

Electrocapillarity Behavior of Au(111) in SO_4^{2-} and F^-

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We present the first set of results measuring the change in interfacial free energy and surface stress for Au(111) electrodes in an electrolyte containing a nonspecifically adsorbing anion and compare this behavior to that in an electrolyte containing an anion known to undergo specific adsorption. Generally, we find that the surface stress is more sensitive to changes in electrode potential and adsorption than the interfacial free energy. The results obtained in fluoride electrolytes are compared to the predictions of a thermodynamic analysis.

Introduction

The classical work of Grahame on electrocapillarity was performed on and formulated for liquid metal electrodes.¹ Solid electrodes are differentiated from liquid electrodes owing to the ability of a solid to support a shear stress. Consequently, the surface free energy of a solid may be altered in two ways. One can add or remove surface at fixed (atom) density or one can stretch or compress a surface, altering its density while maintaining a fixed number of atoms on the surface. In the first case, the reversible work per unit area for such a process is called the specific surface free energy (γ). In the second case, the reversible work per unit area is called the surface stress (f). In the case of liquids, $f = \gamma$, while for solids, this is generally not true. The two quantities are related through the Shuttleworth equation,²

$$f_{ij} = \gamma \delta_{ij} + \partial \gamma / \partial \epsilon_{ij} \quad (1)$$

where ϵ_{ij} is the surface strain tensor and δ_{ij} is the Kronecker delta. For a general surface, the surface stress tensor can be referred to a set of principal axes such that the off-diagonal components are equal to 0. For a surface possessing a 3-fold or higher rotation axis of symmetry, the surface stress is isotropic and can be taken as a scalar, that is, $f = \gamma + \partial \gamma / \partial \epsilon$. For most solids, f is generally of the same order of magnitude as γ (1–4 J m⁻²) and can be positive or negative.³

The Gibbs adsorption equation appropriate for solid/liquid interfaces includes additional specific work terms associated with elastic stretching,

$$d\gamma = -s dT + (f_{ij} - \gamma \delta_{ij}) d\epsilon_{ij} - q dV - \Gamma_k d\mu_k \quad (2)$$

where T is the temperature; ϵ is the linear elastic strain; μ_k is the chemical potential of species k ; and s , Γ_k , and q are respectively the specific surface excesses of entropy, species k , and charge.⁴ A repeated index indicates summation. For an isotropic surface stress, $f_{12} = 0$, $f_{11} = f_{22}$,

and the Gibbs equation takes the simpler form

$$d\gamma = -s dT + (f_{11} - \gamma) d\epsilon_{11} + (f_{22} - \gamma) d\epsilon_{22} - q dV - \Gamma_k d\mu_k$$

or because $f_{11} = f_{22} = f$ and $d\epsilon_{11} = d\epsilon_{22} = d\epsilon$

$$d\gamma = -s dT + 2(f - \gamma) d\epsilon - q dV - \Gamma_k d\mu_k \quad (3)$$

This is the version of the Gibbs adsorption equation first obtained by Couchman and Davidson.⁴ We note that some authors have incorrectly used a version of this equation without a factor of 2 in front of the surface stress term, which assumes that the sample is constrained from deforming along one of two in-plane orthogonal directions. At fixed T and μ_i ,

$$\left(\frac{\partial \gamma}{\partial V} \right)_{T, \mu_i} = -q + 2(f - \gamma) \left(\frac{\partial \epsilon}{\partial V} \right)_{T, \mu_i} \quad (4)$$

This is the electrocapillarity equation for isotropic solid electrodes in analogy with the standard Lippmann equation for fluid/fluid electrochemical interfaces. This relation describes how the solid/electrolyte interfacial free energy changes with electrode potential under the indicated constraints assuming an ideal polarizable interface. Note that the standard equation appropriate for a liquid metal electrode is recovered by setting $f = \gamma$.

Under the additional constraint that $d\epsilon = 0$ (e.g., clamping of the electrode), the change in γ as a function of electrode potential can be measured using several techniques such as chronocoulometry. One measures the current density as a function of the change in potential (e.g., imposing a potential step and measuring the current transient resulting from recharging of the double layer) and integrates to obtain the charge density. The change in the specific surface free energy, $\Delta\gamma$, is obtained from the Gibbs adsorption equation.

