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Host−Guest Interaction at a Self-Assembled Monolayer/Solution Interface: An Electrochemical Analysis of the Inclusion of 11-(Ferrocenylcarbonyloxy)undecanethiol by Cyclodextrins

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A host−guest equilibrium involving the redox guest 11-(ferrocenylcarbonyloxy)undecanethiol (FcSH) in a self-assembled monolayer on gold electrode surfaces and a β-cyclodextrin (β-CD) host in solution is investigated. The effect of varying the ratio of FcSH to a diluent (n-decanethiol) in the self-assembly solution on the electrochemical characteristics of the ferrocene/ferricenium redox process and the inclusion properties of FcSH self-assembled monolayers (FcSH-SAMs) is examined using cyclic voltammetry and chronoamperometry. α- and γ-cyclodextrin have a negligible effect on both the thermodynamics and kinetics of the redox reaction. The electrochemical and ion-pairing behavior of FcSH-SAMs in solutions containing β-CD suggests that an inclusion complex is formed and that the included form of the ferrocenyl group is electroinactive in the potential window investigated. Inclusion results in a decrease in cyclic voltammetric peak currents (surface coverage of electroactive FcSH) and a slight increase in the standard electron transfer rate constant for the ferrocene/ferricenium redox process. The decrease in surface coverage of electroactive FcSH upon addition of β-CD exhibits a response similar to that expected for a Langmuir adsorption isotherm. Stability constants for the inclusion complexes of β-CD and the ferrocenyl or ferricenium forms of an FcSH-SAMs, containing a FcSH surface coverage of 5.2×10^{-11} mol cm^{-2}, have been evaluated as 3.6 (0.4) $\times 10^4$ and 3.2 (0.4) $\times 10^4$, respectively. The stability constants thus evaluated were shown to be dependent on the surface coverage of FcSH in the FcSH-SAMs.

Introduction

The design of tailored surfaces for the transduction of affinity reactions has attracted increasing interest because of potential applications as sensors and for the unraveling of fundamental biological adhesion and transduction mechanisms.[1,2] Receptor−ligand affinity reactions at surfaces have been investigated using indirect methods, such as optical or electrochemical markers of ligands and/or receptors, and directly, by measuring the modulation of the electrochemical, optical, or mass response of the transducer.[1−3] The synthesis of macrocycle-substituted ferrocenes[4] and conducting polymers[5] has also been achieved in an attempt to develop voltammetric-responsive sensors for electroinactive analytes that form inclusion complexes with the macrocycles.

We are interested in the synthesis and characterization of immobilized redox-responsive sensors for environmental and biomedical applications. To this end we have embarked on the study of redox-active self-assembled monolayers (SAMs) containing immobilized receptor ligands. Modulation of the electrochemical response of the redox active probe, immobilized in close proximity to the receptor ligand, is proposed upon binding of the receptor, yielding a redox responsive system for the detection of electroinactive receptor−ligand interactions. We have initially focused on the formation of mixed monolayers of (ferrocenylcarbonyloxy)alkanethiols and alkanethiols by self-assembly at gold electrodes. Stable SAMs can be easily prepared by chemisorption of organosulfur compounds at gold electrode surfaces[6] and ferrocenylthiol SAMs have been the most studied redox-active monolayers to date due to their ease of preparation and the reversible electrochemistry of the ferrocenyl group.[7−11]

The cyclodextrins are cyclic oligosaccharides possessing an interior hydrophobic cavity[12] that can include a wide variety of guest species, among them the environmentally

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important organics.[12,13] The formation of host−guest complexes between ferrocenes and cyclodextrins (CD) in solution has been widely reported.[14,15] The cyclodextrins act as second-sphere ligands for the hydrocarbon cyclopentadienyl rings of the ferrocenes, thus altering the solution redox electrochemistry. Decreased peak currents and shifts in oxidation and reduction potentials in cyclic voltammetry (CV) are observed upon inclusion of ferrocenes into cxyclodextrins, because of the diminished diffusion coefficent and the electrochemical stability of the inclusion complex.[15] The interactions between ferrocenes and β-CD polymers have also been investigated using electrochemistry and the quartz crystal microbalance (QCM).[16]

Host−guest interactions between self-assembled monolayers of thiolated cyclodextrins and redox-active guests in solution have been studied by several groups using CV and impedance analysis.[17] Bernardo et al.[18] have reported on formal potential shifts and current decreases observed for the coprecipitation of an amphiphilic viologen guest and an amphiphilic calix[6]arene host at a gold bead electrode surface. The same group has reported on host−guest interactions between an immobilized ferrocenethiol, self-assembled on gold bead surfaces, and a dodecyl derivative of a sulfonated calixarene.[11] The formation of the host−guest complex in the presence of very low concentrations of the guest in solution (0.4 μM) resulted in a shift in the monolayer ferrocenethiol redox couple. Here we report on an electrochemical analysis of the formation of inclusion complexes between fixed ferrocenyl groups on gold electrodes and cyclodextrin guest species in solution.

