3343

In Situ Monitoring of Diffuse Double Layer Structure Changes of Electrochemically Addressable Self-Assembled Monolayers with an Atomic Force Microscope

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An alkyl disulfide containing two sulfonate-substituted ferrocenes, 7,8-dithiatetradecane-1,14-di-(aminocarbonyl)-bis(1′-ferrocene-1-sulfonic acid), was synthesized and used to form electroactive self-assembled monolayers on gold electrodes. Atomic force microscope (AFM) force curves were employed to measure in situ the change in surface charge as the ferrocene groups were oxidized to compensate for the negative charges on the sulfonate groups. The electrode surface charge density was calculated from the surface coverage measured by electrochemical oxidation of the ferrocene groups, while the diffuse double layer charges were obtained from theoretical fits of the force data to solutions of the complete nonlinear Poisson–Boltzmann (PB) equation with knowledge of the silica probe surface potential. A significant difference between the AFM measured (i.e., effective) surface charge and the surface charge calculated from electrochemical measurements was found. This difference is attributed to a layer of counterions near the surface that screens a large fraction of the surface charge (variously described as "ion condensation" or failure of the nonlinear PB theory). The experimental results also showed that the extent of this ion screening (~97%) was relatively constant and independent of the total electrode surface charge.

Introduction

In numerous interfacial processes (e.g., colloidal stability, electrochemical processes, polyelectrolyte adsorption, and ion partitioning in biological and polymer membranes), electrical double layer phenomena play a crucial role. While double layer theories[1] are well-established, direct measurement of the structure of these double layers and the charge residing at this interface, especially at an electrode surface, has been somewhat limited. However, recent advances in force measurements employing the atomic force microscope (AFM) have allowed direct force measurements between a sphere and a planar surface.[2–4] More recently, the AFM has proven successful in directly measuring the magnitude and potential dependence of diffuse double layer forces at electrode surfaces.[5] These direct measurements of double-layer forces have provided significant insight into this interface and advanced our ability to measure surface charge and address interfacial processes.[1,6]

In a previous study,[7] we applied AFM force measurement to study the surface acid–base properties of carboxylic acid-terminated self-assembled monolayers (SAMs)

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(1) Israelachvili, J. N. *Intermolecular and Surface Forces*, 2nd ed.; Academic Press: New York, 1991.

(2) (a) Ducker, W. A.; Senden, T. J.; Pashley, R. M. *Nature* **1991**, *353*, 239. (b) Ducker, W. A.; Senden, T. J.; Pashley, R. M. *Langmuir* **1992**, *8*, 1831.

(3) (a) Biggs, S.; Mulvaney, P.; Zukoski, C. F.; Grieser, F. *J. Am. Chem. Soc.* **1994**, *116*, 9150. (b) Larson, I.; Drummond, C. J.; Chan, D. Y. C.; Grieser, F. *J. Am. Chem. Soc.* **1993**, *115*, 11885. (c) Li, Y. Q.; Tao, N. J.; Pan, J.; Garcia, A. A.; Lindsay, S. M. *Langmuir* **1993**, *9*, 637.
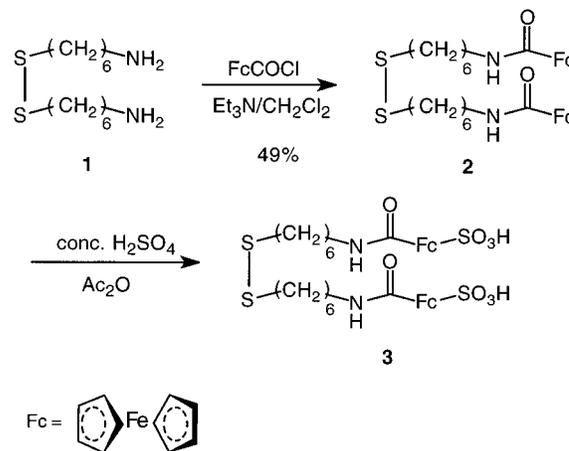
(4) (a) Atkins, D. T.; Pashley, R. M. *Langmuir* **1993**, *9*, 2232. (b) Larson, I.; Drummond, C. J.; Chan, D. Y. C.; Grieser, F. *J. Phys. Chem.* **1995**, *99*, 2114.

