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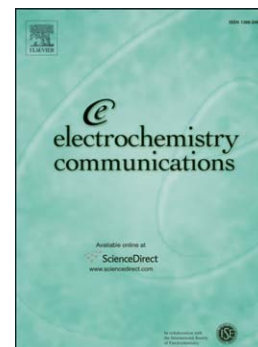
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Effect of external magnetic fields on electron transfer and ion pairing dynamics at ferrocenyl alkane thiol SAM/solution interfaces

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Abstract

The redox behaviour of ferrocene alkane thiol self assembled monolayer modified electrodes in contact with aqueous perchlorate solutions both in the absence of and in the presence of an external magnetic field is examined using both electrochemical and gravimetric techniques. The redox switching process involves an ET reaction involving the ferrocene/ferricinium redox transition coupled with an ion pairing step involving perchlorate ion. The voltammetric response recorded in the latter medium is irreversibly effected by the imposition of a static magnetic field of magnitude 0.5 T applied in a direction parallel to the electrode surface. The magnetic field dependence of the redox behaviour is attributed to structural changes in the monolayer arising from double layer effects involving changes in the spatial distribution of perchlorate counterions at the monolayer/solution interface, brought about by local convective stirring arising from the B field generated magnetohydrodynamic Lorenz body force.

1. Introduction.

Thorough and quantitative studies of electron transfer in single molecule device structures remains extremely challenging¹. On the other hand, redox active molecules tethered to ordered self assembled organic nanostructures of monolayer thickness immobilized on metal electrodes provide a well defined and versatile way to probe the mechanism of molecular electron transfer and tunnelling through organic materials². Mixed monolayer systems containing both redox active and analogous electroinactive structures which serve as diluents can be readily prepared, and so the surface confined redox species can be diluted in a controlled manner to generate an array in which the redox sites are far enough apart so that they do not interact with one another. The application of well established electrochemical techniques to the latter system offers the ability to answer many thermodynamic, kinetic and structural questions relevant to the construction of molecular electronic devices.

Magnetic field effects on electrochemical reactions have been recently reviewed³ and may be divided into three categories-those relating to mass transport, deposit morphology and electrode kinetics. The effect of a magnetic field on mass

transport is well established. The field acts to induce convection in the solution, thereby reducing the diffusion layer thickness and thus increasing the diffusion limited current⁴. In recent years, clear field effects on the morphology and texture of electrodeposits have been reported under various conditions⁵. The effect of external magnetic fields on the dynamics of heterogeneous electron transfer processes is more controversial. Some authors report that the field has no influence⁶ whereas others explain modifications in the exchange current density in a field in terms of transitions between magnetic quantum states in the ions⁷.

In this communication we report the marked effect of an external static magnetic field (0.5 T) on the redox and electron transfer behaviour of a self assembled redox active monolayer (SAM) *n*-(ferrocenylcarbonyloxy) alkane thiol $\text{FcCO}_2(\text{CH}_2)_n\text{SH}$, when $n = 7, 10$ and 11 .

2. Experimental

The complex was synthesised via established methods⁸ and the monolayer was formed on gold support electrodes via adsorption from a dilute (1mM) ethanolic solution of the alkane thiol for some 48 hours. The electron transfer dynamics across the alkane thiol monolayer were probed using cyclic voltammetry, electrochemical quartz crystal microbalance gravimetry and potential step chronoamperometry using a CHI electrochemical workstation, in a standard three electrode electrochemical cell. Electrochemical experiments (facilitated by BAS or CHI computer controlled electrochemical workstations) were performed in aqueous 1.0 M HClO_4 solution at room temperature (293K). A three electrode electrochemical cell was placed in the bore of a permanent magnet which was a Magnetic Solutions HC-500-54 Halbach cylinder made from a $\text{Nd}_2\text{Fe}_{17}\text{B}$ alloy with a fixed static field of 0.5 T transverse to the bore. The bore diameter was 54 mm. The magnetic field was applied parallel to the working electrode surface. Computed magnetic flux lines calculated for the Halbach cylinder used in the present work are presented in fig.1(a). Note the uniformity of magnetic flux within the bore.

