

## Voltammetric Measurement of Interfacial Acid/Base Reactions

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The voltammetric response of a Ag(111) electrode coated with a mixed molecular film of 11-mercaptoundecanoic acid and 1-decanethiol is presented. The voltammetric current arises from the reversible, electric field-driven deprotonation of carboxylic acid groups. Voltammetric peak heights for interfacial protonation and deprotonation are a function of solution pH, obtaining maximum values near the  $pK_{1/2}$  ( $\sim 8.5$ ) of the molecular film.

### Introduction

The acid/base properties of surface-confined molecular species are of fundamental and practical interest in variety of diverse chemical phenomena.<sup>1</sup> It is generally understood that the effective  $pK_a$  of a surface-immobilized molecule may be significantly different than that of the same molecule in solution. The dependence of acidity on spatial location is due to the influence of the local environment on the electrochemical potentials of the acid, its conjugate base, and proton. In particular, the acidity of a surface-confined molecule is influenced by the polarity of the surface, interfacial electrostatic fields, and the local structure of the solvent. Discussions of various factors that influence interfacial acidity have been presented by Bain and Whitesides<sup>2</sup> and by Creager and Clarke.<sup>3</sup>

Quantitative measurement of the acidity of a surface-immobilized species is a challenging analytical problem, requiring methods that are highly specific and sensitive to the composition or properties of the interface. Direct measurement of the surface concentrations of the acid and its conjugate base obviously provides the most straightforward determination of the surface  $pK_{1/2}$  (i.e., the pH at which half of the surface acid groups are deprotonated). For instance, Sukenik and co-workers used in-situ attenuated total reflectance Fourier transform infrared spectroscopy to monitor the titration of an alkyl carboxylic acid anchored to a germanium surface.<sup>4</sup> Other methods used to monitor the degree of acid ionization include contact angle measurements<sup>2,3,5</sup> and quartz crystal measurements of interfacial viscoelasticity.<sup>6</sup> Hu and Bard recently determined the effective  $pK_a$  of a carboxylate acid-terminated monolayer using the atomic force microscope to measure interfacial electrostatic forces as a function of pH.<sup>7</sup>

Previous reports suggest that voltammetric techniques may be useful for quantitative measurements of the acid/base properties of highly organized molecular films, e.g., self-assembled monolayers of alkanethiols containing acid groups.<sup>8,9</sup> Herein, we wish to describe cyclic voltammetric measurements of a Ag(111) electrode coated with a mixed monolayer of 11-mercaptoundecanoic acid and 1-decanethiol. The voltammetric current in this experiment arises from the change in interfacial differential capacitance that occurs upon ionization of the surface-bound species. Theoretical descriptions<sup>8,9</sup> of such an experiment suggest that a peak-shaped voltammetric response may result from the deprotonation and reprotonation of the surface-confined acid groups. Herein, we demonstrate that a

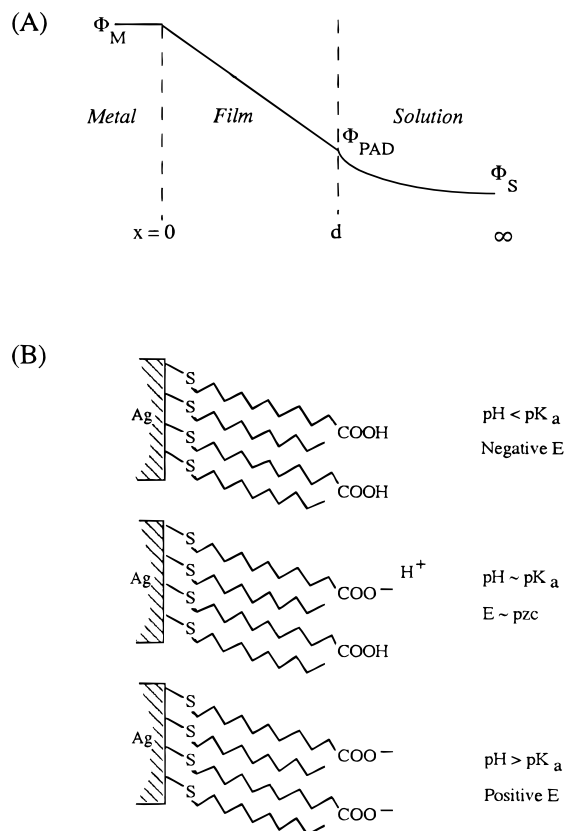
reversible voltammetric wave is indeed observed for the reversible deprotonation of 11-mercaptoundecanoic acid. The voltammetric data are used to measure the fractional degree of ionization of the acid monolayer as a function of pH and electrode potential, providing a direct measurement of the  $pK_{1/2}$  of the surface-confined acid.

