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Ferrocene in oil/water interfaces: An electrochemical approach

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ABSTRACT

This paper aims to understand the differences in the oxidation of ferrocene in several scenarios. The first scenario focuses the direct oxidation of ferrocene in an aqueous conventional support electrolyte and the second one is when ferrocene is directly placed in mineral oil, forming an oil phase and causing an oil/water interface. Additional experiments were also conducted in an emulsion, which was constituted by ferrocene in oil and mixed with conventional electrolytes and tetrabutylammonium chloride (TBAC).

A Boron-Doped Diamond Electrode (BDD) was used as the working electrode. We observed an approximately 0.07 V shift when the ferrocene oxidation was conducted at the oil/water interface compared with the direct oxidation in the conventional aqueous phase. This potential shift was also calculated using the Density Functional Theory (DFT) as a theoretical tool. An additional comparison was conducted related to the interface and emulsions, finding that the ionic strength is the most determining factor in these types of electrochemical studies. Finally, Tafel plots indicated that the reaction mechanisms and reaction geometry are different when the electrode is placed at the interface versus directly in the aqueous phase.

1. Introduction

Electrochemical studies of oil/water interfaces can provide new and interesting insights as they provide direct analyses of oil contaminants without complicated sample pre-treatment steps. These types of interfacial studies are being conducted by various research groups around the world, and the behaviour of ITIES (Interface Between Two Immiscible Electrolyte Solutions) is an interesting example of an fundamental electrochemical study [1–4].

Some other examples include Tasakorn et al. [5], which promoted the detection of ferrocene and Donten et al. [6], who analysed dimethyl-ferrocene detection. Both studies were conducted in a nitrobenzene/water interface. Turek et al. [7] developed a simple method for studying the self-controlled formation of gold nanoparticles in a water/1,2 dichloroethane, and Kohno et al. [8].

A Triple-Phase Boundary (TPB) is formed when an electrode is placed at a junction between two immiscible liquids. This study focuses on ferrocene as a model-molecule because it is largely used as a model in non-aqueous electrochemical systems. The oil phases were contaminated with ferrocene and the aqueous phases (conventional support electrolyte) were uncontaminated for all measurements.

Several phenomena can occur at these polarized interfaces when a contaminated drop of oil is placed on a support electrolyte. However, three major effects dominate: (1) ferrocene can diffuse from the oil to the aqueous phase, contributing to the formation of a partition until an equilibrium is reached (polarization is not important); (2) ferrocene can react at the Triple-Phase Boundary due to the polarization of the working electrode; and (3) ferrocene can interact with the electrode due to the hydrophobic/hydrophilic characteristic of the system.

In this context, several research groups have attempted to understand the mass and charge processes related to organic/water interfacial electrochemistry [9–11].

Several important papers can be found in literature related to organic/water interfaces [12–20]. In this context, we highlight the works published by Scholz et al. [21–23], which were related to oil drop electrochemistry, calculation of free Gibbs energy and interfacial electrochemistry in general. In a specific paper, the authors wrote about a new method to study electrochemical processes at well-defined three-phase junctions [24,25]. Banks et al. [26] published a paper concerning the use of microdroplet modified electrodes in biphasic electrochemistry.

We published our first paper related to electrochemistry subject in 2011 [27]. In that publication, ferrocene was directly detected in biodiesel without the need for a sample pre-treatment.

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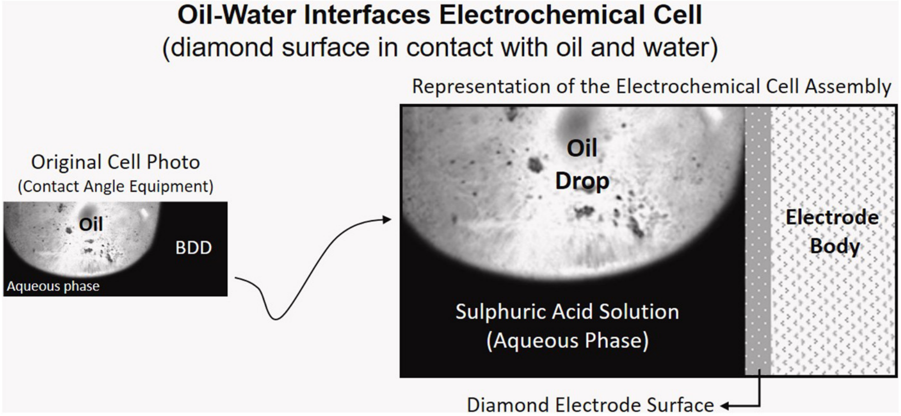

Fig. 1. Contact angle photo and schematic representation of the interfacial electrochemical cell.

Other publications have focused on the detection of Carbendazin in soy oil [28], calculating the ferrocene partition coefficient in an oil/water interface [29] and using single oil drop electrochemistry to promote the detection of 4-nitrophenol in limonene oil [30].