(5) Hillier, A. C.; Kim, S.; Bard, A. J. *J. Phys. Chem.* **1996**, *100*, 18808.

(6) Derjaguin, B. V.; Rabinovich, Y. I.; Churaev, N. V. *Nature* **1978**, *272*, 313.

(7) Hu, K.; Bard, A. J. *Langmuir* **1997**, *13*, 5114.

Scheme 1

and obtained pH-dependent surface force curves. The surface charge and electrostatic potential was then calculated from the force between the SAM-covered gold substrate and a silica sphere on the AFM cantilever. In that study, we found that there was a significant difference between the AFM measured surface charge and the expected surface charge estimated from typical SAM full surface coverage. In the work described here we sought to obtain a better measure of the surface charge electrochemically and compare that to the value found from fitting the force curves to the nonlinear Poisson–Boltzmann (PB) equation. To this end, we synthesized an alkylthiol molecule with a ferrocenesulfonate terminal group (**3**) as the SAM species (Scheme 1). Electrochemical oxidation of the ferrocene groups allowed us to quantitatively measure the SAM surface coverage. With this molecule, we were also able to use AFM to measure in situ a series of surface charges as the ferrocene groups were oxidized to compensate the negative charges on the sulfonate groups (Scheme 2). The experimental results confirmed a sig-

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Scheme 2
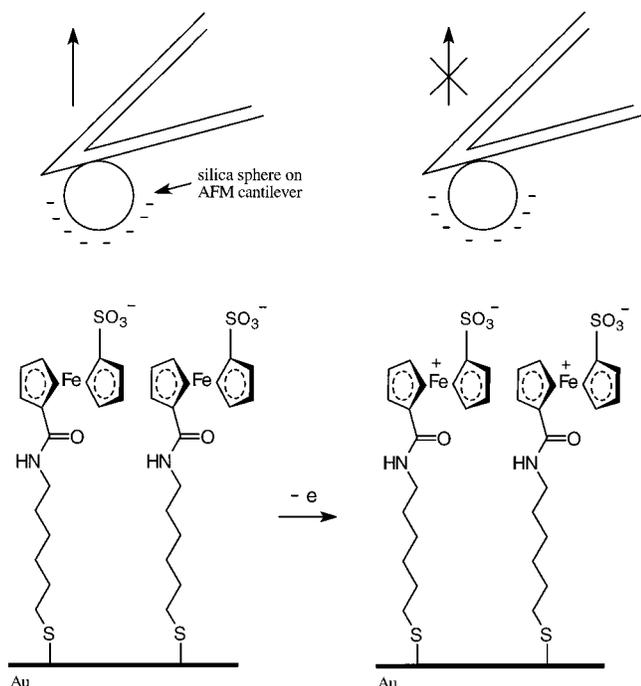
nificant difference between the AFM force curve and the electrochemical surface charge, and the difference was attributed to considerable screening by counterions at the charged SAM/liquid interface. To our knowledge, this is the first demonstration of AFM to monitor in situ diffuse double layer structure changes as a surface layer is changed electrochemically.

Experimental Section

General Procedures for Organic Synthesis. Acetic anhydride, concentrated H_2SO_4, and CH_2Cl_2 were used as supplied by EM Science. ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra were recorded with a Bruker AMX-500 spectrometer. Chemical shifts are reported in ppm using TMS as an internal standard, and coupling constants are reported in hertz. IR spectra were taken with a Nicolet 550 Magna spectrometer. Mass spectra were recorded with a VG ZAB2-E apparatus. The synthetic procedure is indicated in Scheme 1.