Experimental Section

Materials and Reagents. 11-(Ferrocenylcarbonyloxy)undecanethiol (FcSH) was synthesized and purified using literature methods.[10] Its structure was confirmed by ^{1}H NMR spectroscopy. *n*-Decanethiol and α-, β-, and γ-cyclodextrins were purchased from Aldrich Chemical Co. (St. Louis) and used as received. Electrolyte solutions were prepared using deionized water from a Milli-Q purification system. All reagents for supporting electrolytes were of reagent grade and used as received. Gold electrodes were prepared by sealing polycrystalline gold wires (99.99+%, Goodfellow) in soft glass using a gas/air flame. The gold electrodes were abraded with successively finer grades of SiC paper and polished to a "mirror-like" finish with 0.3 and 0.05 μm alumina slurry on microcloth pads (Buehler), followed by rinsing with water and ethanol and removal of traces of alumina from the surface by brief cleansing in an ultrasonic bath. This procedure yields gold disks of macroscopic area of approximately 7×10^{-3} cm^2. Electrical connection was accomplished by soldering, or attaching with silver-loaded epoxy (Epo-Tek), a copper wire to the unexposed side of the gold.

Table 1. Electrochemical Response Characteristics, in 1.0 M NaClO$_4$, of FcSH SAMs Prepared by Self-Asssembly from Ethanolic Solutions Containing Different Ratios of FcSH to Diluent *n*-Decanethiol (mM FcSH/Decanethiol)[a]

FcSH/decanethiol	ΔE_p, mV[b]	$E^{\circ\prime}$, mV[c]	Γ_{Fc}, mol cm^{-2} [d]	k^0, s^{-1} [e]
0.9/0.1	26	550	4.1×10^{-10}	621
0.5/0.5	23	546	1.2×10^{-10}	653
0.1/0.9	148	535	5.2×10^{-11}	174
0.05/0.95	169	548	1.3×10^{-11}	94

[a] Total concentration of thiol in solution was always 1 mM. [b] Cyclic voltammetric peak-splitting at a scan rate of 10 V/s. [c] Cyclic voltammetric formal potential at a scan rate of 10 V/s. [d] Surface coverage of electroactive FcSH groups evaluated from the charge passed during the anodic cyclic voltammetric sweep at 10 V/s. [e] Standard electron transfer rate constant, evaluated from the anodic intercept of a Tafel plot of electron transfer rates, determined from chronoamperograms, versus overpotential.

Monolayer Formation. The electrodes were first pretreated by etching in dilute aqua regia (3:1:4 HCl/HNO$_3$/H$_2$O) for 5 min and then rinsing with water and ethanol. Monolayers were formed by soaking the freshly pretreated electrodes in a coating solution containing various ratios of FcSH to decanethiol in absolute ethanol, with the total thiol concentration of 1.0 mM, at room temperature for more than 48 h. The coating solutions were deaerated with nitrogen for 10 min before the electrodes were soaked and kept O$_2$ free during the self-assembly process.

Electrochemical Measurements. A BAS-100B/W electrochemical analyzer (BAS, USA) was used for all electrochemical measurements. A conventional three-electrode system was employed with a SAM-modified electrode as working, a platinum wire as auxiliary, and a Ag/AgCl in 3.0 M NaCl (BAS) as reference electrode. All potentials are reported versus this reference at room temperature (20 ± 2 °C). A supporting electrolyte of 1.0 M NaClO$_4$, adjusted to pH 6.0, was used except where otherwise indicated. Oxygen was not excluded from the cell.

The microscopic area of the bare polished gold electrodes was determined by measuring the charge that evolved during oxidation of the superficial Au in 1.0 M H$_2$SO$_4$.[19] Roughness factors (ratio of microscopic to geometric area) of 1.4 ± 0.1 were obtained for all electrodes used in this study.

Results and Discussion

Electrochemical Characterization of FcSH SAMs. Cyclic voltammograms, in 1.0 M NaClO$_4$ electrolyte, of FcSH SAMs prepared by soaking the freshly pretreated Au electrodes in ethanolic solutions containing 0.9/0.1 (A) and 0.1/0.9 (B) ratios of FcSH to decanethiol, are shown in Figure 1. All cyclic voltammograms exhibited oxidation/reduction peaks for the ferrocene/ferrocenium redox reaction in the SAMs. The apparent formal potentials, $E^{\circ\prime}$ (estimated from the mean of the oxidation and reduction peak potential), were 550 ± 8 mV for voltammograms in A and 535 ± 6 mV for those in B, respectively. The peak-to-peak splitting (ΔE_p) at a 10 V/s scan rate was approximately 26 mV for electrode A and 148 mV for electrode B (Table 1), indicative of slower heterogeneous electron transfer to the ferrocenyl group in this SAM.

Continuous cycling of the FcSH SAMs at low scan rates (<1 V/s) results in a gradual loss of the ferrocene redox couple due to the reported slow decomposition of the oxidized ferrocenyl group.[11] The monolayers are however extremely stable in this electrolyte if kept in the reduced state. We have minimized the decomposition of the

