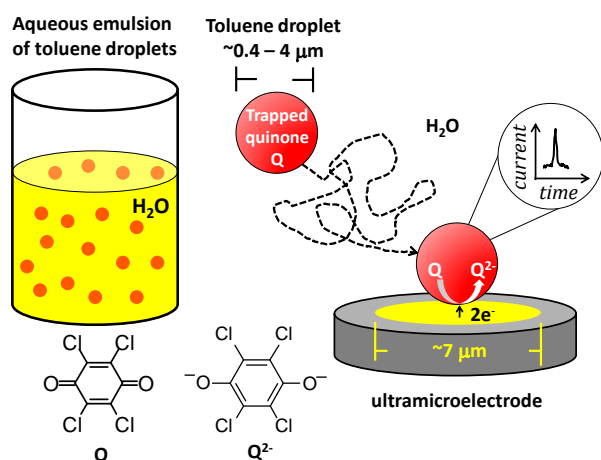**Mechanistic Investigation of the Water-Organic Interface in Aqueous Emulsion Micro-droplets as a Model to Understand "On-Water Catalysis" in Heterogeneous Water-Organic Systems**

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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 September 30 2018 to September 30 2019.

The progress this year was partial because the current students (John Lutkenhaus and Junaid Ahmed) worked only during the summer due to course work needed to be fulfilled in the early stage of their PhD. Therefore, the work presented below is the result of activities mostly done during Summer 2019. We are currently preparing a publication, expected to be submitted around December 2019 summarizing the summer work and anything else that can be done in Fall 2019.

The core principle of this project is an application of what has come to be known as Single Entity Electrochemistry.[4-5] An approach that relies on detecting individual collisions of particles with a disk electrode of micrometer dimensions (0.1 – 10 µm diameter). The collisions originate from the stochastic motion that microscopic
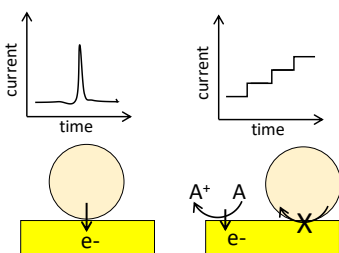

particles undergo in solution, whereas the signal arises from the coupling of an electrochemical reaction with the collision event. Characteristic responses, called chronoamperograms, are displayed as current versus time plots recorded at a potential value for which the electrochemical reaction occurs. The signals can appear as spikes above a baseline or as a staircase, and they may represent single or multiple collisions depending on several factors. Including the underlying mechanism producing the current. For instance, a spike might originate because an electroactive particle transfers a finite number of electrons during the encounter. On the other hand, a non-electroactive particle would partially block the electrode causing a lessening of electrode area. A concomitant decrease in current would be observed if a molecular species is simultaneously reacting at the electrode. The area under the spike or step curve, is controlled by the particle size and the amount of charge (current/time) transferred during the encounter. Likewise, the frequency of collision can be estimated by counting the number of events per unit time. The use of a microelectrode is required on two grounds, first, the noise level that limits the minimum signal measurable for an electrode is given by its charging current, which scales down with electrode area.[6] Therefore, for a collision experiment with an electrode of regular size (~1 mm diameter), the current response would buried below the baseline. Second, because of its small area, a microelectrode limits the collision frequency so that the

interpretation of the chronoamperogram is manageable without having to use extremely dilute solutions of particles. In any case, the power of this technique relies on the freedom to analyze any particle as long as there is way to couple the encounter event with an electrochemical reaction. The first successful example of this approach was demonstrated more than a decade ago using latex nanoparticles of 150 and 500 nm whose adsorption was detected on a Pt electrode of 2.5 µm. This was followed by the first report on characterization of Pt nanoparticles with diameters of just ~4 nm colliding with a carbon fiber electrode of ~8 µm. The current signals were the result of catalytic amplification for the electrochemical reduction of H^+ to H_2 occurring exclusively on the Pt when in contact with the carbon conductive surface. Meanwhile, the carbon surface being inert to this reaction, remained silent just rendering a baseline of charging current. This report accelerated research in this area significantly and soon after that, a plethora of studies started to appear. Given the many variables that can influence the collision response, like particle size, particle composition, electrode surface, electrolyte, charge, etc., in addition to the various mechanisms of interaction, this technique has inspired fundamental studies in a wide range of particle systems. These include DNA,[7] viruses,[8] blood cells,[9] cancer cells,[10] nanoparticles,[11] vesicles[12], emulsion droplets[3], and bacteria.[13]

