

Characterizing Emulsions by Observation of Single Droplet Collisions—Attoliter Electrochemical Reactors

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S Supporting Information

ABSTRACT: We report an electrochemical study of the collisions of single droplets in an emulsion by two methods. In the first method, an electroactive redox species, for example, ferrocene, inside a toluene-in-water emulsion droplet (but not in the continuous phase) is measured by chronoamperometry during a collision with an ultramicroelectrode (UME). Here, a blip or spike type of collision signal is observed, representing electrolysis of the droplet contents. In the second method, electrochemical oxidation of an electroactive redox species in the continuous aqueous phase is hindered by a droplet blocking collision. In this case, a staircase current decrease is observed. From an analysis of single soft particle collision data, one can find the emulsion droplet size distribution and the droplet contents.

A new approach in electroanalytical chemistry involves obtaining information on single events, such as the collisions of “hard particles” like metal nanoparticles (NPs) (Pt, Au, Cu, Ag),^{1–4} oxides (IrO₂, TiO₂),^{5,6} dielectrics (polystyrene),⁷ and carbon (nanotubes, indigo)^{8,9} on an ultramicroelectrode (UME) as opposed to ensemble measurements. We show here that it is also possible to detect “soft particles”, for example, emulsion droplets, for characterizing such systems. Emulsions are widely used and important in many industrial processes. The sizes and distribution of emulsion droplets (the dispersed phase) has a strong impact on its stability, rheology, optical properties, and sensory attributes¹⁰ and is frequently measured. Laser light scattering and microscopic methods are most commonly used to discern the size distribution of emulsions.^{11–13} With dynamic light scattering (DLS), the size distributions can be estimated; however, these types of methods cannot account well for polydisperse samples. Moreover, the overall result is an ensemble average of the entire sample.^{14–16} Because of these factors, other methods, for example, cryo-electron microscopy, are often needed to find the size distribution.¹⁷ We offer the collision approach as an alternative method that can provide information about the droplet chemistry.

Here, we report single emulsion droplet collisions observed electrochemically at a UME by two methods (Figure 1). From these collision current responses, we are able to suggest the emulsion droplet size distribution. In the first method, an electrochemically active redox species, A, only soluble in the dispersed phase, is added to the emulsion (Figure 1A). For example, for an oil-in-water emulsion, A is hydrophobic. When

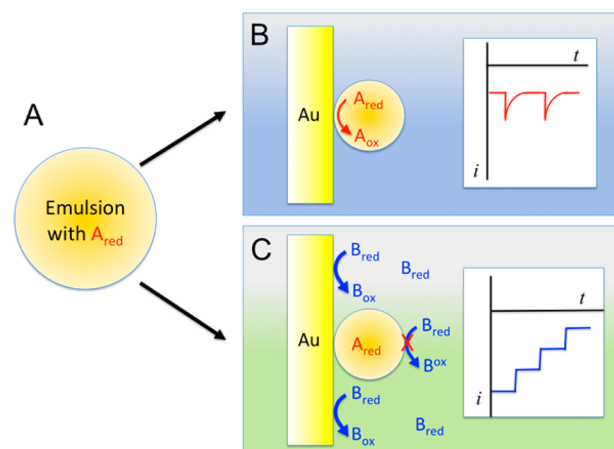


Figure 1. Schematic diagram of two suggested emulsion collision methods. (A) The emulsion droplet contains an electroactive redox species, for example, reduced species A_{red}. (B) Electrochemical oxidation of species A_{red} in droplet occurred at the electrode surface. A “blip” type of current increase can be observed. (C) Electrochemical oxidation of species B_{red} in aqueous solution is hindered by emulsion blocking.

the oil droplet collides with the electrode, an electron transfer reaction—for example, an oxidation—occurs (Figure 1B). Consequently, a current spike is seen as the contents of the droplet are electrolyzed. From the charge in each current spike, we estimate the amount of electroactive species within the droplet. The frequency of the spikes indicates the rate of arrival of the droplets to the electrode. In this first method, the droplet serves as a reactor, so we call this first method the “emulsion droplet reactor (EDR)” method.

In the second method, the emulsion electrochemical cell contains a continuous phase with a high concentration of a redox active species, B (Figure 1C). When the droplet collides with the electrode, the active surface of the UME is blocked and the flux of redox active species B to the electrode surface is decreased. Similar results were previously seen with insulating NPs, for example, of polystyrene or silica.^{7,18} The magnitude of the blocking effect can be observed by the current decrease, which can yield insight into the size distribution of the droplets colliding with the UME. In this second method, the droplet acts as a blocking material, so we call this “emulsion droplet blocking (EDB)”. These two methods can be applied to all

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types of single emulsion droplet collision experiments on UMEs.