### Basic Principles of Voltammetry of Acid Monolayers

The voltammetric response of an electrode coated with a monolayer containing acid groups results from the variation in the interfacial capacitance that occurs during deprotonation and reprotonation of the acid groups. To understand this type of voltammetric measurement, it is useful to briefly outline some basic principles concerning the interfacial potential and charge distributions and how these quantities are influenced by surface-confined acid/base reactions.

Consider the potential distribution across an idealized monolayer containing an acid functionality, as depicted in Figure 1. All of the acid groups lie in a common plane, referred to as the “plane of acid dissociation” or PAD.<sup>8</sup> The PAD is located at a distance  $d$  from the surface. A dielectric region exists between the metal and the PAD, i.e.,  $0 < x < d$ ; the potential in this region is assumed to be described by a linear profile. In previous work, we have assumed that the potential distribution in the solution phase is described by the Gouy–Chapman theory.<sup>8</sup> In a more realistic model, Fawcett and co-workers have considered discreteness-of-charge effects and the presence of a Stern layer adjacent to the molecular film;<sup>9</sup> this layer comprises solvent molecules whose structure is sufficiently different from the bulk liquid that the local dielectric permittivity is significantly lowered.

The key point to be recognized in examining Figure 1 is that the potential distribution across the interface is a function of the degree of dissociation of the acid groups at the PAD. That is, acid dissociation alters the electric field within the monolayer, as well as the potential distribution in the solution phase. Similarly, changing the potential across the interface ( $\phi_M - \phi_S$ ), such as occurs in a voltammetric experiment, will alter the degree of acid dissociation. For instance, one anticipates that sweeping the electrode potential to a value negative of the potential of zero charge (pzc) will tend to result in protonation of the acid groups (Figure 1B), reducing the electrostatic repulsion between the negative charges located on the metal surface and the charges associated with the deprotonated acid



**Figure 1.** (A) Electrostatic potential distribution across a metal/acid monolayer/solution interface. (B) Schematic representation of a mixed monolayer of 11-mercaptopundecanoic acid and 1-decanethiol in contact with an electrolyte solution as a function of electrode potential ( $E$ ) and pH.

groups ( $A^-$ ) at the PAD. Conversely, positive electrode potentials will tend to drive the deprotonation of the surface groups. In general, the surface acid/base equilibrium,  $HA \rightleftharpoons H^+ + A^-$ , is expected to shift in response to the electrode potential in a manner in that minimizes the free energy of the interface. The quantitative relationship between the electrostatic potential at the PAD,  $\phi_{PAD}$  (Figure 1), and the degree of acid dissociation,  $f$ , is given by<sup>8</sup>

$$\log\left[\frac{f}{1-f}\right] = \text{pH} - \text{p}K_a + \frac{F(\phi_{PAD} - \phi_S)}{2.3RT} \quad (1)$$

In eq 1,  $f$  is the fraction of ionized molecules (i.e.,  $f = \Gamma_{A^-}/(\Gamma_{HA} + \Gamma_{A^-})$ , where  $\Gamma_i$  is the surface coverage of the species  $i$ ), the quantity  $(\phi_{PAD} - \phi_S)$  is the potential drop in the solution phase,  $F$  is Faraday's constant,  $\text{p}K_a$  is the dissociation constant of the surface-bound acid in the absence of any interfacial electric fields (i.e., the  $\text{p}K_a$  when  $(\phi_{PAD} - \phi_S) = 0$ ), and pH denotes the proton activity in the bulk solution. Equation 1 is readily derived<sup>8</sup> assuming equilibrium between the interface and bulk solution and using the conventional definition of the electrochemical potential,  $\bar{\mu}_i = \mu_i^0 + RT \ln a_i + z_i F \phi$ .