7,8-Dithiatetradecane-1,14-di(aminocarbonyl)bisferrocene (2). To a mixture of 7,8-dithiatetradecane-1,14-diamine (1)[8] (155 mg, 0.59 mmol) and ferrocenylcarbonyl chloride[9] (292 mg, 1.17 mmol), CH_2Cl_2 (2 mL) was added at room temperature under N_2, followed by Et_3N (340 μL, 4 equiv). The dark-red solution was stirred for 19 h, and more CH_2Cl_2 (10 mL) was added. The mixture was then washed with 2 M HCl, NaHCO$_3$, and brine successively, dried with Na$_2$SO$_4$, and concentrated. Precipitation of the residue from EtOAc yielded a yellow powder (200 mg, 49%). ^{1}H NMR (CDCl$_3$): δ 1.44 (m, 8 H), 1.61 (m, 4 H), 1.70 (m, 4 H), 2.68 (t, $J = 6.2$ Hz, 4 H), 3.37 (dd, $J = 13.2$ Hz, $J = 6.8$ Hz 4 H), 4.20 (s, 10 H), 4.33 (m, 4 H), 4.67 (m, 4 H), 5.88 (bs, 2 H). ^{13}C NMR (CDCl$_3$): δ 26.6, 28.2, 29.1, 29.9, 39.0, 39.5, 68.1, 69.7, 70.3, 76.5, 170.1. HRMS (CI positive ion mode): calcd for $C_{34}H_{44}N_2O_2S_2Fe_2$ [M$^+$] 688.1543, found 688.1549. IR (KBr): $\nu = 3500, 3318, 2927, 2853, 1629, 1543, 1453, 1301$.

7,8-Dithiatetradecane-1,14-di(aminocarbonyl)bis(1′-ferrocene-1-sulfonic acid) (3). To **2** (21 mg, 0.03 mmol) in a minimum amount of acetic anhydride (just enough to cover **2** in the reaction vial), concentrated H_2SO_4 (24 mg, 0.24 mmol) was added at room temperature and the mixture was allowed to stand for 5 min. The resulting deep-red solution was cooled with an ice

bath and water (2 mL) was added. The aqueous solution was then washed with CH_2Cl_2 (10 × 2 mL), followed by neutralization with concentrated NH$_4$OH to bring the pH to 9 while cooling in an icebath. The basic aqueous phase was again washed with CH_2Cl_2 (10 × 2 mL) and dried with a stream of N_2 for 3 h. MeOH (4 mL) was added to the residue and the mixture was filtered through a cotton plug to give a clear solution. Evaporation of solvent with a N_2 stream and drying with a high vacuum pump afforded a quantitative yield of a yellow oil (the ammonium salt form of the sulfonic acid). ^{1}H NMR (CD$_3$OD): δ 1.44 (m, 8 H), 1.63 (m, 4 H), 1.71 (m, 4 H), 2.69 (t, $J = 7.2$ Hz, 4 H), 3.30 (overlapped with solvent peak, 4 H), 4.28 (s, 4 H), 4.50 (m, 8 H), 4.77 (s, 4 H). ^{13}C NMR (CD$_3$OD): δ 27.8, 29.2, 30.2, 30.6, 39.7, 40.7, 70.7, 71.2, 71.9, 73.4, 79.1, 95.6, 173.0. HRMS (FAB positive ion mode): calcd for $C_{34}H_{45}N_2O_8S_4Fe_2$ [M$^+$ + H] 849.0758, found 849.0766. IR (thin film on a salt plate): $\nu = 3414, 3189, 3089, 3057, 2929, 2856, 1643, 1555, 1439, 1215, 1184$.

Electrochemistry. Large, flat, template-stripped gold surfaces prepared by the procedure of Hegner et al.[10] were immersed into a 0.5 mM solution of **3** in methanol for 24 h. Immediately before use, the SAM-covered gold substrate was rinsed with methanol for 30 s and dried with a stream of argon. The SAM-covered gold substrate, mounted on a Teflon cell, served as the working electrode (with an exposed area of 0.30 cm^2). The electrolyte was a 0.1 M NaClO$_4$ aqueous solution at pH 6.0 degassed with argon. Cyclic voltammograms were collected on a BAS 100 B/W electrochemical analyzer using a Pt wire as the counter electrode and an Accument double junction Ag/AgCl electrode as the reference electrode.

For in situ electrochemical measurements, experiments were carried out in an AFM fluid cell (Digital Instruments, Santa Barbara, CA) with Teflon tubing. A three-electrode design was used for electrochemical measurements: the SAM-covered gold substrate, which served as the working electrode, a Pt counter electrode, and an Ag/AgCl reference electrode. The counter and reference electrodes were placed in a saturated KCl solution, which was connected through a salt bridge to the outlet of the fluid cell. All electrode potentials are given with respect to this Ag/AgCl reference. Electrochemical control of the cell was effected with a PAR 173 potentiostat and 175 universal programmer (EG&G Instruments, Princeton, NJ).