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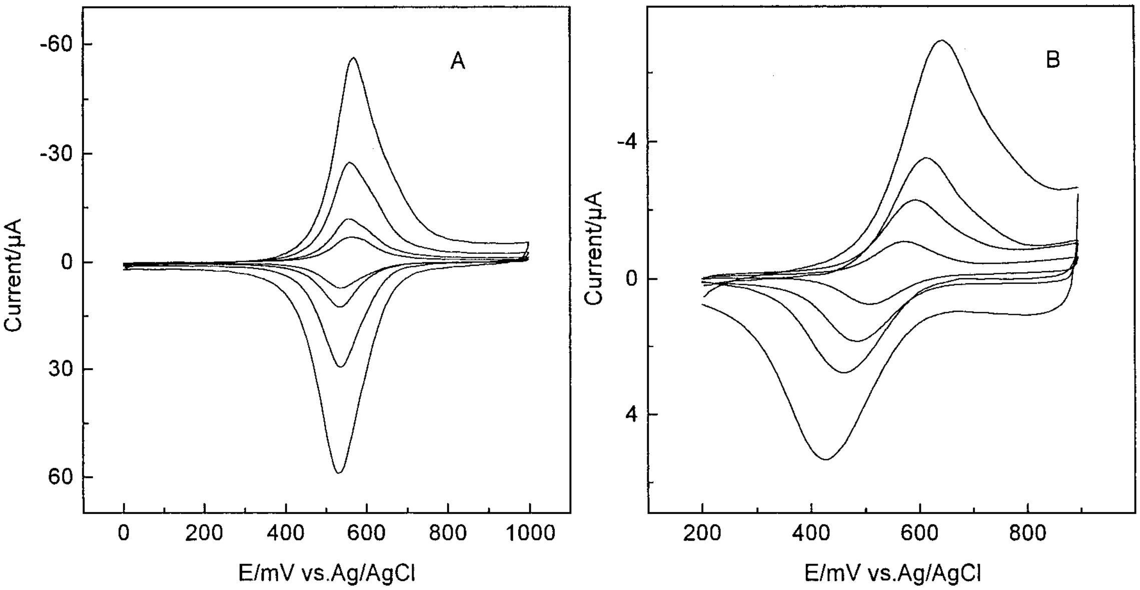

Figure 1. Cyclic voltammograms of FcSH SAMs with FcSH surface coverages of 4.1 × 10^{-10} (A) and 5.2 × 10^{-11} (B) mol cm^{-2} in 1.0 M $NaClO_4$ at scan rates of 2, 5, 10, and 20 V/s (currents increase in that order).

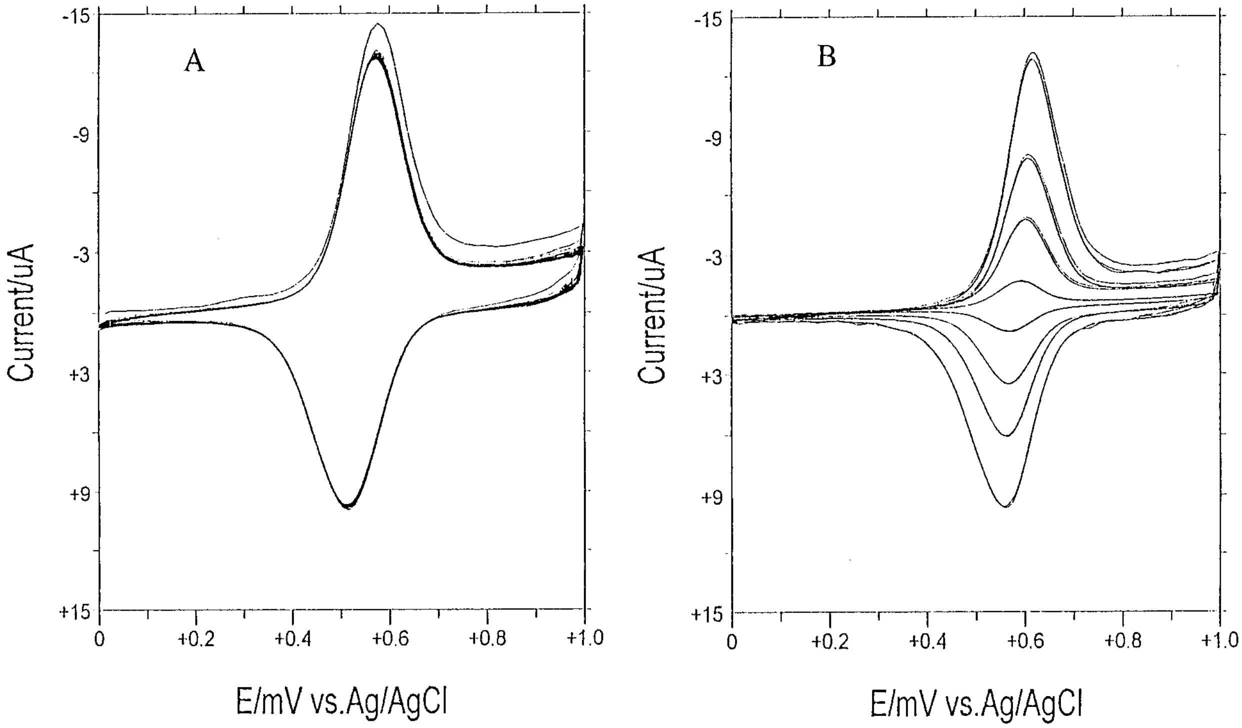

Figure 2. Repetitive cyclic voltammograms at a FcSH SAM with FcSH surface coverage of 2.1 × 10^{-10} mol cm^{-2} in 1.0 M $NaClO_4$. Scanning for 30 cycles at 10 V/s (A) and for 3 cycles at 1, 3, 6, and 10 V/s (increasing peak heights in that order) (B).

ferrocenyl form of the monolayer by cycling the potential at fast scan rates (10 V/s) where no decay in the signal is apparent for up to 30 continuous scans (Figure 2A). Consecutive cycles (3) at various scan rates also demonstrate the stability of these monolayers (Figure 2B).

