

Electrochemistry@Soft Interfaces. Sensing and Fabrication for Electroanalysis.

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In the electrochemical community, the liquid-liquid interface is known as the interface between two immiscible electrolyte solutions (ITIES). The interfacial charge transfer (either ion or electron crossing the soft junction) can be followed with all available electrochemical techniques. ITIES based systems are unique. From the electroanalytical point of view, (a) detection at ITIES is not restricted to oxidation/reduction reaction but can arise from the simple interfacial ion transfer; (b) soft junctions are resistive to fouling given by their self-healing, renewability, and anti-scratch properties; (c) excellent reproducibility of the interface geometry translates into high experimental repeatability and reproducibility; and (d) phenomena happening at electrified soft junctions can be described and understood with existing electrochemical theory. Some chemical species which are difficult to detect at conventional solid electrodes (reaction irreversibility, lack of redox signals, surface fouling) can be easily followed at pristine ITIES. Such systems are especially attractive when it comes to amine-group holding chemical species detection. Many relevant compounds hold ionizable/permanently charged amine group(s) within their structure. Examples include food additives, antibiotics, medicines, illicit drugs among many others.

In this work, I will present a few examples proving the utility of the polarized liquid-liquid interface for amine group-containing drugs detection we have developed over the last few years. My focus will be given to the following aspects: (i) brief introduction to the theory behind ITIES based systems; (ii) ITIES miniaturization platforms which are based on the patterned membranes or single μ -capillaries;¹ (iii) application of a 3D printing technology to electrochemistry at the ITIES² and finally (iv) sensing protocols developed for the detection of fluoroquinolone antibiotics,^{1,3} cocaine together with its cutting⁴⁻⁶ and ephedrine.²

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The electrodes modified with a mesoporous silica thin film and a polyelectrolyte multilayer - preliminary results.

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Electrodes modified with mesoporous silica-based deposits possess unique properties that can be exploited in many fields such as energy and sensing. Especially promising are the mesoporous silica films created *via* sol-gel processing in the presence of a soft template, for which pH-dependent hydrolysis and condensation reactions of alkoxy- and organo-silane reagents can be controlled via, e.g., the Electrochemically Assisted Self-Assembly (EASA).^{1,2} We have found that layer-by-layer assembly of oppositely charged polyelectrolytes (poly(diallyldimethylammonium chloride - PDADMA - and poly(styrene sulfonate) - PSS) over an electrode modified with a mesoporous silica thin film leads to the amplification of the change in the redox signals when using various redox probes in solution, and even provides switchable on-off electroanalytical platforms. The electrochemical properties of the designed platforms were studied in the presence of positively charged ($\text{Ru}(\text{NH}_3)_6^{3+}$), neutral (FcMeOH), and negatively charged ($\text{Fe}(\text{CN})_6^{4-}$) redox probes. The surface and electroanalytical properties of the modified electrodes are adjustable in a highly controllable manner and are defined by the charge of the terminating polymeric layer. Polyelectrolyte multilayer deposition was followed with different characterization techniques XPS, FTIR-ATR, and SEM.

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Electrochemical determination of quinine in water tonic samples at the polarized and miniaturized liquid-liquid interface

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The electrochemical platforms that are based on the interface between two immiscible electrolyte solutions (ITIES) are still under development, especially in electroanalytical laboratories. It is important to underline that detection at ITIES is not restricted to oxidation/reduction processes and can result from simple interfacial ion transfer reaction (truly unique property). Quinine (QN) is a naturally occurring alkaloid, mostly found in the bark of the cinchona tree. QN was the first specific drug for malaria disease given to people who have been bitten by an infected mosquito. QN is a very popular food additive used for flavoring. QN is commonly added to soft fizzy drink, known as a tonic water, giving them characteristic bitter taste.

Within this work, the electrochemical behavior of QN at the macro- and microITIES has been investigated using ion-transfer voltammetry (ITV). In this work, 10 mM HCl in 10 mM NaCl and the solution of hydrophobic organic phase background electrolyte salt dissolved in 1,2-dichloroethane were used as the aqueous and the organic phase, respectively. The influence of concentration of the tested compound on the analytical signal was investigated. In order to plot ion partition diagrams, the effect of pH of aqueous phase on recorded QN signals in wide range of Britton-Robinson buffer was checked. The applicability of the elaborated ITV procedure was tested in the determination of QN in tonic water samples purchased from three independent producers. Finally, the validation of the proposed method was successfully performed. Based on obtained results validation parameters were determined.

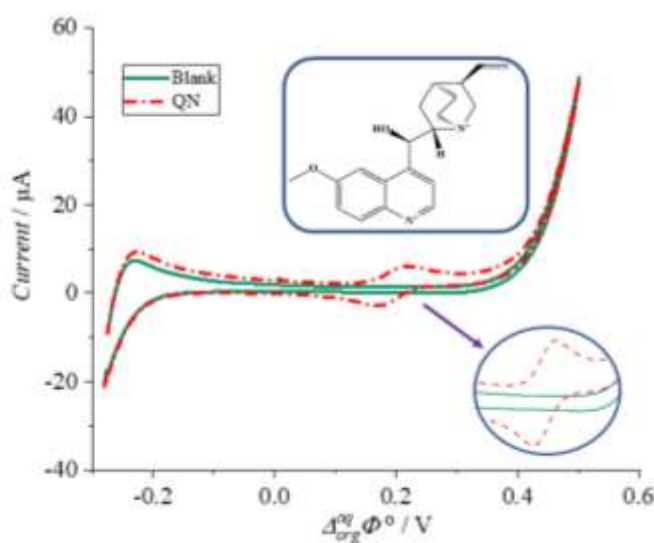


Fig. 1. Chosen ITVs recorded in the presence of QN (dash-dot line) and blank (solid line) at the macroITIES system. The inset shows the chemical structure of QN.

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