Changes in the surface stress as a function of electrode potential can be measured by using wafer curvature techniques. Typically these experiments are performed by arranging the electrode as a cantilever in an electrochemical cell. Electrodes for these experiments are usually thin films (~200 nm) that have been vacuum deposited onto a thick (~200 μm) substrate. The Stoney equation⁵

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relates curvature change to the change in surface stress,

$$\Delta f = \Delta \sigma t_f = (1/6) M_s t_s^2 \Delta \kappa \quad (5)$$

Here, σ is the mean in-plane stress in the electrode film, t_f is the film thickness, t_s is the substrate thickness, κ is the curvature, and M_s is the appropriate elastic modulus of the substrate determined by the nature of the bending. We will return to this point later. The change in strain is related to the change in curvature by $\Delta \epsilon = \Delta \kappa t_s/2$. In such experiments, $\Delta \epsilon$ is typically of order 10^{-6} so that the $2(f - \gamma) d\epsilon$ term in the Gibbs equation makes a negligible contribution ($\sim 0.1\%$ or less) to $d\gamma$ in comparison to the $q dV$ term.

If we consider the simplest model of the electrical double layer that assumes a constant capacity, c , then $\Delta \gamma = -cV^2/2$, where V is the voltage measured with respect to the potential of zero charge (pzc). Taking the double-layer capacity for Au(111) to be in the range of 0.2 – 0.4 F m^{-2} ,⁶ over a voltage change of 0.5 V , there is a corresponding $\Delta \gamma$ of -0.025 to -0.05 J m^{-2} . If specific anion adsorption occurs as is usually the case, this change in specific surface free energy will be larger as dictated by the Gibbs adsorption equation.

Unfortunately there is no corresponding simple manner to estimate changes in surface stress with electrode potential. Consider the Gibbs adsorption equation for the interface (isotropic electrode surface at fixed T and μ_d) and the Maxwell relation that we can derive from it:

$$d\gamma = -q dV + 2(f - \gamma) d\epsilon \quad (6)$$

$$\left(\frac{\partial f}{\partial V}\right)_\epsilon = \left(\frac{\partial \gamma}{\partial V}\right)_\epsilon - \frac{1}{2} \left(\frac{\partial q}{\partial \epsilon}\right)_V$$

Generally, the second term on the right-hand side of the Maxwell relation is unknown. Making use of the reciprocity relation, $(\partial q/\partial \epsilon)_V = -(\partial V/\partial \epsilon)_q (\partial q/\partial V)_\epsilon$,

$$\left(\frac{\partial f}{\partial V}\right)_\epsilon = \left(\frac{\partial \gamma}{\partial V}\right)_\epsilon + \frac{1}{2} \left(\frac{\partial V}{\partial \epsilon}\right)_q \left(\frac{\partial q}{\partial V}\right)_\epsilon \quad (7)$$

Additionally, because $(\partial \gamma/\partial V)_\epsilon = -q = -c(V) V$ and $(\partial q/\partial V)_\epsilon = c(V) + V(\partial c/\partial V)_\epsilon$, we can rewrite the Maxwell relation as

$$\left(\frac{\partial f}{\partial V}\right)_\epsilon = -c(V) V + \frac{1}{2} \left(\frac{\partial V}{\partial \epsilon}\right)_q \left[c(V) + V \left(\frac{\partial c}{\partial V}\right)_\epsilon \right] \quad (8)$$

If we evaluate the Maxwell relation at the pzc ($V = 0$), the equation reduces to $(\partial f/\partial V)_\epsilon = (c_{\text{pzc}}/2)(\partial V/\partial \epsilon)_q$. Physically, the $(\partial V/\partial \epsilon)_q$ term corresponds to the change in the pzc as the surface is elastically strained. This number is difficult to measure because the amount of applied elastic strain that a metal crystal can withstand prior to plastic deformation is less than 10^{-3} . However, we can estimate this parameter owing to the work of Kolb and Schneider.⁶ They measured the pzc for reconstructed and bulk-terminated Au(111) in 0.01 M HClO_4 and reported a difference of 90 mV . The reconstruction corresponds to a biaxial elastic compression of 4.5% . Therefore, $(\partial V/\partial \epsilon)_q \sim -2 \text{ V}$. Taking $c_{\text{pzc}} = 0.2$ – 0.4 F m^{-2} , we estimate $(\partial f/\partial V)_\epsilon = -0.2$ to -0.4 C m^{-2} at the pzc. If owing to clamping or