The apparent heterogeneous electron transfer rate constant, k_{app}, can be conveniently evaluated from chronoamperometric experiments if the RC cell time constant is sufficiently short. The standard heterogeneous rate constant, k^0, can be evaluated from the intercept of a semilog plot (Tafel plot) of k_{app} versus overpotential, η, according to the Butler–Volmer formalism.[20] The values of k^0 are dependent on the amount of ferrocene in the monolayer, with k^0 similar at FcSH SAMs containing more than 25% coverage of FcSH. When the coverage is further reduced the electron transfer rate constant quickly decreases. An average value for the standard heterogeneous rate constant in 1 M $NaClO_4$ of 640 ± 30 s^{-1} was estimated for monolayers prepared from solutions of 0.9/0.1 and 0.5/0.5 FcSH/decanethiol ratios. This value is similar to the value of approximately 660 s^{-1}, estimated by extrapolation of data (Figure 11 in ref 21) obtained for mixed monolayers of $FcCOO(CH_2)_nSH$ and $CH_3(CH_2)_{n-1}SH$ by an indirect laser-induced temperature jump method.

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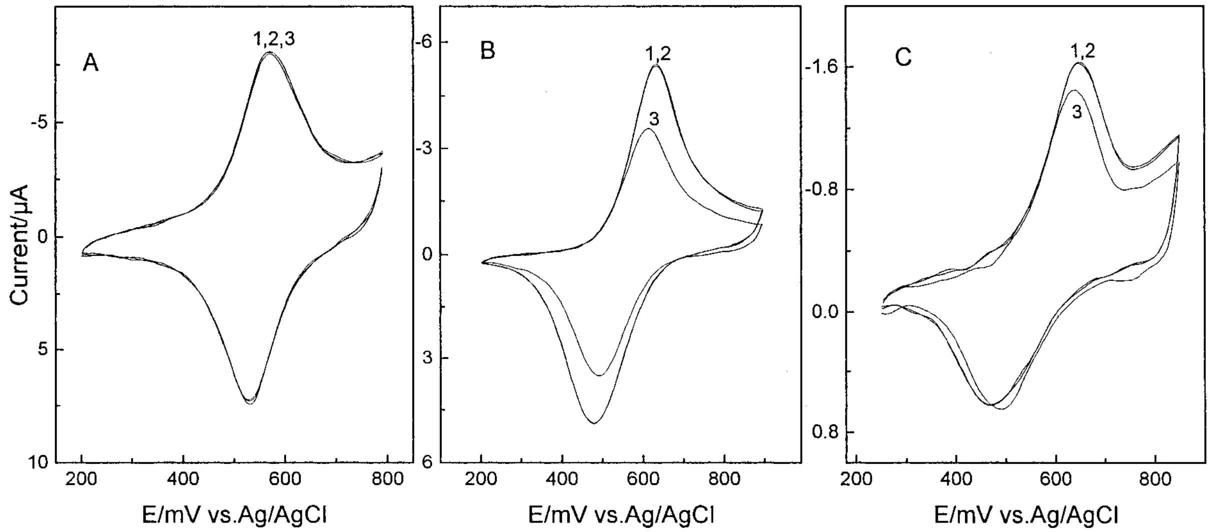

Figure 3. Cyclic voltammograms, recorded at a scan rate of 10 V/s, at FcSH SAMs with FcSH surface coverages of 9.2×10^{-11} (A), 4.9×10^{-11} (B), and 1.3×10^{-11} (C) mol cm^{-2} in 1.0 M $NaClO_4$ containing 10 mM of α-CD (curve 1), γ-CD (curve 2), and β-CD (curve 3).

The observed dependence of the rate constant on surface coverage has been proposed to be due to the formation of a more densely packed monolayer at lower coverages of FcSH.[9]

Host−Guest Interaction at FcSH SAM/Solution Interface. A 2:1 inclusion complex of α-CD with ferrocenemonocarboxylic acid can be formed in solution, each cyclopentadienylferrocene ring occupying one cyclodextrin cavity.[15] Equatorial inclusion of the ferrocenemonocarboxylic acid in γ-CD occurs in solution to yield a 1:1 inclusion complex.[15] No changes in cyclic voltammograms of the FcSH SAM, at any FcSH surface coverage, were observed upon addition of either α-CD or γ-CD to the electrolyte solution (Figure 3, curves 1 and 2). This indicates that equatorial inclusion of the tethered ferrocene in γ-CD is not possible and that the stability constant of the α-CD/ferrocene complex is low at the FcSH SAM/solution interface.

The radius of the ferrocenyl group is 3.3 Å,[22] yielding a maximum theoretical ferrocene coverage of 4.8×10^{-10} mol cm^{-2} for a densely packed monolayer of FcSH alone. The radius of the outer periphery of the β-CD molecule is approximately 7.7 Å,[14,15] resulting in a maximum possible β-CD surface coverage of approximately 9×10^{-11} mol cm^{-2}. Thus, the formation of inclusion complexes between ferrocene and β-CD is more probable when the FcSH coverage is less than 9×10^{-11} mol cm^{-2}, assuming that the FcSH molecules are uniformly distributed throughout the monolayer. This is demonstrated in Figure 3, where no change in the cyclic voltammogram (10 V s^{-1}) at the FcSH SAM upon addition of β-CD is observed for a FcSH coverage of 9.2×10^{-11} mol cm^{-2} (Figure 3A), while changes were observed for FcSH coverages of 4.9×10^{-11} (Figure 3B) and 1.2×10^{-11} mol cm^{-2} (Figure 3C). From Figure 3 (B3 and C3), the redox peak currents decrease upon addition of β-CD. However, no difference is found in the apparent formal potential, 545 ± 7 mV, in the presence or absence of β-CD, although the peak splitting changes slightly. This indicates that the electroactive species in these FcSH SAMs is the uncomplexed FcSH. This is consistent with previous reports that the ferrocenemonocarboxylic acid/β-CD inclusion complex cannot be directly oxidized in the potential window studied (up to 1.0 V vs SCE) and that a CE scheme is observed, where the ferrocene must dissociate from the cyclodextrin prior to electron transfer.[15,17a] The rapid scan rates that are used in this study do not allow us to observe the typical sigmoidal voltammograms associated with CE-type reactions upon addition of cyclodextrin. This may be an indication that the host−guest dissociation rate is slower than the time scale of the experiment. Unfortunately, decreasing the scan rate also decreases the stability of the SAMs. Simulations of CE reactions are in progress in an attempt to address this issue. The addition of β-CD to the electrolyte does however reduce the peak splitting of the FcSH SAM cyclic voltammograms, indicative of a slight increase in the rate of electron transfer. Subsequent rinsing of the electrode with water results in an increase in the peak current and peak splitting (not shown). Regeneration of the original signal has not however been achieved, possibly because of the solubilization of a portion of the FcSH by β-CD over the duration of the experiments.