To exemplify these two suggested methods, we used a toluene in water emulsion, which has been the subject of many studies.^{19–23} Toluene has a dielectric constant, ϵ of 2.38 and it is difficult to find a supporting electrolyte for electrochemical studies in such a low dielectric medium.²⁴ To overcome this problem, we chose a hydrophobic ionic liquid, trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl)amide (IL-PA), as the supporting electrolyte (Supporting Information Figure S1). Cyclic voltammetry (CV) on a 10 μm Au UME was used to demonstrate the oxidation of 20 mM ferrocene (Fc) in neat toluene with 400 mM IL-PA (Supporting Information Figure S2) for comparison with the observation of the same reaction within an emulsion droplet. The CV shows a clean wave for Fc oxidation and is only slightly perturbed by uncompensated resistance ($E_{3/4} - E_{1/4} = 86$ mV). The same toluene composition, made by mixing 5 mL water with a 0.1 mL toluene containing 20 mM Fc and 400 mM IL-PA, was used to create the emulsion for collision experiments. An ultrasonic processor was used to form the emulsion that was stable for at least 16 h.

In the EDR method, chronoamperometry was used to observe Fc oxidation in the emulsion droplet (Figure 2A) with Au UME at 0.5 V. Before addition of the emulsion to the

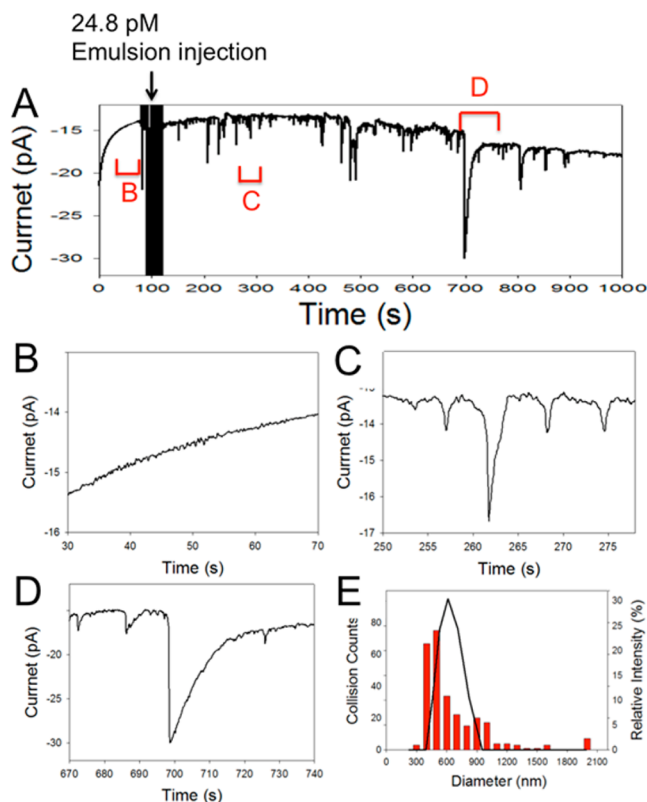


Figure 2. (A) The $i-t$ curve of single droplet collisions at Au UME. A 24.8 pM toluene (Fc + IL-PA)/water emulsion was added after 100 s. The large noise around 100 s comes from opening of the faraday cage, injection of emulsion, and Ar bubbling to mix emulsion and water. (B) Before injection of the emulsion, (C) and (D) are magnified $i-t$ curves showing clear current spikes. (E) Comparison of calculated data vs DLS data. Red bar is representative of calculated data and black solid line is representative of DLS data. The UME potential was +0.5 V vs Ag/Ag⁺ applied at zero time.

aqueous system, we observed a steady current level of 14.2 ± 0.074 pA (Figure 2B). After 100 s, a toluene (20 mM Fc + 400 mM IL-PA)/water emulsion equivalent to a concentration of droplets of 24.8 pM was introduced into the system. We observed many current spikes, which were attributed to Fc oxidation in the droplets (Figure 2A, Supporting Information Figure S5). To confirm that these current spikes are only due to Fc oxidation in the emulsion droplet, a background experiment was conducted under identical experimental conditions, except without Fc. As shown in Supporting Information Figure S5A, current spikes were not detected. The number of current spikes in Figure 2A is related to diffusion (and possibly migration) of emulsion droplets to the UME. The diffusion coefficient of a spherical emulsion droplet (D_{ems}) can be estimated by the Stokes–Einstein eq 1.