At constant electrode potential, the electronic charge density on the metal surface is a function of the ionic charge density at the PAD. It immediately follows that the differential capacitance of the electrode will be a function of the degree of acid dissociation,  $f$ , albeit in a relatively complex fashion.<sup>8,9</sup> For the model depicted in Figure 1, we have shown that the capacitance of the interface may be written as<sup>8</sup>

$$C_T^{-1} = C_F^{-1} + (C_S + C(f))^{-1} \quad (2)$$

where  $C_T$  is the total interfacial capacitance,  $C_F$  is the capacitance of the dielectric region of the molecular film ( $=\epsilon_0\epsilon_F/d$ , where  $\epsilon_F$  is the dielectric constant of the film and  $\epsilon_0$  is the permittivity of vacuum), and  $C_S$  is the capacitance of the solution region. For a solution containing a symmetrical 1:1 electrolyte, the latter is given by Gouy–Chapman theory,  $C_S = \epsilon_0\epsilon_S\kappa \cosh[(\phi_{PAD} - \phi_S)/2kT]$ , where  $\kappa$  is the inverse Debye length and  $\epsilon_S$  is the dielectric of the solution. The quantity  $C(f) = f(1-f)(F^2\Gamma_T/RT)$  is the capacitance associated with the acid group at the PAD.  $C(f)$  is a function of any factor that influences the surface acid/base equilibrium. In particular,  $C(f)$  is a function of the pH of the bulk solution.

When  $f \rightarrow 1$  or 0 (i.e., when the film is either fully deprotonated or protonated; see Figure 1B), the differential capacity reduces to that expected for a chemically inert monolayer, eq 3.

$$C_T^{-1} = C_F^{-1} + C_S^{-1} \quad (3)$$

Physically, the limiting behavior at  $f \rightarrow 1$  or 0 corresponds to a solution pH much larger or smaller than the  $\text{p}K_a$ , respectively, or to an electrode potential far removed from the pzc (positively or negatively, respectively). For either of these conditions, the dependence of  $C_T$  on electrode potential arises solely from the variation in the capacitance associated with the solution phase,  $C_S$ . In many instances, the capacitance of the film will be much smaller than that of the solution, i.e.,  $C_F \ll C_S$ ; the total interfacial capacitance,  $C_T$ , in this limiting case will be independent of the electrode potential since  $C_F$  is assumed to be constant valued. For conditions corresponding to intermediate values of acid dissociation, e.g.,  $0.1 < f < 0.9$ , the capacitance associated with the acid group,  $C(f)$ , will vary in response to the electrode potential, obtaining a maximum value when half of the acid groups are ionized, i.e., when  $f = 0.5$ . The pH of the bulk solution that corresponds to  $f = 0.5$  is defined as the  $\text{p}K_{1/2}$ . From eq 1, it follows that  $\text{p}K_{1/2} = \text{p}K_a - (F(\phi_{PAD} - \phi_S)/2.3RT)$ . Intermediate values of  $f$  are obtained when the solution pH is adjusted to a value near the monolayer  $\text{p}K_a$  and the electrode potential is biased at a value near the pzc of the electrode.

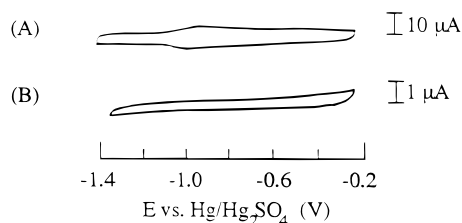
From eq 2 and the definition of  $C(f)$ , it is clear that the maximum in  $C(f)$  at  $f = 0.5$  corresponds to a maximum in  $C_T$ . The capacitive current for an electrode scanned at a constant rate,  $\nu$ , is given by

$$i = \nu AC_T \quad (4)$$

where  $A$  is the electrode area. Thus, the voltammetric response of an electrode coated with a monolayer containing an acid group should display a reversible peak-shaped voltammogram, the current peak corresponding to the maximum in  $C_T$ . The voltammetric wave corresponds to deprotonation (anodic currents on the positive-going scan) and reprotonation (cathodic currents on the negative-going scan).