At our FcSH SAM electrodes, inclusion of the ferrocene into the β-CD cavity decreases the effective coverage of uncomplexed FcSH, resulting in the decrease in peak currents and charge passed observed in Figure 3 (B3 and C3). The decrease in cathodic peak currents observed at FcSH SAMs upon addition of β-CD to the electrochemical cell was less than that of the anodic peak current. This reflects the previous finding that the oxidized ferricenium ion is included to a lesser extent than the reduced form in the β-CD cavities.[15] The magnitude of the current decrease also varied with FcSH surface coverage (see Figure 3). At high coverages no decrease is observed. At low coverage ($<2 \times 10^{-11}$ mol cm^{-2}) a smaller decrease is observed compared to that seen at intermediate coverage (approximately 5×10^{-11} mol cm^{-2}).

Electron Transfer Kinetics of FcSH SAMs in β-CD Solutions. The decrease in the CV peak splitting of FcSH SAM upon addition of β-CD to the electrolyte (see for example Figure 3) could be indicative of increased electron transfer rates in these solutions. We further examined this effect using chronoamperometry to evaluate the kinetics of electron transfer, as described above. Plots of ln *i* vs time following excursions of the potential step to different overpotentials (η) at an FcSH SAM electrode of 5.2×10^{-11} mol cm^{-2} FcSH surface coverage, in the absence (A) and presence of varying concentrations of β-CD (B and C) are shown in Figure 4. The plots show good

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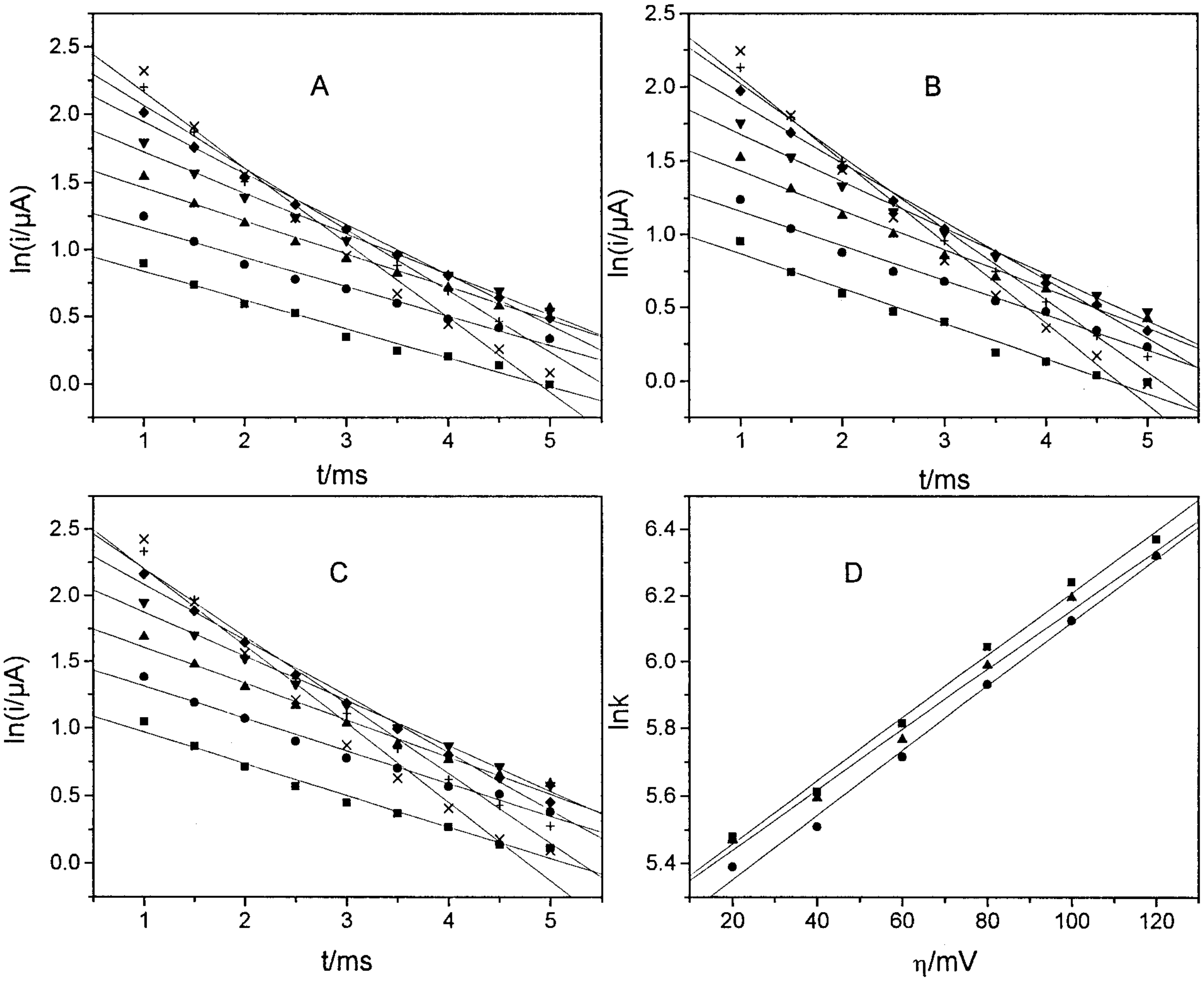