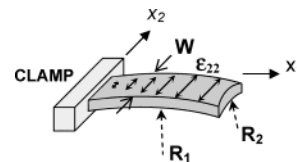


Figure 1. Schematic drawing of the cantilever electrode for measurement of the surface stress change. The clamp constrains deformation along the x_2 direction over distances of order W , the width of the beam. Arrows qualitatively indicate the magnitude of ϵ_{22} along the x_1 direction. R denotes the radius of curvature of the bent beam. R_1 is uniform along the length of the beam. At the clamp, R_2 is infinite, while far enough away from the clamp, $R_2 = R_1$, which defines equal bi-axial bending.

geometry of the electrode beam, the deformation along one of two orthogonal directions is constrained; the factor of $1/2$ does not appear in eq 7 (see Discussion). In that case, we estimate $(\partial f/\partial V)_\epsilon = -0.4$ to -0.8 C m^{-2} .

There are several measurements that have been reported in the literature for $\Delta \gamma$ and Δf for single crystal electrodes. Most of these measurements have been made on gold surfaces, and here we briefly focus on the behavior of bulk-terminated $1 \times 1 \text{ Au}(111)$ in perchloric acid. The literature indicates that the ClO_4^- anion undergoes weak specific adsorption on this surface.^{7,8} Measurements over a voltage of 300 mV positive of the pzc indicate a variation in $\Delta \gamma$ of 0.05 J m^{-2} . This is about a factor of 5 larger than what would be predicted on the basis of the simple model ($\Delta \gamma = -cV^2/2$) discussed above. There is data in the literature from three separate groups that allow us to estimate the magnitude of $(\partial f/\partial V)_\epsilon$ at the pzc. Results of Haiss⁹ indicate a value of -0.3 C m^{-2} , while results of both Friesen et al.¹⁰ and Ibach et al.^{11,12} yield values closer to -0.7 C m^{-2} . Presently we cannot explain these different values for nominally the same measurement; however, it seems possible that an inappropriate selection of M_s may be at least partly responsible. Nevertheless, it seems likely that measurements for both $\Delta \gamma$ and Δf were affected by adsorption.

We return now to the question of the appropriate form for the elastic modulus, M_s , to be used in the Stoney equation. Figure 1 shows the typical situation for a working electrode in the form of a cantilever. Conventionally, the cantilever length is about 3–5 times larger than its width. At the point of clamping, deformation along the x_2 direction is constrained, R_2 is infinite ($\kappa_2 = 1/R_2 = 0$), and only R_1 takes on a finite value. As one moves away from the clamp along the x_1 direction, κ_2 approaches κ_1 , and at distances of order $3W$, $\kappa_2 \cong \kappa_1$. Recall that the strain is related to the curvature by $\epsilon = \kappa t^2/2$, where t is the thickness of the beam. Near enough to the clamp, bending is one-dimensional and the appropriate form for M_s (assuming an elastically isotropic cantilever) is $E/(1 - \nu^2)$, where E is Young's Modulus and ν is Poisson's ratio. This combination of elastic constants is often termed the flexural modulus. Accordingly, for the case of one-dimensional bending the appropriate form of the Gibbs adsorption equation is missing the factor of 2 on the right-hand side of eq 3 because $\epsilon_{22} = 0$. Far enough away from the clamp,

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(6) Kolb, D. M.; Schneider, J. *Electrochim. Acta* **1986**, *31*, 929. The double-layer capacitance is known to be a function of the electrolyte concentration. Kolb and Schneider reported a value of $\cong 0.25 \text{ F m}^{-2}$ in a 0.01 M perchloric acid electrolyte. In our 0.1 M electrolyte, the capacitance could be as much as a factor of 3 larger, but our own measurements of $\Delta \gamma$ suggest the appropriate value is closer to 0.30 F m^{-2} .

$\kappa_2 \cong \kappa_1$, the bending is two-dimensional, and the appropriate form for M_s is $E/(1 - \nu)$. This combination of elastic constants is termed the biaxial modulus. Now the appropriate form of the Gibbs equation is given by eq 3. These are important considerations in data analysis. From an experimental point of view, one should know where along the beam a measurement of curvature or displacement is being made because this determines the appropriate form of M_s (for the Stoney equation) and the Gibbs adsorption equation. Dahmen et al.¹³ have performed a finite-element analysis that parametrizes the appropriate M_s value in terms of the measurement location and the experimental method used to determine the degree of bending (curvature, slope, displacement).