AFM Force Measurement. Force measurements were performed with a Nanoscope III AFM (Digital Instruments) equipped with a piezo scanner having a maximum scan range of 15 μm × 15 μm × 2 μm. The standard AFM silicon nitride tip was modified by the attachment of a spherical silica bead. The AFM force measuring technique is well-documented,[2−4] and the experimental details have been described elsewhere.[5,7] Typically, in an AFM force measurement, the deflection of a microfabricated cantilever is measured as a function of its separation from a surface. The spring constant of the silica sphere modified cantilever, determined using the method of Cleveland et al.,[11] was 0.65 ± 0.12 N/m. The SAM-covered gold surfaces were used as the substrates for the force measurements.

During the force measurement, the measured experimental parameters were the cantilever deflection, obtained from the voltage of the sectored photodiode detector, and the substrate displacement, which was given by the piezo scanner voltages. These data were converted to a table of normalized force (force/radius) vs tip−substrate separation for further analysis. Derjaguin−Landau−Verwey−Overbeek (DLVO) theory[12] was employed to calculate the surface electrostatic potentials between the similarly charged surfaces, i.e., the interaction between two silica surfaces to calibrate the bead. The electrical double layer interaction energy between dissimilarly charged surfaces such as silica and gold was calculated for the constant-charge limit of the complete nonlinear Poisson−Boltzmann equation using

(8) (a) Owen, T. C. *J. Chem. Soc. C* **1967**, *15*, 1373. (b) Kono, M.; Saitoh, Y.; Kasai, M.; Shirahata, K.; Morimoto, M.; Ashizawa, T. *J. Antibiot.* **1993**, *46*, 1428.

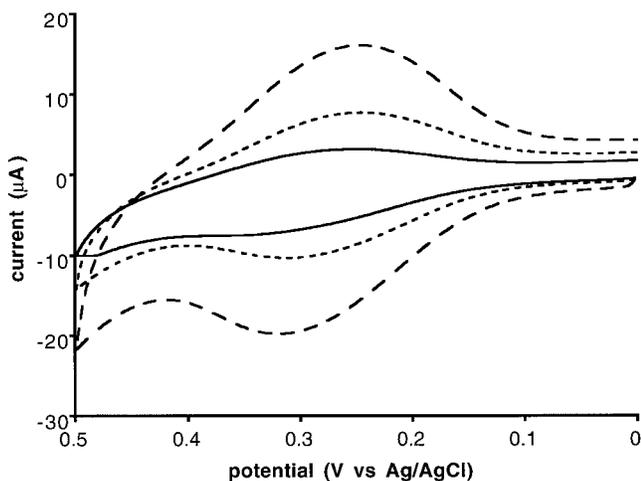(9) Lau, H. H.; Hart, H. *J. Org. Chem.* **1959**, *24*, 280.

(10) Hegner, M.; Wagner, P.; Semenza, G. *Surf. Sci.* **1993**, *291*, 39.

(11) (a) Cleveland, J. P.; Manne, S.; Bocek, D.; Hansma, P. K. *Rev. Sci. Instrum.* **1993**, *64*, 403. (b) Sader, J. E.; Larson, I.; Mulvaney, P.; White, L. R. *Rev. Sci. Instrum.* **1995**, *66*, 3789.

(12) (a) Derjaguin, B. V. *Trans. Faraday Soc.* **1940**, *36*, 203. (b) Derjaguin, B. V.; Landau, L. D. *Acta Phys. Chem.* **1941**, *14*, 633. (c) Derjaguin, B. V.; Landau, L. D. *J. Exp. Theor. Phys.* **1941**, *11*, 802. (d) Verwey, E. J. W.; Overbeek, J. T. G. *Theory of the Stability of Lyophobic Colloids*; Elsevier: New York, 1948.
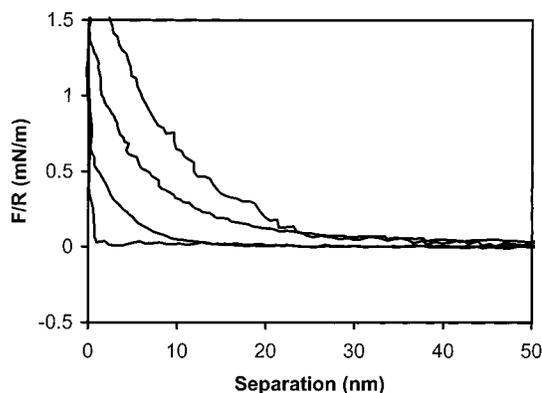
Figure 1. Cyclic voltammograms of a SAM of **3** on a gold substrate (surface area, 0.3 cm^2) in 0.1 M aqueous NaClO$_4$ solution at pH 6.0. Scan rates were (—) 0.1, (- - -) 0.25, and (— — —) 0.5 V s^{-1}.