Figure 4. Data analysis of chronoamperometric currents upon stepping the potential from 100 mV to overpotentials of 0 (■), 20 (●), 40 (▲), 60 (▼), 80 (◆), 100 (+) and 120 (×) mV at a FcSH SAM (FcSH surface coverage of 5.2 × 10^{-11} mol cm^{-2}) in 1.0 M $NaClO_4$ containing 0 (A), 1 (B) and 10 (C) mM β-CD. The anodic portions of Tafel plots for A (●), B (▲), and C (■) are shown in (D).

Table 2. Standard Electron Transfer Rate Constants (k^0) at FcSH SAMs of Different FcSH Surface Coverages in 1.0 M $NaClO_4$ Electrolyte Containing Various β-CD Concentrations ($C_{\beta\text{-CD}}$)[a]

$C_{\beta\text{-CD}}$, mM	k^0, s^{-1}	
	$\Gamma_{Fc} = 5.2 \times 10^{-11}$ mol cm^{-2}	$\Gamma_{Fc} = 1.3 \times 10^{-11}$ mol cm^{-2}
0	174 (5)	94 (7)
0.2	182 (5)	101 (5)
1	193 (6)	122 (15)
10	194 (6)	149 (14)

[a] Rate constants were evaluated as described in the text and are an average of three determinations at one surface coverage (standard deviation).

linearity, with deviations at short times possibly due to residual charging currents. Estimates of k^0 for each electrolyte solution, tabulated in Table 2, are obtained from the intercept of the Tafel plots (Figure 4D). It can be seen that the inclusion of ferrocenyl groups of the FcSH SAM by β-CD can increase slightly the electron transfer rate, possibly by improving the microenvironment for the electrochemical oxidation of the FcSH SAM. This increase in k^0 was larger at electrodes with lower surface coverages of FcSH.

Ion-Pairing Properties of FcSH SAMs. The electrochemical oxidation of the FcSH SAM produces ferrocenium cations in the SAM. These cations may form ion pairs with anions in the supporting electrolyte to neutralize the excess positive charge in the SAM, resulting in a negative shift in the redox potential with increasing anion concentration.[7,8] The changes in the cyclic voltammetric response of a FcSH SAM (FcSH surface coverage of 4.7 × 10^{-11} mol cm^{-2}) in the presence and absence of 10 mM β-CD upon addition of increasing $NaClO_4$ concentration are shown in Figure 5. In this experiment 1.0 M Na_2SO_4 was selected as supporting electrolyte to maintain a constant ionic strength, as the SO_4^{2-} anion is both a weak ion-pairing agent for ferrocenium in FcSH SAMs[8] and a poor guest for the β-CD host molecule.[23] Figure 5A gives a comparison of formal potential shifts in the presence and absence of β-CD. The shift in formal potential with increasing perchlorate concentration is due to the formation of ion pairs. The slopes of the plots in Figure 5A are equal within experimental error, 50 and 53 mV in the presence and the absence of β-CD, respectively. They are close to the theoretical Nernst slope of 59 mV that would indicate the formation of an ion pair between the oxidized ferricenium and a perchlorate anion.[8] The FcSH SAM CV peak splitting (5B) and anodic peak currents (5C) decreased upon addition of 10 mM β-CD to 1.0 M Na_2SO_4 as described above for $NaClO_4$ electrolyte. The increase in peak currents and decrease in peak splitting upon subsequent addition of $NaClO_4$ to the cell in the presence or absence of β-CD is due to faster electron transfer rates in $NaClO_4$ than in Na_2SO_4. The important point to note

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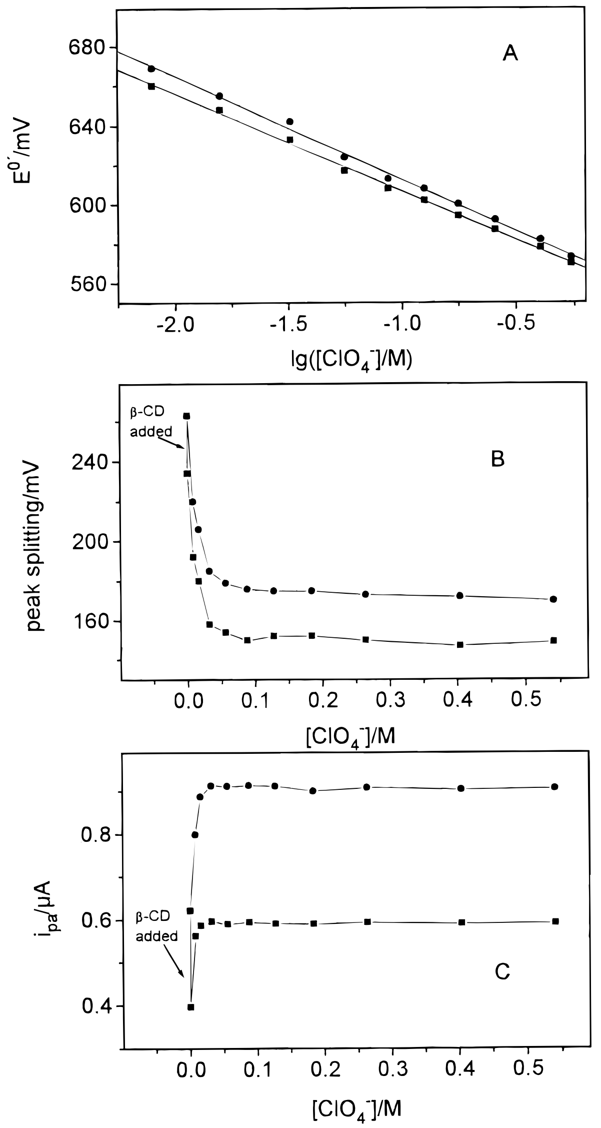