3. Results and Discussion

In fig.1(b) the voltammetric behaviour recorded at a sweep rate of 20 mVs⁻¹ for the ferrocene thiol SAM (n=7) in the absence and in the presence of an external magnetic field ($B = 0.5$ T) is outlined. Redox peaks corresponding to the ferrocene/ferricinium surface redox transition are clearly discerned with E^0 having a value close to 582 mV (vs Ag/AgCl) at slow sweep rates. The latter does not change when an external magnetic field is applied, hence the thermodynamics of the surface redox transformation is not field dependent.

A marked decrease in surface coverage of attached electroactive ferrocene species was observed in the presence of the magnetic field ($\Gamma = 0.79$ nmol cm⁻² ($B = 0$ T) and $\Gamma = 0.52$ nmol cm⁻² ($B = 0.5$ T)). Hence $\Gamma_B/\Gamma_0 = 0.60$. Similar results were observed for other ferrocene alkane thiol SAM films of the type $\text{FcCO}_2(\text{CH}_2)_n\text{SH}$, and typically $\Gamma_B/\Gamma_0 = 0.8$ for $n = 11$ and 0.7 for $n = 10$. Little variation in surface coverage is observed when the alkanethiol films are continuously multicycled between 0.3 and 0.8 V in HClO_4 electrolyte in the absence of an external magnetic field. However an irreversible decrease in surface coverage is observed even after one cycle in the presence of an external field of 0.5 T applied parallel to the electrode surface.

Figure 1(c) shows the corresponding EQCM response. The oxidation of the pendant ferrocene group in ferrocene terminated SAMs is accompanied by an ion pairing event in perchloric acid electrolytes⁸ The process involves negatively charged perchlorate ions (ClO_4^-) ions forming an ion pair with the positively charged ferricenium ions (Fc^+) in order to maintain charge neutrality. This event causes an increase in mass loading atop of the pendant ferrocene canopy and may be recorded using an EQCM. It is clear that the application of the external magnetic field has implications not only on the surface coverage observed using CV, but also has an effect on the amount of ion pairing that occurs. We have determined values of the redox group surface coverage Γ as determined from CV analysis and both the frequency change Δf and the mass change Δm corresponding to ion pairing events as determined from EQCM both in the presence and in the absence of an external magnetic field. We note from fig.1(c) that the mass change in the SAM layer accompanying the redox switching of the immobilized redox groups is less in the presence of a static magnetic field than in the field free environment. This means that the quantity of charge compensating

counterions and solvent molecules in the oxidized SAM film is less when the voltammetry is performed in the finite field environment as compared with the same procedure conducted in the absence of the magnetic field.

Given $\Gamma_0 = 0.79 \text{ nmol/cm}^2$ for the $n = 7$ SAM when $B = 0$ then assuming complete charge compensation via ion pairing between ferricinium and perchlorate ions during layer oxidation, we can predict an expected film mass change of 76 ng arising from oxidative redox switching of the layer, which was very close to that actually observed (77 ng). When voltammetry is performed within the bore of the magnet $\Gamma_B = 0.52 \text{ nmol/cm}^2$ and again assuming all oxidized sites are paired with counterions a layer mass change of ca 50 ng is predicted. The actual mass change observed experimentally is considerably less (35 ng). This observation indicates that the packing and order within the monolayer has been significantly affected by the magnetic field environment. Many of the oxidized ferricinium groups are not ion paired and may well be buried within the hydrocarbon structure.