Results from Summer 2019: our first paper on this topic describes the collisions of toluene droplets (0.4 to 4 µm)
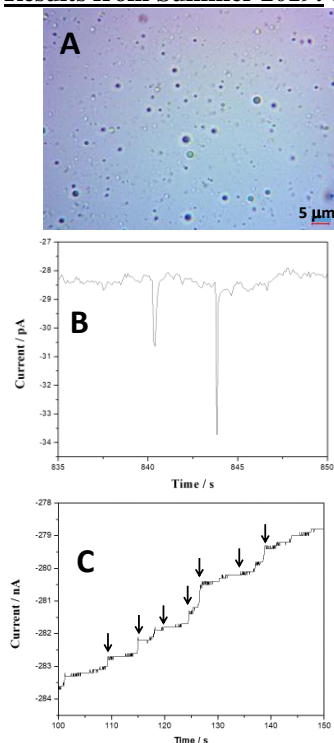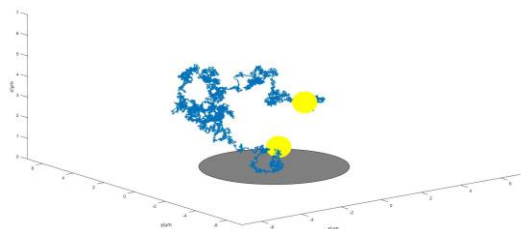
dispersed in water to determine chemical effects across the organic-water interface.[14] The droplets were detected by loading them with a hydrophobic quinone that upon collision, reacted with a carbon fiber electrode of 8.6 µm in diameter. Current spikes were produced in proportion to the droplet size, which was matched with the size obtained by Dynamic Light Scattering. Because the redox potential of the quinone shifts upon hydrogen bonding with carboxylic acids, we added acids of opposite hydrophobicity to observe the effect of differential partition between the two phases. The results showed that the acid inducing the largest shift (oleic acid) was the one that remained trapped in the toluene droplet, while the shift by acetic acid was smaller because it went into the water. Though this result was expected, the purpose of this paper was to illustrate that the collision technique when applied to emulsions could detect changes on the chemical interactions between two phases. In Figure 1, panel A a microscopic image of toluene droplets dispersed in water is shown. Panel B is the spike response when the toluene droplets are loaded with ferrocene. When these droplets collide with the electrode poised at the oxidation potential of ferrocene, the droplet content is oxidized rendering a peak whose area is related to the size of the particle.[3] Panel C shows a staircase response, in which the toluene droplets are without redox species, so that they merely block the electrode upon collision. The current response is from the oxidation of $K_4Fe(CN)_6$ which is only dissolved in the aqueous phase. We expect that these results will be compared with the simulations below, to determine the collision dynamics for droplets in different conditions, so that the chemical effects described in our first and future papers regarding this project can be interpreted correctly.

Figure 1. A. Microscopic image of toluene droplets in water. B. Spike response for toluene droplets loaded with ferrocene 20 mM at a carbon electrode 6 µm. C. Staircase response for pure toluene droplets in aqueous $K_4Fe(CN)_6$ 0.2 M at a Pt electrode 10 µm.

Theoretical Model of Collisions. The objective here is to determine how frequency collision is affected by particle size, concentration and microelectrode diameter. We are performing digital simulations by modeling the droplet motion

Figure 2. Simulated random walk of a single emulsion droplet undergoing collision at a 6 µm Carbon ultramicroelectrode.

as a random walk. The Brownian motion of spherical particles in solution is described by the Einstein−Smoluchowski relationship between the one-dimensional particle step length, δx, and step time, τ,

$$\delta x^2 = 2D\tau \qquad (1)$$

where D is the diffusion coefficient of the particle of radius r, as given by the Stokes−Einstein equation.[15]

$$D = \frac{k_B T}{6\pi\eta r} \qquad (2)$$

Where k_B is the Boltzmann constant (1.381 × 10−23 J·K−1), η is the viscosity of water, and T is the

temperature (298.15 K). Our model uses equation 2 at arbitrary values of δx and τ. For instance, Figure 2 shows a simulation made with Matlab® in which the kinetic energy (1/2 k_BT) of a toluene droplet with a radius of 1 μm. In this case, the electrode diameter was set at 6 μm. In the upcoming weeks, simulations will change the electrode diameter to estimate the collision frequency as a function of electrode size and compare with experimental values obtained so far.

Impact of Research in PI's Career:
During the second year, this grant allowed the support of two new graduate students to continue the project.

Impact of research on the career of students who worked and are currently working in this project:
Two new students that joined the PI's lab were supported during summer 2019 and were able to continue with the project. We expect to produce a publication describing the work during summer in the upcoming months.

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