Figure 5. Effect of changing [ClO$_4^-$] on the formal potential, $E^{o\prime}$ (A), the peak splitting, ΔE_p (B), and the anodic currents, $i_{p,a}$ (C) of cyclic voltammograms at a FcSH SAM with FcSH surface coverage of 4.7 × 10^{-11} mol cm^{-2} in the presence of 1.0 M Na$_2$SO$_4$ containing 0 (●) and 10 (■) mM β-CD.

is that the curves for the dependence of the anodic peak current and peak splitting on the perchlorate ion concentration parallel each other in the presence and absence of β-CD, a further indication that the included form of the ferrocene is electroinactive. If the inclusion complex of FcSH−β-CD was electroactive, the ion-pairing property of the FcSH SAMs would be greatly affected.

Determination of β-CD Inclusion Constants at FcSH SAMs. In order to further investigate the inclusion of the surface-attached ferrocenyl groups in the FcSH SAM by β-CD in solution, we performed fast scan rate (10 V s^{-1}) cyclic voltammetry at FcSH SAM electrodes in solutions containing increasing β-CD concentrations (Figure 6). Both anodic and cathodic peak currents and peak areas (surface coverage of electroactive FcSH) decreased with increasing β-CD concentration, eventually reaching a steady value at concentrations above 8.0 mM β-CD. The peak splitting also decreased with increasing β-CD concentration, reaching a steady value of 120 ± 5 mV above 4.0 mM β-CD. A plot of the decrease in FcSH surface coverage against β-CD concentrations exhibited a shape similar to that of a Langmuir adsorption isotherm. Therefore, the inclusion

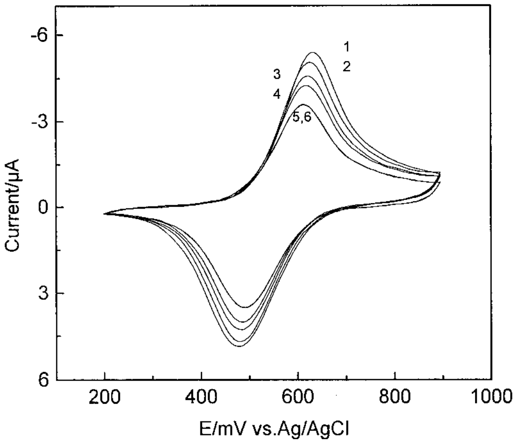

Figure 6. Cyclic voltammograms, recorded at a scan rate of 10 V/s, at a FcSH SAM (FcSH surface coverage of 5.2 × 10^{-11} mol cm^{-2}) in 1.0 M NaClO$_4$ containing 0 (1), 0.2 (2), 0.6 (3), 1.0 (4), 8.0 (5), and 10 (6) mM β-CD.

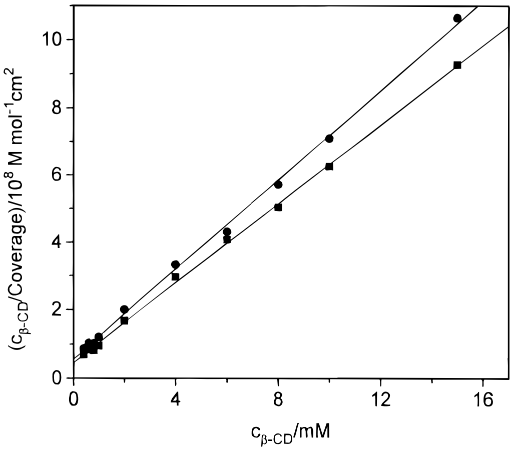

Figure 7. Linearized Langmuir plots for the ferrocenyl (■) and ferricenium (●) forms of FcSH, from the data obtained from the cyclic voltammograms in Figure 5. See text and Figure 6 for details.

process can be considered as a sorption equilibrium at the SAM/solution interface. The conditional equilibrium constants, *K*′, can be determined using the Langmuir adsorption equation[20]

$$\theta = \frac{KC_{\beta\text{-CD}}}{(1 + KC_{\beta\text{-CD}})} \qquad (1)$$

where θ is the ratio of the coverage (Γ) of β-CD at a concentration $C_{\beta\text{-CD}}$ to its maximum coverage ($\Gamma_{\max}$). Equation 1 can be linearized to yield[20]

$$\frac{C_{\beta\text{-CD}}}{\Gamma} = \frac{1}{K\Gamma_{\max}} + \frac{C_{\beta\text{-CD}}}{\Gamma_{\max}} \qquad (2)$$