This study analyses electrochemical signal differences when experiments are directly conducted in aqueous media or oil/water interfaces. Hydrodynamic (square-wave voltammetry) and steady-state electrochemical measurements (Tafel Plots) were conducted to support the analysis. A boron-doped diamond (BDD) electrode was chosen because it is robust and does not undergo significant changes when used in electrochemical studies, thereby constituting a stable and reproducible electrochemical surface.

2. Experimental Section

2.1. General

All electrochemical measurements were conducted using high purity chemical reactants. Ferrocene ($Fe(C_5H_5)_2$) was purchased from Aldrich®, and sulphuric acid (95.0-98.0%, Synth®) was used to prepare the conventional aqueous electrolyte solutions (0.5 mol L^{-1} or 1×10^{-3} mol L^{-1}). All aqueous solutions were prepared using water from the Milli-Q® (Direct-Q) system. The oil phases were created using pure mineral oil (Aldrich®), including a 1×10^{-2} mol L^{-1} ferrocene solution, which was prepared in the same mineral oil. Appropriate quantities of tetrabutylammonium chloride (TBAC) from Aldrich® were added to the oil phase in several experiments.

Emulsions were obtained via the agitation of 1×10^{-2} ferrocene in mineral oil solution + 0.1 mol L^{-1} BTAC + 0.5 (or 1×10^{-3}) mol L^{-1} H_2SO_4 aqueous solution. All experiments were conducted in Pyrex® glass cells, which included three electrodes. A 0.1 cm^2 boron-doped diamond (BDD) flat plate as used as a working electrode and a 0.7 cm^2 Pt foil was used as the counter electrode. The Ag/AgCl (KCl saturated) system was used as a reference. The BDD electrode was submitted to an anodic pre-treatment (3.0 V vs. HESS, Hydrogen Electrode in the Same Solution) for 150 seconds before use in 25 mL of the 0.5 mol L^{-1} H_2SO_4 solution. This anodic pre-treatment was followed by a cathodic pre-treatment at −3.0 V vs. HESS at the same acidic solution. The goal of this pre-treatment is to clean the surface by oxidizing contaminants via an anodic treatment and to promote the H-termination of the carbon surface at −3.0 V vs. HESS. This routine is commonly applied and is similar to the methods used in our previous publications [27,28].

Electrochemical measurements were conducted using PGSTAT MicroAutolab potentiostat. The hydrodynamic technique utilized was Square Wave Voltammetry (SWV) because these types of measurements were previously optimized by our research group. The optimized parameters include an amplitude of 50 mV, increment of 5 mV and frequency of 20 Hz.

Steady-state measurements were recorded as Tafel plots. Data were collected in potentiostatic mode. The fixed potentials varied from 0.0 to 0.4 V vs. Ag/AgCl and intervals of 100 s were applied to each measurement, aiming to reach the stationary currents. All experiments were conducted at least three times.

2.2. Interfacial Electrochemical Cells Assembly

The electrochemical cell assembly scheme analysed in this study can be seen in Fig. 1.

In all electrochemical cells, the counter and reference electrodes are located in the aqueous phase (conventional support electrolyte). The aqueous phase is composed of 25 mL of the conventional support electrolyte. 1.5 mL of quantities of mineral oil, which contains ferrocene, were inserted in the aqueous phase. The electrochemical studies were often directly conducted in the aqueous phase or at the interface, as represented in Fig. 2.

The electrode position at the interface was held constant, corresponding to the upper end of electrode. Thus, the electrochemical area does not change when the electrode is submerged in the aqueous phase or when it is placed at the interface because only the border contacts the oil phase. A contact-angle measurement is ever carried out prior to start the electrochemical measurements, as described in Fig. 1. It is important to pull the electrode from the aqueous phase to the oil phase in this type of interfacial study, avoiding electrode contamination via the oil.

In “I” and “II”, the aqueous phases were composed of 25 mL of the 1×10^{-3} mol L^{-1} H_2SO_4 solutions. In “I”, the system does not contain an oil phase and the measurement using the BDD electrode was directly conducted in the conventional aqueous electrolyte.

On the other hand, scheme “II” represents a system with 1.5 mL of oil with a concentration of 1×10^{-2} mol L^{-1} of ferrocene. This system forms an oil/water interface. These measurements were conducted in only the aqueous phase (not at the interface). The main goal was to observe the formation of the partition due to the diffusion of ferrocene from the oil to the aqueous phase.

The aqueous phases in “III” and “IV” are composed of 0.5 mol L^{-1} of H_2SO_4 solutions, with higher ionic strengths than I and II. Note that the higher aqueous phase ionic strength dramatically decreases the ferrocene diffusion from the oil to the aqueous phase. The oil phases also possess the same initial concentration of 1×10^{-2} mol L^{-1} of ferrocene in “III” and “IV”. However, a quantity of 1×10^{-3} mol L^{-1} of TBAC was added to the oil phase in “IV”. Thus, “III” and “IV” allowed us to analyse the ionic strength differences of the aqueous phase (III) and the effect of charging the oil phase with a surfactant (IV). Figures “V” and “VI” describe the