the method of Hillier et al.[5] The Hamaker constants (A_H) used for the theoretical calculations were 0.88×10^{-20} J[13] and 1.1×10^{-19} J[5,7] for the silica—silica and silica—gold interactions, respectively. Previous AFM measurements of the template-stripped Au substrates indicated a mean roughness of 0.25 nm/μm^2, with a maximum peak-to-valley height of 2.7 nm of a 1 μm $\times$ 1 μm area, with the silica sphere probably having a similar roughness. We previously estimated that this uncertainty in distance results in an error of 5—10% in the charge measurement.[14]

Results and Discussion

Electrochemistry. Chidsey et al.[15] first studied the electrochemistry of ferrocene alkanethiol SAMs in 1 M HClO$_4$ using cyclic voltammetry. The electrochemical oxidation peak potential of the surface-confined ferrocene groups is around +0.6 V vs Ag/AgCl. Based on a close-packed layer of 0.66 nm diameter spheres, they estimated that the maximum theoretical coverage should be 4.5×10^{-10} mol/cm^2. The actual measured value of their system was 5.5×10^{-10} mol/cm^2. Related SAMs prepared by other workers show coverages ranging from 3 to 7×10^{-10} mol/cm^2.[2,16] This variation probably reflects uncertainty in the true surface area and the presence of some disorder in the SAM, which prevents all of the ferrocenes from lying in a common plane.

With ferrocenesulfonate-terminated SAMs, cyclic voltammograms at different scan rates were obtained in a 0.1 M NaClO$_4$, pH 6.0, solution (Figure 1). The peak current was proportional to the scan rate, indicating that the oxidation of ferrocenes is indeed a surface process. Note that the potential for oxidation of **3** was +0.3 V vs Ag/AgCl, compared to +0.6 V for the neutral ferrocene groups. This potential shift might be attributed to the presence of a sulfonate anion on each ferrocene group. A surface charge density of 26 μC/cm^2 was obtained by integration of the voltammograms. A ferrocene surface coverage of 2.7×10^{-10} mol/cm^2 was then extracted from
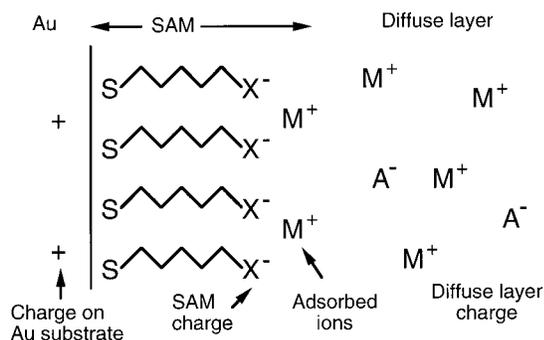
(13) (a) Grabbe, A.; Horn, R. G. *J. Colloid Interface Sci.* **1993**, *157*, 375. (b) Hunter, R. J. *Foundations of Colloid Science*; Oxford University Press: Oxford, 1987. (c) Hough, D. B.; White, L. R. *Adv. Colloid Interface Sci.* **1980**, *81*, 285.
(14) Hu, K.; Pyati, R.; Bard, A. J. *Anal. Chem.* **1998**, *70*, 2870.
(15) Chidsey, C. E. D.; Bertozzi, C. R.; Putvinski, T. M.; Mujsce, A. M. *J. Am. Chem. Soc.* **1990**, *112*, 4301.
(16) For a recent review, see: Finklea, H. O. In *Electroanalytical Chemistry*; Bard, A. J., Rubinstein, I., Eds.; Marcel Dekker: New York, 1996; Vol. 19, p 248.