In fact, the coverage of β-CD is equal to the coverage of electroinactive ferrocene included in the β-CD cavity which can be evaluated from the difference in FcSH surface coverage measured in the presence and absence of β-CD. Linear plots of $C_{\beta\text{-CD}}/\Gamma$ versus $C_{\beta\text{-CD}}$ for both oxidation and reduction at an initial ferrocene surface coverage of 5.2 × 10^{-11} mol cm^{-2} are shown in Figure 7. The values obtained for β-CD conditional equilibrium constants for inclusion of ferrocene ($K'_{\text{Fc−CD}}$) and ferricenium ($K'_{\text{Fc}^+\text{−CD}}$) forms of FcSH along with the maximum surface coverages of included complexes at electrodes of various FcSH surface

Table 3. Conditional Stability Constants (K'), Stability Constants (K), Maximum Surface Coverages (Γ_{max}), and Standard Free Energies of Adsorption (ΔG°) for Inclusion Complexes between Ferrocenyl (Fc) or Ferricenium (Fc^+) Forms of FcSH SAMs and β-CD at Different FcSH Surface Coverages[a]

	$\Gamma_{Fc} = 5.2 \times 10^{-11}$ mol cm^{-2}	$\Gamma_{Fc} = 4.9 \times 10^{-11}$ mol cm^{-2}	$\Gamma_{Fc} = 1.3 \times 10^{-11}$ mol cm^{-2}
K'_{Fc}, M^{-1}	$1.3\ (0.1) \times 10^3$	$1.1\ (0.1) \times 10^3$	$5.0\ (0.4) \times 10^2$
K'_{Fc+}, M^{-1}	$1.2\ (0.1) \times 10^3$	$9.8\ (1.0) \times 10^2$	$2.2\ (0.3) \times 10^2$
K_{Fc}, M^{-1}	$3.6\ (0.4) \times 10^4$	$3.1\ (0.4) \times 10^4$	$1.4\ (0.2) \times 10^4$
K_{Fc^+}, M^{-1}	$3.2\ (0.4) \times 10^4$	$2.8\ (0.4) \times 10^4$	$9.0\ (0.1) \times 10^3$
$\Gamma_{max,Fc}$, mol cm^{-2}	$1.9\ (0.1) \times 10^{-11}$	$2.0\ (0.1) \times 10^{-11}$	$6\ (1) \times 10^{-12}$
Γ_{max,Fc^+}, mol cm^{-2}	$1.6\ (0.1) \times 10^{-11}$	$1.4\ (0.1) \times 10^{-11}$	$2\ (1) \times 10^{-12}$
ΔG°_{Fc}, kJ mol^{-1}	−26.0	−25.6	−23.6
$\Delta G^\circ_{Fc^+}$, kJ mol^{-1}	−25.7	−25.3	−22.6

[a] See text for details.

coverages are given in Table 3. The maximum surface coverages obtained indicate that only approximately 40−50% of the ferrocene in the monolayer forms an inclusion complex with β-CD.

It has been found that the type of electrolyte has a significant influence on the stability constants of inclusion complexes.[23] Several anions such as ClO_4^-, I^-, NO_3^-, SCN^-, and Br^- can be complexed by β-CD, with stability constants of 27.0, 18.1, 5.6, 10 and 6.7 M^{-1}, respectively.[24] The concentration of uncomplexed β-CD in solution, [β-CD], prior to complexation with the FcSH SAM is thus given by

$$[\beta\text{-CD}] = \alpha C_{\beta-\text{CD}} \tag{3}$$

where $\alpha = 1/(27[ClO_4^-] + 1)$. In our electrolyte solutions the effect of the addition of millimolar concentrations of β-CD to a 1.0 M solution of $NaClO_4$ on $[ClO_4^-]$ was assumed to be negligible; thus an α value of appproximately 0.036 can be estimated. The conditional stability constants, K', determined above are equal to the product of α and the true stability constants for the β-CD inclusion complexes at the FcSH SAM, K. The corrected values of K for both the ferrocene and ferricenium forms of the FcSH SAM are listed in Table 3, together with the free energy of adsorption, ΔG°_{ads} ($= -RT \ln K$).

The values obtained for the stability constants and free energies of adsorption for FcSH SAMs of 5.2×10^{-11} mol cm^{-2} FcSH coverage were close to that obtained for ferrocene inclusion into a self-assembled thiolated β-CD monolayer at gold electrodes.[17a] These values are larger than those observed for the equilibrium binding of the ferrocenecarboxylate anion to β-CD in solution ($K = 2200$ M^{-1}).[15a] The origin of the additional free energy observed for the host−guest equilibrium at the electrode interface for our system is unclear. Additional free energy may be released because of positive interactions between the adsorbed cyclodextrins at the monolayer surface. From Table 3 it can be found that with decreasing coverage of FcSH, the stability constant decreased, which could correspond with decreasing interactions between the more widely spaced cyclodextrins. At all electrodes both the stability constant values and the maximum coverages of inclusion complexes for ferrocene are larger than those for ferrocenium, which is consistent with the results reported previously.[15] The ratio between the stability constants for inclusion of the ferrocene and ferrocenium forms at low FcSH surface coverage is similar to that seen in solution.[16b] At the higher surface coverages, however, the ratio is larger than that obtained from solution studies. This may again be related to the rather rapid scan rates used in this study. At high scan rates relative to dissociation rates, a large proportion of the ferrocenium form remains included in the cyclodextrin and is therefore not available for rereduction. The instability of the SAMs at lower scan rates unfortunately hampers confirmatory investigations.

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