## Experimental Section

Ag(111) surfaces were prepared by thermal evaporation of 250 nm of Ag (99.99% Alpha/Aesar) onto muscovite mica by a procedure previously described in detail.<sup>10</sup> The surfaces were thermally annealed under vacuum to increase the (111) orientation and to produce a smoother surface. Characterization of the Ag(111) films by scanning tunneling microscopy, glancing angle X-ray diffraction, and electrochemical measurements has been previously reported.<sup>10,11</sup> STM images display 100 nm wide atomically flat terraces. Glancing angle X-ray diffraction



**Figure 2.** Voltammetric responses of (A) a bare and (B) 1-decanethiol-coated Ag(111) electrodes in 0.1 M NaF solution. Scan rate: 100 mV/s. Electrode areas: (A) 0.40 cm<sup>2</sup> and (B) 0.56 cm<sup>2</sup>.

measurements indicate that these films are predominately (111)-oriented. X-ray photoelectron spectroscopy measurements performed on Ag(111) surfaces exposed to air for several days reveal only trace amounts of adsorbed oxygen, indicating that these films are oxidized very slowly in air.<sup>12</sup>

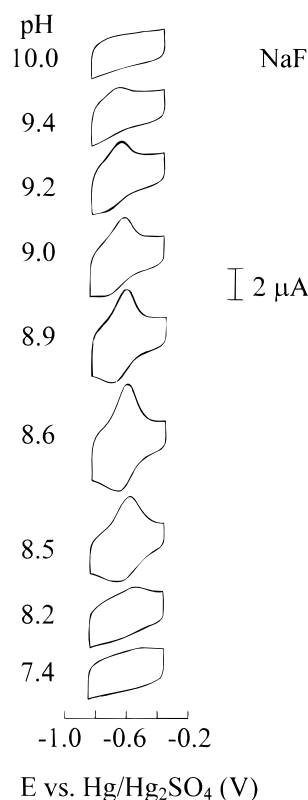
Sodium fluoride, 1-decanethiol, cesium fluoride, tetramethylammonium nitrate, sodium hydroxide, and nitric acid were reagent grade and used as received. 11-Mercaptoundecanoic acid was synthesized from the corresponding  $\omega$ -bromoundecanoic acid (Aldrich) following a previously published procedure.<sup>5a</sup> All aqueous solutions were prepared using water obtained from a Barnstead water purification system ("E-pure") with the feed-water inlet connected to an in-house deionized water line.

The voltammetric results reported herein are for mixed molecular films prepared by immersing a Ag(111) electrode for 15 h in an ethanol solution containing a 5:1 mole ratio of 11-mercaptoundecanoic (5 mM) and 1-decanethiol (1 mM). Immersion times (5–20 h) and solution composition (1:1 to 20:1 mole ratio) were varied in order to determine the approximate optimal conditions for preparing monolayers, as judged by the voltammetric response. The 15 h immersion time and 5:1 mole ratio correspond to films associated with the largest voltammetric currents; however, other solution conditions and reaction times yielded qualitatively similar results. Using the data of Bain and Whitesides for mixed monolayers prepared at Au surfaces under similar conditions,<sup>13</sup> we estimate that this deposition procedure yields a mixed monolayer consisting of ca. 0.75 mole fraction of 11-mercaptoundecanoic acid. The electrodes were removed from solution, rinsed with chilled ethanol and deionized water, and dried with nitrogen.