Figure 2. Forces between a silica probe and a SAM-covered gold electrode in 1 mM aqueous NaClO$_4$ solution at pH 6.0 as a function of electrode potential. The force is scaled to the probe radius of 8.0 μm. The force curves correspond to controlled potentials of, from top to bottom, 0.0, 0.35, 0.40, and 0.50 V vs Ag/AgCl.

the charge density assuming one electron transferred per ferrocene. This surface coverage is somewhat lower than the values typical for ferrocene-bearing alkanethiols and is probably due to the larger terminal groups and the existence of repulsive forces between adjacent terminal groups, which prevent a more compact packing.

Since each sulfonate group is attached to a ferrocene, their surface densities are the same. This coverage corresponds to a surface charge value of -26 μC/cm^2 with each sulfonate group having a -1 charge, when all of the ferrocenes remain unoxidized. Therefore, the electrochemical measurement offers an independent measure of the actual surface charge density of the SAM.

AFM Force Measurement. We now compare the known charge density of the film to that obtained by the AFM force curve method. Typically, to measure quantitatively the surface charge of a substrate, the surface electrostatic potential of the probe must be known. As in earlier publications, force measurements between a silica sphere and a silica substrate were conducted to determine the silica surface potential (ψ_p) under solution conditions similar to those used while probing the diffuse double layers at the SAM-covered gold substrates. The silica surfaces have an isoelectric point at about pH 2.0 and are negatively charged in a 1.0 mM NaClO$_4$ solution of pH 6.0 with positively charged diffuse double layers forming at the silica/solution interfaces. AFM force measurements can probe the double layer structure and thickness as the tip moves toward the substrate. Generally, these force—distance curves exhibit an exponential dependence with distance that agrees with standard DLVO theory.[12] The measured silica surface potential was -41 mV under these conditions. The corresponding Debye length, κ^{-1}, of the diffuse double layer was 9.6 nm, in good agreement with that calculated from the salt concentration (C) of the solution, where for a dilute aqueous solution containing 1:1 electrolyte at 25 °C, κ^{-1} (nm) = $0.3045/C^{1/2}$ (C in M).[17]

The interaction between a silica probe and a gold substrate covered with **3** was a strong function of electrode potential. In Figure 2, we show typical force—separation curves at several controlled electrode potentials obtained in an aqueous solution of 1 mM NaClO$_4$ at pH 6.0 with the force scaled to the probe radius ($R = 8.0$ μm). At a controlled potential of 0.0 V vs Ag/AgCl where ferrocene oxidation did not occur, a strong electrostatic repulsive

(17) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*; John Wiley & Sons: New York, 1980.

Figure 3. Schematic representation of charge distribution at electrode surface.

force was observed, suggesting that the gold substrate was negatively charged. As reported in early studies,[5,7] the interaction between a silica probe and a clean gold surface in deionized water at neutral pH at open circuit exhibits an attractive interaction. Therefore, the negative charge on the gold substrate can be attributed primarily to the anchored terminal sulfonate anions. A similar strong electrostatic repulsive force was also observed under open circuit conditions. When the controlled potential was increased positively, i.e., to where the surface ferrocene groups can be oxidized, the electrostatic repulsive force decreased correspondingly. We recorded these force curves at different controlled potentials representing different extents of oxidation of the SAM. This decrease in repulsive force is due to a decrease in negative charge of the substrate, caused by the partial oxidation of ferrocenes in the SAM. Each oxidized ferrocene group (ferricinium cation) compensates a surface negative charge from a sulfonate group and thus produces an attenuation of the negative charge on the gold substrate. When the controlled potential reached at 0.45 V, there were no measurable long-range electrostatic interactions between silica and a SAM-covered gold substrate, showing that the gold substrate did not have an overall net charge; i.e., surface ferrocene groups were completely oxidized, and the positive ions and negative ions were equally distributed over the substrate. After complete oxidation of ferrocene groups, we could reduce the ferricinium ions back to ferrocenes and recover those repulsive force curves by scanning the potential back to 0.0 V. However, an appreciable decrease in repulsive force was observed after four or five cycles, indicating the loss of surface ferrocene sulfonate groups, probably caused by the decomposition of the ferricinium ions or desorption of some molecules from the surface.