$$D_{\text{ems}} = \frac{k_{\text{B}}T}{6\pi\eta r_{\text{ems}}} \quad (1)$$

where k_{B} is the Boltzmann constant, T is temperature, η is the viscosity of water at 25 °C, and r_{ems} is the radius of an emulsion droplet. From this equation, the diffusion coefficient of a 600 nm diameter emulsion droplet is 8.2×10^{-9} cm² s⁻¹. The collision frequency by diffusion of the emulsion droplet can be calculated by eq 2

$$f_{\text{ems}} = 4D_{\text{ems}}C_{\text{ems}}r_eN_A \quad (2)$$

where C_{ems} is the concentration of droplets, r_e is the radius of the working electrode, and N_A is Avogadro's number. From this equation, the predicted frequency of emulsion droplet collisions is 0.24 Hz. The experimentally observed frequency, 0.34 Hz, is close to this value, given the usual variation in stochastic measurements, suggesting that any migration effects are not significant compared with diffusion.⁷ In previous results, the experimentally observed frequency of polystyrene spheres (diameter, 310 nm; ζ potential, -58.9 mV) was nearly 3 orders of magnitude larger than the frequency predicted by diffusion alone. However, migration is less important with emulsion droplets under the conditions of the experiment because of the larger particle size, the small ζ potential, and the fact that there is small background faradaic reaction responsible for the major contributor of the migrational electric field.

Integrating the current spike yields the charge transferred to the electrode for a given collision from Fc oxidation in the droplet (Supporting Information Figure S6). We can, therefore, use this charge data to measure the total amount of Fc oxidized. Assuming that the concentration of Fc is 20 mM throughout the range of droplet sizes with each having spherical geometry, and complete consumption of all Fc within a droplet on collision, we can estimate the volume and the radius of each droplet from the charge and Fc concentration (Supporting Information Figure S7). The droplet diameter (d_{drop}) can be calculated by eq 3

$$d_{\text{drop}} = 2 \sqrt[3]{\frac{3Q}{4\pi FC_{\text{redox}}}} \quad (3)$$

where Q is measured charge, F is the Faraday constant, and C_{redox} is the concentration of redox species in the dispersed phase (obtained from the amounts of Fc and toluene used). The droplet size distribution calculated by eq 3 is compared to DLS data in Figure 2E. This overlay suggests that most of the droplets are 400–600 nm in diameter. The DLS data indicate that the peak diameter is 624 nm (Supporting Information

Figure S4A). The distributions from the two techniques are quite similar.

The shape of the current spike shows either a sharp decrease or a longer decay after a fast increase (Figure 2C and 2D, respectively). We speculate that the shape of the current spike and the different decay times are related to the nature of the emulsion droplet collision process with the UME, the contact area, and droplet volume. When the emulsion droplet collides, the contact area between the droplet and the UME may vary (Supporting Information Figure S8A(ii)). The contact area represents a disk electrode touching the electrochemical reactor (volume, roughly 100 μL). Diffusion in this tiny droplet is rapid, so one can assume the familiar bulk electrolysis model with the concentration of reactant Fc uniform within the droplet.²⁵ An increase in contact area will result in an increase in the current at each current spike for the first 0.45 to 0.6 s (Supporting Information Figure S8B). Once the droplet is fixed stably on the UME, the Fc oxidation currents start to decay because Fc in the droplet becomes depleted during the electrolysis. In fact, the exponential current decay is consistent with the $i-t$ behavior of bulk electrolysis in the droplet assuming the contact area, the electrode size, and the droplet volume remain constant (Supporting Information Figure S8B). Overall, these two processes govern the shape of the current spike. In a second experiment, after 100 s, a 12.9 μM emulsion was introduced into the system. Similar results were observed as outlined above (Supporting Information Figures S9, S10, and S11). Note that the process of oxidizing Fc to Fc^+ probably results in the expulsion of Fc^+ from the toluene droplet into the water phase to maintain electroneutrality.