A conventional one-compartment, three-electrode glass cell was used for the electrochemical measurements. Pt wire and Hg/Hg<sub>2</sub>SO<sub>4</sub> (saturated K<sub>2</sub>SO<sub>4</sub>) electrodes were employed as the counter and reference electrodes, respectively. A small spring-loaded Cu clip was used to make electrical contact to one end of the Ag(111) electrode. The electrode was immersed to a depth of  $\sim 0.5$  cm in the electrolyte solution, taking precaution not to contact the Cu clip. The electrolyte solution was purged for  $\sim 30$  min with N<sub>2</sub>, and a positive N<sub>2</sub> pressure was maintained over the solution during electrochemical measurements. Voltammetric measurements were performed with an EG&G Princeton Applied Research model 173 potentiostat/galvanostat, a model 175 universal programmer, and a Kipp & Zonen model BD 90 XY recorder. The solution pH was maintained between 7 and 11, being adjusted in increments of  $\pm 0.3$  pH units by addition of either 5 mM NaOH or 5 mM HNO<sub>3</sub>. pH was measured using an Orion model 910600 combination pH electrode connected to a model 320 pH meter.

## Results and Discussion

Figure 2 shows the voltammetric responses of a bare Ag(111) electrode and a Ag(111) electrode coated with a monolayer of 1-decanethiol. The voltammograms were recorded with the

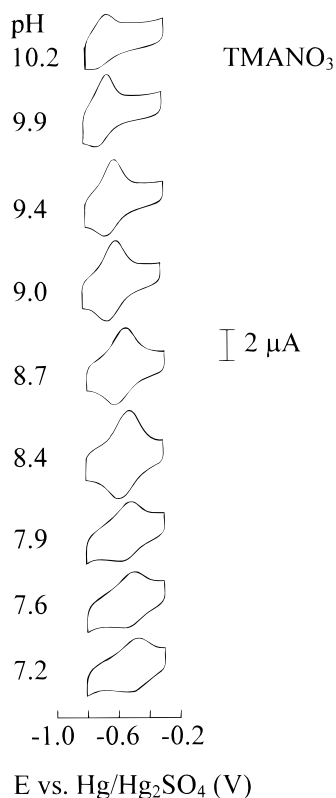


**Figure 3.** pH dependence of the voltammetric response of a Ag(111) electrode (0.65 cm<sup>2</sup>) coated with a mixed monolayer of 11-mercaptoundecanoic acid and 1-decanethiol. Measurements were made in a 0.1 NaF solution at a scan rate of 100 mV/s.

electrodes immersed in 0.1 M NaF solutions (pH = 8.1). The voltammetric currents for both electrodes are essentially purely capacitive. A small wave associated with weak adsorption of fluoride on the bare Ag(111) electrode is observed at ca.  $-1.0$  V vs Hg/Hg<sub>2</sub>SO<sub>4</sub>.

The capacitances of the bare Ag(111) and 1-decanethiol-coated Ag(111) electrodes can be estimated from the voltammetric current using the expression  $C_T = \frac{1}{2}(i_a - i_c)A\nu$ , where  $i_a$  and  $i_c$  are the anodic and cathodic charging currents, respectively. This analysis yields  $C_T \approx 86$  and  $3.2 \mu\text{F}/\text{cm}^2$  for the bare and 1-decanethiol-coated Ag(111) electrodes, respectively. The smaller capacitance of the 1-decanethiol-coated Ag(111) electrode reflects the low dielectric constant ( $\epsilon_F \sim 3$ ) associated with the molecular film.<sup>14</sup> Since the 1-decanethiol film does not contain ionizable acid groups, the total capacitance of the interface is simply that expected for an electrode coated by a chemically inert film, i.e.,  $C_T^{-1} = C_F^{-1} + C_S^{-1}$ .