Herein we will describe a set of experiments aimed at measuring these surface quantities on well-prepared 1×1 bulk-terminated Au(111) surfaces in two electrolytes: one containing sulfate anions, which are known to adsorb, and the other containing fluoride anions, the prototypical nonadsorbing or (very) weakly adsorbing anion. We will compare the results of measurements in these electrolytes and to the analysis just described.

Experimental Methods

All electrochemical measurements except for those relating to surface stress were performed using a Au(111) single crystal (Monocrystals Co.) disk of diameter 10 mm and 2 mm in thickness. The gold crystal was electrochemically polished by anodic direct current treatment in a two-electrode cell using an 8-cm² platinum sheet as a cathode. This procedure was performed at a constant temperature of 60 °C. The polishing solution was a mixture of ethylene glycol and concentrated hydrochloric acid in a volume ratio 2.5:1. The crystal was polarized at a potential of 10 V with pulses (20–30 s in duration) until a shiny bright surface was observed. After electropolishing, the crystal was thoroughly rinsed with Barnstead Nanopure water (> 18 M Ω) and hydrogen flame annealed for 5–7 min. The crystal was cooled in an ultrahigh purity H₂/N₂ gas mixture, covered with a drop of Nanopure water, and then mounted on a Teflon holder, exposing an area of 0.3 cm².

The technique used for making surface stress measurements has been described previously.¹⁰ Briefly, gold-coated cantilevers were made by electron-beam evaporation (200-nm thickness) onto freshly cleaved mica substrates at 340 °C, at a deposition rate of 0.02 nm/s. This produced films with exclusively {111} texture. A specially designed wafer curvature apparatus and an electrochemical cell were used to determine the change in beam curvature as a function of the applied potential under deaerated conditions. The dimensions of the cantilever used were 1.0 cm \times 4.0 cm \times 150 μ m thick, and measurements were taken at \sim 1 cm from the free end so that the geometry conformed to two-dimensional bending.

The working electrolytes were 0.1 M solutions of NaF and Na₂SO₄ (Aldrich ultrapure reagents). The pH was adjusted to a value of 2 by acidifying each solution with the appropriate acid. The HF and H₂SO₄ were double-distilled and obtained from GFS Chemicals. All solutions were made with > 18 M Ω Barnstead Nanopure water. Prior to each experiment, the electrolyte was deaerated for 2 h using high purity nitrogen gas. A mercury sulfate electrode (MSE) was used as a reference electrode. All potentials referred to in the text are presented versus MSE unless stated otherwise.

Results

Cyclic voltammograms (CVs) in the two electrolytes for Au(111) are presented in Figure 2. The CV in sulfate is consistent with results previously published in the literature.^{14–16} The waves correspond respectively to the

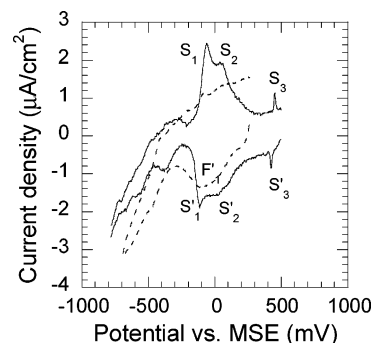


Figure 2. Cyclic voltammetry for the Au(111) single crystal in 0.1 M, pH 2 solutions of NaF (dashed line) and Na₂SO₄ (solid line). Scan rate 10 mV s⁻¹.

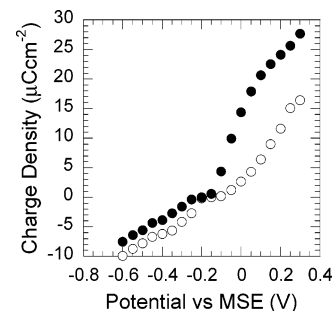


Figure 3. Charge density versus electrode potential determined from chronoamperometric measurements for the Au(111) single crystal in 0.1 M, pH 2 solutions of NaF (open circles) and Na₂SO₄ (solid circles).

lifting of the Au(111) reconstruction (S1), the specific adsorption of sulfate anions (S2), and the formation of an ordered sulfate adlayer (S3). The lifting of the reconstruction coincides with the pzc for Au(111) in the sulfate electrolyte. The CV in the fluoride electrolyte is comparatively featureless except for the broad peak (F'1) that occurs near the pzc. It is likely related to the Au(111) reconstruction.