Although it is possible to utilise well established theory⁹ to evaluate the electron transfer rate constant from CV data as a function of sweep rate or experimental time scale, it is less complicated to use potential step chronoamperometry. In the latter experiment the potential was stepped from an initial value of ca. 0.44 V to a final value some 400 mV more positive. In effect the potential was stepped across the redox peak, and an oxidative redox transformation ferrocene \rightarrow ferricinium established. The current flow arising from the latter is subsequently measured as a function of time. The time varying, chronoamperometric response expected by a surface immobilized redox group arising from a potential step is given by: $i(t) = k_{ET} \Delta Q \exp[-k_{ET}t]$, where k_{ET} denotes the potential dependent electron transfer rate constant and ΔQ represents the charge passed during the current transient. Hence the ferrocene/ferricinium surface redox transformation should exhibit first order kinetics, and a plot of the natural logarithm of the current should vary linearly with the elapsed time. The results obtained for the ferrocenethiol SAM modified electrode under both zero and 0.5 T magnetic field conditions are outlined in semi-logarithmic form in fig 1 (d) below.

We note that the semi-logarithmic curve corresponding to the oxidative ferrocene/ferricinium redox transformation decays more rapidly in the presence of an 0.5 T magnetic field than in the field free situation. The heterogeneous rate constant recorded for the ferrocene/ferricinium redox transformation was ca. 17 s^{-1} when $B = 0 \text{ T}$

but was significantly increased to *ca.* 47 s^{-1} when $B = 0.5\text{ T}$. In contrast, little effect of magnetic field could be found on the rate constant ($k_{\text{ET}} = 47\text{ s}^{-1}$ for $B = 0$ and $B = 0.5\text{ T}$) for the corresponding reductive ferricinium/ferrocene transformation. The rate constant values are obtained via linear extrapolation at times longer than *ca.* 4 ms . This result provides a firm confirmation for the first time that the rate of long range electron transfer across molecular barriers (the insulating hydrocarbon chains) is directly effected by the presence of a magnetic field. However the surface redox reaction is also accompanied by ion pairing equilibria so the net kinetic situation is complex.

It is also significant that the semi-logarithmic plots presented in fig.1(d) are non-linear and so the simple linear plot expected for first order kinetic decay is not observed. Indeed the semilogarithmic plots exhibit a distinct ‘dog-leg’ character consisting of two distinct temporal regions. This observation leads to the suggestion that the chronoamperometric response is best expressed in terms of a multiexponential expression where to a first approximation one can indentify a fast and a slow ET process. More generally the non linearity may be explained in terms of kinetic dispersion and interfacial potential drop effects as discussed by Albery et al¹¹ and by Creager and Weber¹².

The theory developed some time ago by Smith and White¹³ which extends the original work of Laviron⁹ enables SAM modified electrode voltammetry to be quantitatively examined. Specifically, the approach enables the shape of the voltammetric wave and the position at which it is observed to be computed from a simple double layer model. It has been shown that the shape and peak position depend on the thickness and dielectric constant of the adsorbate film, the surface concentration of electroactive adsorbate, the concentration and type of charge compensating solution phase counterion, the solvent dielectric constant and the potential of zero charge. This type of analysis was further developed by Ohtani and co-workers¹⁴ who considered the effect of ion association within the SAM layer, and by Calvente and co-workers¹⁵ who considered the effect of a spatial distribution in redox site positions within the layer. Hence keeping this work in mind we note that the shape of the voltammetric response recorded for a redox active SAM film such as the systems discussed in the present paper is strongly dependent on the distribution of potential at the monolayer/solution interface. The potential distribution in turn is determined by the distribution of charge compensating counterions in the solution adjacent to the monolayer. The voltammetric profile will also be directly affected by

the degree of ion pairing and ion association and on whether the immobilized redox groups are buried within the dielectric thiol film. Clearly the counterion distribution will be disturbed by the local stirring effect brought about by the magnetohydrodynamic Lorentz force. This will directly affect the number of local available counterions which can engage in ion pairing with oxidized ferricinium groups (since convective stirring will decrease the number of counterions in the depletion layer) and hence, as Smith and White¹³ and White and co-workers¹⁶ have shown, affect the nature of the interfacial potential distribution. Indeed the packing quality and structure of the monolayer film may well suffer irreversible change as a result of this local stirring. A situation corresponding to insufficient charge compensation by counterions will pertain corresponding to diminished peak currents and distorted voltammograms as compared to the field free case^{13,15}. Hence we suggest that the effect of magnetic field on the observed redox response of the electroactive ferrocenyl alkane thiol SAM film can be largely attributed to local magnetohydrodynamic effects involving charge compensating counterions at the layer/solution interface.