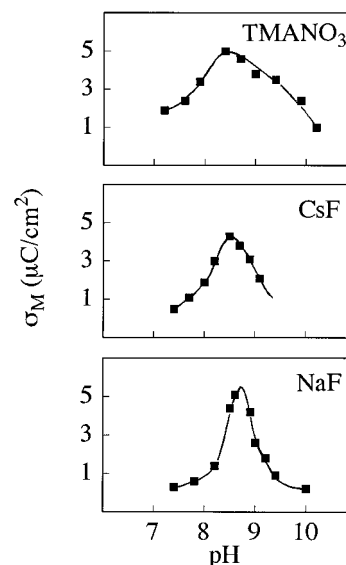
Figure 3 shows the voltammetric response of a Ag(111) electrode coated with a mixed monolayer of 11-mercaptoundecanoic acid and 1-decanethiol in an aqueous solution containing 0.1 M NaF. Figure 4 shows the results of the same measurement in a 0.1 M tetramethylammonium nitrate (TMANO<sub>3</sub>) solution. A reversible voltammetric wave is observed at ca.  $-0.6$  V vs Hg/Hg<sub>2</sub>SO<sub>4</sub>, independent of the supporting electrolyte. We assign this wave to the reversible deprotonation of the terminal carboxylic acid group. The magnitude of the voltammetric peak currents and half-wave potential,  $E_{1/2}$ , are both strong functions of the solution pH.  $E_{1/2}$  is observed to shift to more negative potentials with increasing pH, while the voltammetric currents are largest at a solution pH between 8 and 9. At more extreme pH values, the peak currents decrease to background levels. Qualitatively similar behavior is observed in 0.1 M CsF solutions (not shown).



**Figure 4.** pH dependence of the voltammetric response of a Ag(111) electrode ( $0.60 \text{ cm}^2$ ) coated with a mixed monolayer of 11-mercaptopundecanoic acid and 1-decanethiol. Measurements were made in a 0.1 tetramethylammonium nitrate (TMAO<sub>3</sub>) solution at a scan rate of 100 mV/s.

The voltammetric behavior observed for the mixed monolayers containing carboxylic acid groups is qualitatively consistent with theoretical expectations outlined above and in previous studies.<sup>8,9</sup> The finding that the voltammetric wave is only observed for the carboxylic acid-terminated monolayer strongly supports our conclusion that the voltammetric response is due to the reversible, electric-field-driven deprotonation of the monolayer. At electrode potentials far removed from  $E_{1/2}$ , the acid groups remain fully deprotonated ( $f \rightarrow 1$ ) or fully protonated ( $f \rightarrow 0$ ), regardless of the electrode potential or pH. The molecular film is chemically inert under these conditions (see eq 3). The capacitance of the film in this limit is  $\sim 6 \mu\text{F}/\text{cm}^2$ , slightly larger than that of the Ag(111) electrode coated with 1-decanethiol. This difference in capacitance is due to substitution of the terminal methyl group of the adsorbed molecule by the more polar carboxylic acid group.

A feature of the voltammetric response that is *not predicted* by our simplified model is the dependence of the voltammetric peak height on pH. According to eqs 1 and 2, the total interfacial capacitance,  $C_T$ , is anticipated to be independent of pH at constant ionic strength; thus, the voltammetric peak heights are not expected to depend on pH. The discrepancy between the theoretical predictions and the experimental data clearly indicates a deficiency in our model of the interface. Specifically, the observed dependence of peak height on pH suggests that the term  $(C_S + C(f))$  in eq 2 increases at high or low pH. This is consistent with an increase in the diffuse layer capacitance,  $C_S$ , as  $E_{1/2}$  is shifted away from the pzc of the monolayer-covered Ag(111) surface; i.e., at potentials removed from the pzc, the film capacitance dominates the overall interfacial capacitance. The effect is entirely analogous to that predicted by the Gouy–Chapman–Stern model of a bare



**Figure 5.** pH dependence of the surface charge density,  $\sigma_M$ , of a Ag(111) electrode coated with a mixed monolayer of 11-mercaptopundecanoic acid and 1-decanethiol.  $\sigma_M$  is determined by integration of the voltammetric waves. Measurements were made in 0.1 M solutions of TMAO<sub>3</sub> (top), CsF (middle), and NaF (bottom) solutions.

electrode, in which the inner layer Helmholtz capacitance dominates the overall electrode capacitance at potentials removed from the pzc.