The total charge on the electrode depends on the electronic charge of the gold substrate, the charge of the SAM, and any ions that are adsorbed or tightly ion-paired with the SAM (Figure 3). This net charge, which in general is a function of the potential of the Au electrode, is compensated by a diffuse double layer of counterions that is measured in the AFM experiment. To obtain some feeling of the effect of substrate charge, in a separate experiment, 2-mercaptoethanesulfonic acid, sodium salt was used as the SAM species which contains no ferrocene group. Force measurements of this SAM-covered gold substrate were conducted in the same aqueous solution (1 mM NaClO$_4$, pH 6.0). A strong repulsive force was again observed between the silica probe and the gold substrate at open circuit, indicating that the negative charge on the substrate was from the terminal negative sulfonate groups. However, there were no measurable changes in repulsive force when the potential was controlled between 0.0 and 0.6 V. This experiment suggests that the charge on the Au remains constant over this potential region, which

should span the potential of zero charge, and that the change in repulsive force in the experiment in Figure 2 was indeed caused by electrochemical oxidation of the ferrocenes. Therefore, AFM is capable of monitoring the diffuse double layer structure change caused by an electrochemical reaction that affects a modifying layer.

In Figure 2, the diffuse double layer force change with the controlled electrode potential between the negatively charged silica tip and SAM-covered gold substrate can be explained in terms of both the nature of the double layer and the charge state of the substrate. In the force measurement, the silica spherical tip, as it moves through the double layer, probes the diffuse double layer near the gold substrate. For example, at a controlled potential of 0.0 V where ferrocene oxidation does not occur, the net surface charge of the gold substrate is negative and a diffuse double layer with a net positive charge, consisting of a higher local concentration of Na$^+$ (and H$^+$) and a lower local concentration of ClO$_4^-$ (and OH$^-$), forms near the gold substrate. Therefore, as the negatively charged silica probe (with its own positively charged diffuse double layer) penetrates this double layer near the gold substrate, the overlap and interaction of the two positively charged double layers results in an electrostatic repulsive force.

The diffuse double layer reflects the magnitude of surface charge of a substrate immersed in a solution. Theories describing the forces between interacting double layers in electrolytic solutions are well-developed. In this work, the method of Hillier et al.[5] was used to calculate the electrical double layer interaction between silica and gold surfaces. This model of the interaction force between two dissimilarly charged surfaces has proven very useful in fitting AFM force curves for a variety of systems.[5,7,18−21] With the knowledge of silica probe surface potential, the surface electrostatic potentials (ψ_s) of the SAM-covered gold substrates were obtained by fits of the force data to solutions of the complete nonlinear Poisson−Boltzmann equation, assuming a constant surface charge boundary condition. All calculations include both electrostatic and van der Waals interactions, with $A_H = 1.1 \times 10^{-19}$ J (for the silica−gold interaction) and $\kappa^{-1} = 9.6$ nm. While the A_H value for the silica−SAM interaction, rather than the silica−gold interaction, would be more appropriate in the theoretical fitting of the experimental force data, this A_H value is not available and is difficult to determine experimentally independent of any electrostatic interaction. The best reasonable assumption we can make at present is that the interaction can be approximated by using the A_H value for the silica−gold interaction. Because the van der Waals interaction is only important at small distances (several nanometers), while the force data fitting is primarily based on larger separations, i.e., beyond 10 nm, this approximation does not significantly affect the accuracy of the charge calculation. The best-fit parameters for all force data are given in Table 1. Note that, as in the case for 2-mercaptoethane sulfonic acid, the gold substrate charge does not change between 450 and 600 mV. The surface charges (σ) in Table 1 were calculated from the corresponding surface potentials and the measured Debye lengths of the diffuse double layers.[22]

(18) Hu, K.; Bard, A. J. *Langmuir* **1997**, *13*, 5418.
(19) Hu, K.; Fan, F.-R. F.; Bard, A. J.; Hiller, A. C. *J. Phys. Chem.* **1997**, *101*, 8298.
(20) Hu, K.; Brust, M.; Bard, A. J. *Chem. Mater.* **1998**, *10*, 1160.
(21) Hu, K.; Bard, A. J. *Langmuir* **1998**, *14*, 4790.
(22) (a) The surface charge (σ) in Table 1 is calculated from the following relationship,[22b] $\sigma = \epsilon_0\epsilon_s\kappa(2kT/e)\sinh(e\psi/2kT)$, where κ is the reciprocal Debye length of the electrolyte solution with a dielectric constant, ϵ_s, taken to be 78.49 and assumed to be independent of surface charge change, and ϵ_0 is the permittivity of free space. (b) Bard, A. J.;

