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# Electrochemical formation and electron transfer through self-assembled monolayers of 4-mercaptophenol on mercury

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This work is dedicated to Professor Ron Fawcett on the occasion of his 65th birthday

## Abstract

Formation and reductive desorption of self-assembled monolayers of 4-mercaptophenol on mercury have been studied by using cathodic stripping voltammetry. Voltammetric peak shapes and integrated areas are consistent with a sequential reorientation of adsorbed molecules from a flat to a perpendicular orien tation as their surface concentration increases. The rate of $Ru(NH_3)_6^{3+}$ reduction in the presence of full grown thiol monol ayers has been determined by impedance measurements. The frequency dispersion of the electrode admittance was found to obey Randles' behavior, though the parallel capacitance was observed to depend on the redox probe concentration when the monolayers became ionized at $pH > 4$. Non-ionized 4-mercaptophenol monolayers are more effective electron conductors than alkanethiol monolayers of the same thickness. After correcting for the diffuse layer potential drop, faster electron transfer rates are observed in the presence of ionized monolayers. This increase of reactivity correlates with results obtained from quantum chemical calculations performed on a model system, which predict an increase of donor–acceptor electronic coupling when the intervening molecular bridge becomes deprotonated.

*Keywords:* Thiol monolayer; Electron transfer; 4-Mercaptophenol; Impedance measurements; Electronic coupling

## 1. Introduction

Understanding the physical and chemical factors that determine the rates of electron transfer through molecular bridges has become a key issue in Biology [1] and in the growing field of Molecular Electronics [2]. To obtain meaningful results, both the donor–acceptor separation and the intervening bridge orientation have to be carefully controlled. In order to meet these requirements, several experimental strategies have been devised, including the use of binuclear complexes [3] and thiol monolayers deposited on electrode surfaces [4–6]. A significant advantage of the later approach is that thiol molecules, upon adsorption on a metallic surface, spontaneously form robust and well-ordered surface structures, known as self-assembled monolayers (SAM) [7,8].

In the last decade, the work of Miller et al. [4,9–11] showed how tunneling currents recorded at gold electrodes modified with alkanethiol SAMs, in the presence of a redox probe in solution, could be interpreted in terms of the non-adiabatic Marcus-DOS (density of states) theory [5]. Advantage was taken of the lateral interactions between the adsorbed hydrocarbon chains, which force a reproducible and nearly perpendicular orientation of the molecular spacer, and of the exponential decay of the electron transfer rate with donor–acceptor

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distance, which limits the possibility of electron exchange to those redox probe molecules that are in close contact with the organic monolayer. Alternatively, the redox moiety can be covalently attached to an alkanethiol chain, which is usually deposited together with a non-electroactive diluent thiol to form a mixed monolayer on the electrode surface [12–14]. To achieve a desirable uniformity of the donor–acceptor electronic pathways in this configuration, the hydrophilicity of the redox terminus should be enhanced, so that a chain folding of the electroactive thiol into the organic film becomes less likely [15].

Electronic coupling between the electrode and a redox probe, either in solution or tethered to an adsorbed thiol, is strongly dependent on the chemical nature of the molecular bridge. Variation of the chain length of alkanethiol spacers has produced values of the exponential decay constant $\beta$ lying within the 0.8–1.0 $\text{Å}^{-1}$ range [5,13,16–18]. Lower $\beta$ values were observed when the alkane chains were replaced by unsaturated oligophenyleneethynylene bridges ($0.4 \leqslant \beta \leqslant 0.6\ \text{Å}^{-1}$) [19,20], or by fully conjugated and more rigid oligophenylenevinylene bridges. In this last case, nonlinear decay plots, approaching a kinetic saturation regime, have been reported [21]. Insertion of single ether, alkyne or alkene linkages into alkanethiol chains has been shown to reduce the electronic coupling across the monolayer [22], whereas extensive amide–amide hydrogen bonding interactions between neighboring organic chains results in higher electron transfer rates [23].

Most studies on thiol self-assembled monolayers have been carried out on gold substrates, but mercury offers some unique advantages as substrate for thin-film deposition [24]. Mercury provides a highly reproducible, defect free and atomically flat surface, and it allows to mimic Langmuir balance experiments by expanding/contracting its surface [25–27]. In a recent report [27], the electrochemical formation and reductive desorption of 6-mercaptohexanol SAMs on mercury were studied, and evidence was given for the presence of three sequential stages during SAM formation. These three stages were associated with the growth of: (i) a low surface density monolayer, (ii) a high surface density monolayer and (iii) a passivating highly ordered monolayer, respectively. Majda and coworkers [26,28,29] have shown that electron tunneling experiments can be successfully performed on these highly ordered thiol monolayers deposited on mercury.

In this work, we will explore the electron tunneling characteristics of 4-mercaptophenol monolayers, which are expected to facilitate a fast electron exchange since they combine the presence of π-electron conjugation and small molecular size. Their formation under potential control will be monitored at different times during the deposition process, by comparing the areas and shapes of the corresponding cathodic stripping voltammograms. As it was shown previously in the case of 6-mercaptohexanol monolayers [27], 4-mercaptophenol SAMs grow satisfactorily on mercury in the presence of the $\mathrm{Ru(NH_3)_6^{3+}}$ redox probe in solution, so that tunneling experiments on freshly prepared monolayers can be performed in a straightforward way. Besides, the acid character of the phenolic group offers the possibility to assess the influence of the molecular bridge protonation on its efficiency as a molecular wire.

## 2. Experimental and computational aspects

### 2.1. Experimental aspects

4-Mercaptophenol (MPH) and $\mathrm{Ru(NH_3)_6Cl_3}$ were purchased from Aldrich and Alfa Aesar, respectively. Sodium sulfate ($\mathrm{Na_2SO_4}$), phosphoric acid ($\mathrm{H_3PO_4}$) and sodium hydroxide (NaOH) were purchased from Fluka, and they were used as received. Aqueous solutions were prepared from water purified with a Millipore Milli-Q system. Working solutions of thiols in sodium phosphate buffer were prepared from 5 mM stock solutions of MPH in ethanol (Merck). They were prepared daily and intensively deaerated with a presaturated nitrogen stream prior to the measurements for at least 20 min. Mercury was distilled three times under vacuum after treatment with dilute nitric acid and mercurous nitrate.

Self-assembled monolayers of MPH were built under potentiostatic control, by holding the hanging mercury drop electrode (HMDE) at −0.05 V (vs. Ag/AgCl, saturated NaCl) for ca. 100 s in the presence of a 30 μM thiol solution in sodium phosphate buffer, which may also contain the redox probe.

Electrochemical measurements were carried out in a three-electrode, water-jacketed glass cell, thermostated at 25 ± 0.2 °C with a Haake D8.G circulator thermostat. A sodium saturated Ag/AgCl electrode and a platinum foil were used as reference and auxiliary electrodes, respectively. The working electrode was a hanging mercury drop electrode (EG&G PAR 303A) whose area (0.0261 $\mathrm{cm^2}$) was determined by weighing three sets of 10 drops. Voltammetric and cell impedance measurements were carried out with an Autolab PGSTAT30 (Echo Chemie). UV–vis spectra were recorded with a 8452A Hewlett-Packard diode array spectrophotometer.

### 2.2. Computational aspects

Density-functional theory calculations at the 6-311G basis set level were performed to compute the molecular geometry of MPH. The molecular thickness of a MPH monolayer was calculated as the distance between the sulfur atom and the hydrogen atom of the phenol group, then a value of 2 Å was added to account for the distance between the sulfur atom of the thiol and the mer-