Various electrochemical techniques have been employed for the investigation of the electrocapillarity behavior of solid electrodes. Cyclic voltammetry, double-layer capacitance measurements, chronocoulometric measurements, radiochemistry, and electrochemical quartz crystal microbalance are among the methods most frequently used.¹⁷ In our work, the surface free energy of the Au(111) surface as a function of potential was determined from chronoamperometric measurements where the charge density was obtained by integration of current–time data. An initial potential, E_0 of -450 mV, was chosen for each pulse where anions are desorbed from the Au(111) surface. The current response of the system to a potential pulse of a prescribed magnitude (50-mV increments) was measured in both anodic (to 300 mV) and cathodic (to -600 mV) potential directions. The charge density values were obtained by integration of each current transient. The charge density as a function of potential measured with respect to the pzc is shown in Figure 3. The values of the pzc for the cases considered were chosen using results of chronocoulometric measurements published by Lipkowski et al.^{15,18} In that work, the pzc in each electrolyte was determined independently from differen-

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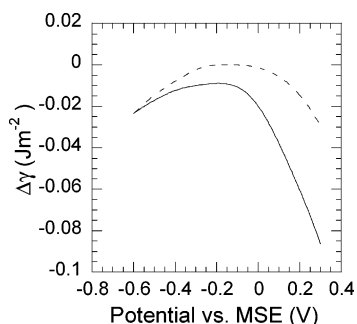


Figure 4. Change in interfacial free energy, $\Delta\gamma$, versus electrode potential for the Au(111) single crystal in 0.1 M, pH 2 solutions of NaF (dashed line) and Na_2SO_4 (solid line).

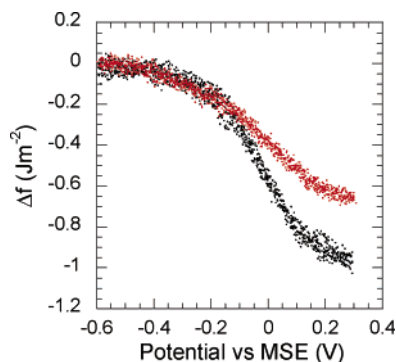


Figure 5. Change in the surface stress, Δf , as a function of electrode potential for the Au(111) cantilever electrode in 0.1 M, pH 2 solutions of NaF (red) and Na_2SO_4 (black).

tial capacitance measurements. In addition, comparison between charge densities obtained from integration of differential capacitance data (considered as the most accurate), integration of cyclic voltammetry curves, and chronocoulometry suggested no significant differences in the final shape of the charge–potential plots. The shape and the number of inflection points of charge–potential curves were invariant to the anion concentration.¹⁶ On the basis of those findings, the values of the pzc for our results have been chosen to coincide with the corresponding inflection point of the charge density plots.

The data in Figure 3 were fit to a high-order polynomial and integrated to obtain values for $\Delta\gamma$ versus electrode potential as shown in Figure 4. The $\Delta\gamma$ values in the electrolytes were matched at the most negative potential (−600 mV) and aligned such that the maximum in the fluoride electrolyte was set at a $\Delta\gamma$ of 0. This somewhat arbitrary procedure simply allows for a convenient presentation of results. Because we are only concerned with the magnitude of the change in $\Delta\gamma$ with the potential, this procedure will be of no consequence in our interpretation and discussion of results.

Figure 5 shows our results for the change in surface stress, Δf , versus electrode potential in the sulfate and fluoride electrolytes. The curves were matched at Δf of 0 at the most negative potential investigated. Again, because we are only concerned with the relative changes in Δf versus potential this procedure will not affect our data interpretation or discussion of results.