4. Conclusions

We have shown in this communication that the electrochemical response of a pendant ferrocene group in an alkane thiol SAM thin film is irreversibly effected by the presence of a 0.5 T static magnetic field applied parallel to the electrode surface. In situ EQCM analysis indicates that the extent of ion pairing decreases in the presence of the magnetic field which suggests that the decrease in electroactivity manifested in the voltammetry can be attributed to local magnetohydrodynamic stirring which effects the counter-ion distribution at the film/solution interface and hence the interfacial potential distribution.

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Figure legends

Figure 1. (a) Magnetic flux lines calculated for Halbach cylinder of the type used in the present work. (b) Cyclic voltammetric response for the ferrocene thiol $\text{FcCO}_2(\text{CH}_2)_7\text{SH}$ SAM recorded both in the presence (blue trace) and in the absence (black trace) of an external magnetic field of magnitude 0.5 T, Electrolyte 0.1 M HClO_4 , sweep rate 20 mV/s. (c) EQCM response showing the frequency change corresponding to the oxidation/reduction of the pendant ferrocene groups of a $\text{FcCO}_2(\text{CH}_2)_7$ SAM both in the presence (blue trace) and in the absence (black trace) of an externally applied magnetic field of magnitude 0.5 T directed parallel to the electrode surface. Electrolyte 0.1 M HClO_4 , sweep rate 20 mV/s. (d) PS chronoamperometric transients recorded in semi-logarithmic (base 10) format for surface bound Ferrocene/ferricinium redox transition in the absence and presence of an external magnetic field. Potential step 300 – 850 mV. 0.1 M HClO_4 .

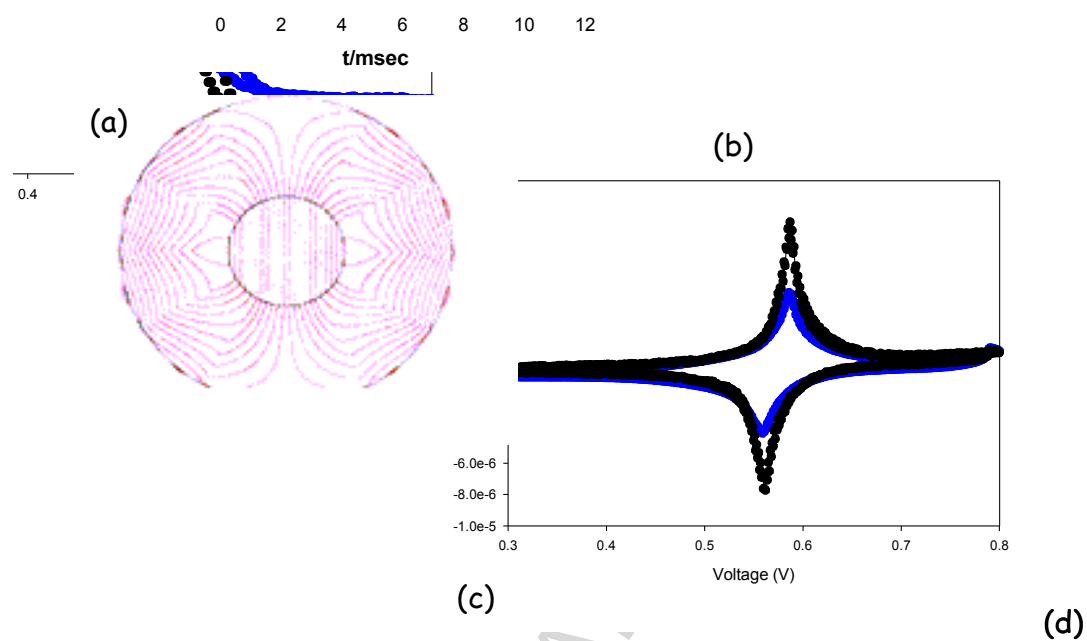


Figure 1