In the EDB method, the droplets block the oxidation of 200 μM $\text{Fe}(\text{CN})_6^{4-}$ in the aqueous phase. $\text{Fe}(\text{CN})_6^{4-}$ shows a Nernstian, one-electron wave CV (Supporting Information Figure S12). A steady-state current was obtained at 0.2 V at a 10 μm Au UME. Although $\text{Fe}(\text{CN})_6^{4-}$ in water can be oxidized at 0.2 V, Fc in the toluene droplet cannot, allowing an EDB measurement to complement the EDR measurement. During chronoamperometry at 0.2 V the $\text{Fe}(\text{CN})_6^{4-}$ oxidation at the UME yielded a steady-state current. When an emulsion droplet collided with the electrode, oxidation of $\text{Fe}(\text{CN})_6^{4-}$ at that position was blocked, producing a current step. After the addition of a 24.8 μM droplet solution, current steps were observed (Figure 3A and Supporting Information Figure S13). The observed frequency with the EDB method was 0.33 Hz, close to (i.e., 1.3 times) the value from the EDR measurements. The EDB method was conducted in a high concentration of $\text{Fe}(\text{CN})_6^{4-}$ and a larger current, but migration of the droplet is probably still negligible compared to diffusion. Without emulsion, in the same aqueous solution, background current was -251.9 ± 0.023 nA (Figure 3B). The current steps shown in Figure 3A are related to the size of the emulsion droplets. In most cases, we observed a current decrease in the shape of a staircase (Figure 3C). However, in rare cases, we also observed a current increase step (Figure 3D), which we attribute to a droplet leaving the electrode surface. In principle, the magnitude of the current step caused by blocking can also give information about the droplet size. However, because the current density across the UME disk varies and is especially high at the edges, there is a good deal of uncertainty in estimating the droplet size. This will be addressed in a future publication.

In summary, we report two different methods to observe single emulsion droplet collisions at a UME. In the EDR

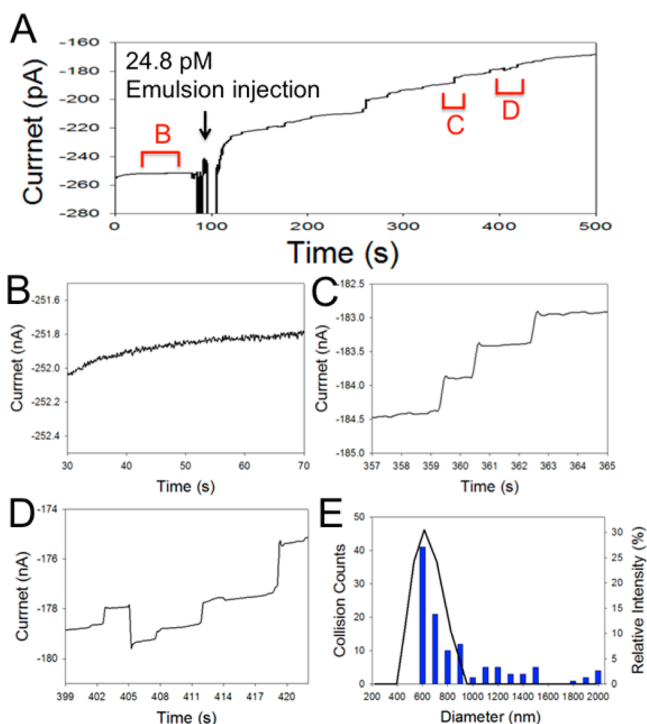


Figure 3. (A) The $i-t$ curve of single droplet collisions at a Au UME. A 24.8 μM toluene (Fc + IL-PA)/water emulsion added after 100 s. The large noise around 100 s comes from opening of the Faraday cage to inject emulsion and Ar bubbling to mix emulsion and water. (B) Before injection of emulsion, the current level is -251.9 ± 0.023 nA. (C) Staircase current decrease is shown by droplet blocking. (D) A rare staircase current increase is shown by droplet leaving at 405 s. (E) Comparison of calculated data vs DLS data. Blue bars are representative of calculated data and black solid line is representative of DLS data. The UME potential was +0.2 V vs Ag/Ag^+ applied at zero time.

method, we use toluene, ferrocene, ionic liquid droplets in water. When these droplets collide with the UME, oxidation of the ferrocene occurs. In the EDB method, with a redox couple in the aqueous continuous phase, blockage of the UME surface occurs on droplet collision. Both methods allow the observation of single collision events. The results from the two methods agree and also with DLS results. With the EDR method, many other immiscible organic solvent/aqueous electrolyte/analyte systems can be envisaged, which allow flexibility in selecting different redox species and electrolytes in relation to solubility in the organic solvent. With the EDB method, it is possible to design emulsions with various hydrophobic materials, such as oil (silicone, mineral), aromatic compounds, and alkanes as well as vesicles, micelles, and cells.

■ ASSOCIATED CONTENT

📄 Supporting Information

Experimental details and additional figures and photographs. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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