Table 1. Data Analysis Results of Electrochemical and AFM Force Measurements[a]

potential vs Ag/AgCl (mV)	electro-chemical charge passed (μC/cm²)	surface charge (μC/cm²)	AFM ψ (mV)	AFM σ (μC/cm²)	counter ion binding (%)
600	26.0	0	0	0	
500	26.0	0	0	0	
450	25.7	−0.3	0	0	
400	21.9	−4.1	−19	−0.14	96.6
350	14.2	−11.8	−40	−0.32	97.3
300	11.8	−14.2	−53	−0.45	96.8
250	6.5	−19.5	−61	−0.55	97.2
200	2.7	−23.3	−71	−0.69	97.0
100	0	−26.0	−75	−0.76	97.1
0	0	−26.0	−75	−0.76	97.1

[a] Full surface coverage, measured from the electrochemical experiments, is about 2.7×10^{-10} mol/cm².

Clearly the electrochemically measured surface charge for the SAM monolayer, 26 μC/cm², is much larger than the charge determined from the AFM force measurements, 0.76 μC/cm² for the reduced form of the SAM. Initially the film in the $Fc\sim SO_3^-$ form is negatively charged, with this charge compensated by the diffuse double layer charge and, as discussed below, a large extent of counterion binding. The electrochemical oxidation does not depend on ion pairing of the film by counterions so that on complete oxidation the film is in the $Fc^+\sim SO_3^-$ form, and the coulombs required represent the total number of Fc groups on the surface. Any difference in charge determined by the two methods must involve charge in the gold (e.g., image charge induced by the SAM) and counterion charge not taken into account by the nonlinear Poisson−Boltzmann (PB) model. The latter has been the subject of considerable discussion in the literature.[23] For example, in treatments of polyelectrolytes, one can deal with counterion binding to the highly charged species in terms of "adsorbed" or "condensed" ions.[23c,d] Alternatively, the system can be treated by a PB model with a reduced surface charge. For example,[23a] the repulsion between two uniformly charged walls with a surface charge of 22.4 μC/cm² will fit the PB model if the "effective" surface charge is taken to be 6.2 μC/cm². The difference between these

charges represents "nonspecific electrostatic adsorption of ions to the surface".[23a] If this is the case for the SAM in question here, then 97% of the surface charge would be compensated by tightly paired counterions. This amount is much larger than that usually found with equivalent amounts of surface charge in other systems. Moreover, the extent of this compensation appears independent of the extent of oxidation of the SAM, i.e., of the total charge of the monolayer, as shown in Table 1. It seems likely that at least a part of the counter charge resides in the gold substrate, and the insensitivity of the double layer charge to potential represents screening of this charge by the adsorbed monolayer. Additional experiments with different substrates need to be carried out before a clearer picture of the detailed nature of the surface charge for systems such as this can be obtained.

Conclusions

AFM force measurements were employed to monitor in situ diffuse double layer structure changes of electrochemically addressable SAMs in aqueous solutions. A series of double layer charges were measured as the ferrocene groups were partially oxidized to compensate the charges on the sulfonate groups. The SAM-covered electrode surface charge density was calculated from the surface coverage measured by electrochemical oxidation of the ferrocene groups, while the diffuse double layer charges were obtained by theoretical fits of the force data to solutions of the complete nonlinear Poisson−Boltzmann equation with the knowledge of silica probe surface potential. The significant difference between the AFM-measured surface charge and the expected surface charge calculated from SAM full surface coverage is attributed to considerable counterion binding at the charged SAM/liquid interface.

Faulkner, L. R. *Electrochemical Methods*; J. Wiley: New York, 1980.
(23) (a) Kjellander, R.; Marcelja, S. *J. Phys. Chem.* **1986**, *90*, 1230. (b) Zimm, B. H.; LeBret, M. *J. Biomol. Struct. Dyn.* **1983**, *1*, 461. (c) Manning, G. S. *Acc. Chem. Res.* **1979**, *12*, 443. (d) Spitzer, J. J. *Colloids Surf.* **1984**, *12*, 189 and references therein.