The surface charge density,  $\sigma_M$ , associated with the acid/base reaction was obtained by integration of the anodic portion of the voltammetric waves. Plots of the dependence of  $\sigma_M$  on pH are shown in Figure 5. Independent measurements using different electrodes were performed in solutions containing 0.1 M NaF, TMAO<sub>3</sub>, or CsF. The maximum value of  $\sigma_M$  occurs at  $\text{pH} \sim 8.5$  in each of these solutions, a value that we believe corresponds approximately to the  $\text{p}K_{1/2}$  of the surface-bound acid groups. As noted above, our simplified model does not predict any dependence of  $\sigma_M$  on pH; thus, there is no theoretical basis for interpreting the pH at which  $\sigma_M$  is a maximum as being equal to the monolayer  $\text{p}K_{1/2}$ . This assignment is based on comparison of our data to  $\text{p}K_{1/2}$  values for similar systems reported in the literature (*vide infra*).

It is interesting to note that the  $\text{p}K_{1/2}$  and maximum value of  $\sigma_M$  ( $4\text{--}5 \mu\text{C}/\text{cm}^2$ ) are essentially independent of the nature of the supporting electrolyte cation, suggesting that ion pairing between carboxylate groups and supporting electrolyte cations has a small effect of the voltammetric behavior.<sup>15</sup> However, we observe that the plot of  $\sigma_M$  vs pH is significantly wider ( $\sim 3.5$  pH units) for the TMAO<sub>3</sub> solution than for the NaF solution ( $\sim 2$  pH units) (Figure 5). This finding suggests a significant difference in the strengths of interaction of the inorganic and organic cations with the monolayer carboxylate groups.

The measured  $\text{p}K_{1/2}$  of  $\sim 8.5$  is ca. 4 pH units higher than  $\text{p}K_a$  values typically associated with carboxylic acids in aqueous solutions.<sup>16</sup> This larger value reflects the fact that the organic monolayer provides a less polar environment for dissociation, in addition to the influence of the interfacial potential distribution. Both factors are contained in eq 1: the inherent  $\text{p}K_a$  of the surface-bound acid is an implicit function of the interface polarity, while a nonzero value of  $(\phi_{\text{PAD}} - \phi_s)$  has an explicit influence on the pH at which the film is half-oxidized. The measured value of  $\text{p}K_{1/2} \approx 8.5$  for the mixed 11-mercaptopundecanoic acid/1-decanethiol monolayer on Ag(111) is slightly larger than the corresponding value of  $\sim 7$  measured by Creager and Clarke, using contact angle titration, for the same mixed

monolayer deposited on Au.<sup>3</sup> Ward and co-workers estimated a  $pK_{1/2}$  of ca. 8 for a monolayer of HS(CH<sub>2</sub>)<sub>15</sub>COOH on Au;<sup>6</sup> Hu and Bard recently estimated an effective  $pK_a$  of 7.7 for HS(CH<sub>2</sub>)<sub>3</sub>COOH adsorbed on Au. Although our value is in reasonable agreement with these published values, we anticipate that the  $pK_{1/2}$  may be a function of the chemical identity of the metal, since the pzc of different metals may be significantly different. For instance, the reported pzc of Au(111) and Ag(111) in NaF solutions are -0.068 and -1.1 V vs Hg/Hg<sub>2</sub>SO<sub>4</sub>, respectively.<sup>17</sup> Such a large difference in pzc will clearly influence the potential distribution across the acid/base monolayer and, thus, the degree of acid dissociation on Au(111) and Ag(111) at any specified potential. Furthermore, subtle differences in the chain length and packing density may influence the acidity of the monolayer, as recently reported by Creager and Clarke.<sup>3</sup> A more complete understanding of the dependence of surface  $pK_{1/2}$  on these factors requires further experimental studies.

## Conclusion

We have shown that the reversible deprotonation of a surface-bound carboxylic gives rise to a voltammetric response when the pH of the solution is adjusted to be approximately equal to the  $pK_{1/2}$  of the monolayer. The voltammetric currents have a non-Faradaic origin, arising solely from the dependence of the interfacial capacitance on the degree of acid dissociation. The voltammetric method has been used to estimate a surface  $pK_{1/2}$  of ca. 8.5 for a mixed monolayer of 11-mercaptoundecanoic acid and 1-decanethiol on Ag(111) in aqueous solutions.

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