



Investigation of the oxidation of hydroquinone at the liquid/liquid interface

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Abstract

The oxidation of hydroquinone (QH₂) was investigated for the first time at liquid/liquid (L/L) interface by scanning electrochemical microscopy (SECM). In this study, electron transfer (ET) from QH₂ in aqueous to ferrocene (Fc) in nitrobenzene (NB) was probed. The apparent heterogeneous rate constants for ET reactions were obtained by fitting the experimental approach curves to the theoretical values. The results showed that the rate constants for oxidation reaction of QH₂ were sensitive to the changes of the driving force, which increased as the driving force increased. In addition, factors that would affect ET of QH₂ were studied. Experimental results indicated ion situation around QH₂ molecule could change the magnitude of the rate constants because the capability of oxidation of QH₂ would be affected by them.

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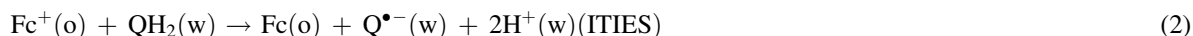
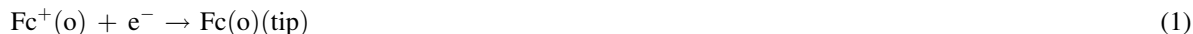
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Quinones are very important compounds that are involved in a variety of biological energy metabolism [1]. They are acting as a shuttle for electrons to move one place to another in photosynthesis or respiration, resulting an electron transport process feasible [2,3]. As we all know, QH₂ is one of the most important species in quinones, which is involved in many metabolic processes where it acts as an electron donor. Because the reaction often occurs in biomembranes or membrane surfaces, choosing the L/L interface to study the redox reaction and assess its specific function or capability in biological electron transport processes is clearly the approach of choice. Furthermore, the L/L interface has been suggested as a simple model for biological and artificial membranes to understand charge transfer processes in biological systems, which include not only ion transfer but also ET. ET at the L/L interface is fundamentally important for understanding the energy conversion in biomembranes [4,5], and the kinetics of ET at immiscible electrolyte solutions (ITIES) could be probed directly by SECM. In the present report, the electrochemical oxidation of QH₂ has been studied by cyclic voltammetry and differential pulse voltammetry at glassy carbon electrodes and platinum electrodes. However, up to now, there is little report about ET of QH₂ at ITIES measured by SECM. In this paper, ET process of QH₂ was observed at the L/L interface by SECM.

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SECM, a technique which has been invented and extensively applied by Bard and co-workers [4–9] is a powerful tool for the characterization of ET occurring at the ITIES via a bimolecular reaction between redox species confined to the two different solutions. The reactions both at the tip and at the ITIES can be summarized as follows:



where $\text{Q}^{\bullet-}$ is the free radical of hydroquinone. In the electrochemical systems, QH_2 has been known to undergo a totally irreversible 2e^- oxidation at electrodes [10,11]. However, in our work, the ITIES is assumed to act as an electrode and $\text{Q}^{\bullet-}$ produced at the interface is relatively unreactive and decays by disproportionation to QH_2/QH^- in aqueous solution. So only the first one electron procedure played mainly role in the interface reaction, and the second irreversible oxidation could not act as the dominating step in ET at ITIES.

The experimental system for investigation of ET at the interface can be represented as follows:

Ag/AgCl/10 mmol/L phosphate buffer (pH 7.0) 0.5 mL, 0.1 mol/L LiCl, x mmol/L NaClO_4 , y mmol/L QH_2/NB 0.5 mL, 10 mmol/L TBAClO₄, 1 mmol/L Fc/tip.

The SECM feedback mode has been well established and is applicable to the study of interfacial redox reactions. As shown in Fig. 1, the approach curves (solid squares are experimental points) at several concentrations appeared as different tip currents. When the concentration of QH_2 in aqueous phase is higher, the reaction between Fc^+ and QH_2 carried out at the interface and as the electrode approached the interface (where $d=0$) the current had a sharp enhancement, which showed a positive feedback. In Fig. 1 are feedback curves of the reacted system at interface with various K_r ($K_r = C_{\text{w}}/C_{\text{o}}$); $K_r = 15, 10, 5, 2$ and 1 , which were all at the interface dynamic controlled region. The obtained k_f values within the range $0.0009\text{--}0.08 \text{ cm s}^{-1}$ from a diffusion coefficient of Fc in nitrobenzene (NB) of $5.9 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ gotten by steady-state voltammetry. In our research system, the diffusion coefficient of QH_2 in water obtained by steady-state voltammetry was $1.2 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$. The experimental results demonstrated that the k_f values depended on the potential drop across the ITIES, which increased with an increase of the concentration of QH_2 . Because the interface reaction is a bimolecular reaction and bimolecular reaction rate is proportional to the bulk concentration of redox reactant in two phases, under constant composition model, as the concentration of reactant in two phases increased, bimolecular reaction rate increased.

Ion transfer is often happening during the biological electron transport process. In our study, the concentration of common ion was changed to stimulate the biological system and investigate whether the conditions of ion would influence ET. In SECM measurements, the potential across the interface is adjusted by varying the concentration of common ion (ClO_4^-) in two liquid phases, which would provide a controllable driving force for ET reactions. And the

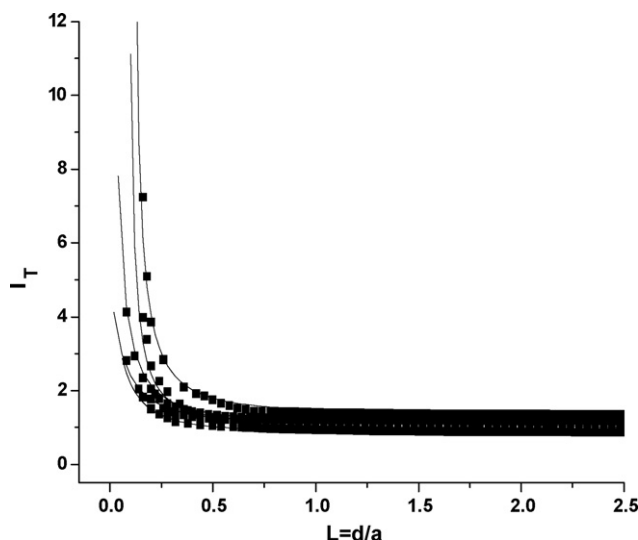


Fig. 1. Experimental SECM approach curves for the heterogeneous ET reaction between QH_2 and tip generated organic phase reactants at the NB/water interface for various reactant concentration ratios $K_r = 15, 10, 5, 2, 1$ (from top to bottom). The supporting electrolyte in NB was 10 mmol/L TBAClO₄ and in aqueous phase were 0.1 mol/L NaClO_4 + 0.1 mol/L LiCl. Solid lines show the simulated curves.

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