Discussion

The results for $\Delta\gamma$ versus electrode potential correlate remarkably well with the simple model discussed in the introduction. In the fluoride electrolyte between the pzc (−150 mV) and +300 mV, we observe a change in $\Delta\gamma$ of about 0.03 J m^{-2} , which is about what we would expect

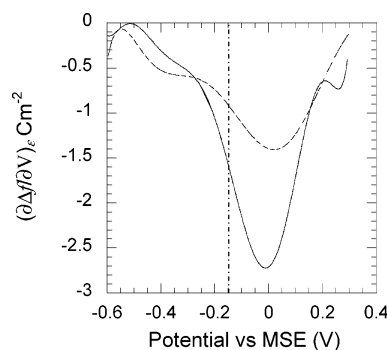


Figure 6. Parameter $[(\Delta f/\Delta V)_\epsilon]$ as a function of electrode potential for the Au(111) cantilever electrode in 0.1 M, pH 2 solutions of NaF (dashed line) and Na_2SO_4 (solid line). The vertical line corresponds to the location of the pzc.

in an electrolyte containing a nonadsorbing anion. This behavior contrasts with that observed in the sulfate electrolyte, for which over the same voltage range $\Delta\gamma$ varies by 0.08 J m^{-2} . This difference is a result of the relatively strong adsorption behavior of sulfate compared to fluoride. Nevertheless, if we consider the changes observed in $\Delta\gamma$ compared to the absolute magnitude of γ for Au(111), which is 1.25 J m^{-2} ,³ the changes correspond to about 6% of the absolute value. Thus, we conclude that, for the case of Au(111) in the electrolytes examined, γ is weakly affected by changes in electrode potential or adsorption.

The results for Δf versus electrode potential (Figure 5) are in sharp contrast to the behavior observed for $\Delta\gamma$. The absolute value of the surface stress for Au(111) is about 2.7 J m^{-2} .³ The magnitude of the potential/adsorption-induced changes in Δf is in the range of 0.7 (for fluoride)–1.0 J m^{-2} (for sulfate) or about 25–37% of the absolute magnitude of f . Thus, for the cases reported herein, f is much more strongly affected by changes in electrode potential and adsorption.

We consider now the magnitude of $(\partial\Delta f/\partial V)_\epsilon$ at the pzc in the electrolytes examined. Figure 6 is derived from the data presented in Figure 5 for the fluoride and sulfate electrolyte. The figure shows that at the pzc $(\partial\Delta f/\partial V)_\epsilon$ is -0.91 C m^{-2} while that in the sulfate electrolyte is -1.60 C m^{-2} . In the case of a nonadsorbing anion, the analysis discussed in the introduction predicts values that range from -0.2 to -0.4 C m^{-2} for the case of two-dimensional equi-biaxial bending.

Let us consider the possible sources of disagreement between the prediction of the analysis and the measurement for the quantity $(\partial\Delta f/\partial V)_\epsilon$ at the pzc in the case of the fluoride electrolyte. One possibility is that the double-layer capacitance at the pzc is larger than our estimate of 0.2 – 0.4 F m^{-2} . Recall that we measured a value of $\Delta\gamma$ over a 450 mV change in electrode potential of -0.030 J m^{-2} , which is in good agreement with the simple model where the double-layer capacitance is about 0.3 F m^{-2} . Because the measurements for $\Delta\gamma$ were made on a carefully prepared single-crystal surface and those for Δf were made on a thin film, which is a (111) textured Au polycrystal, it seems possible that the double-layer capacitance of the polycrystal could be larger. In the case of two-dimensional bending of the cantilever electrode, the capacitance would have to be $\sim 0.9 \text{ F m}^{-2}$ to bring the analysis in line with the measurement. Another possibility for the disagreement is our estimate of the $(\partial V/\partial \epsilon)_q$ term in eq 7. Because this is based on the transition from a reconstructed to a bulk-terminated 1×1 Au(111) surface, there is a structural change of the surface associated with this estimate. Ideally, we would like a measurement of this term not involving a structural change of the surface,

but such a measurement would be difficult to make. Mechanical straining of the surface would never suffice because plastic deformation would set in at very low values of applied strain. In principle, one could make the measurement by placing coherently strained gold layers (at least three or four monolayers) on suitable substrates and measuring the pzc as a function of strain in the coherent overlayer. The strain in the overlayer could be tuned by using an alloy for the substrate and adjusting the composition, thereby varying the lattice parameter and, accordingly, the strain in the coherent Au overlayer. Nevertheless, it seems reasonable to argue that, because our estimate of $(\partial V/\partial \epsilon)_q \cong -2 V$ involves a structural transformation, this number is likely an upper bound and is, therefore, probably not the cause of the disagreement. Finally, the third possibility is specific adsorption of the F^- anion. While the experimental values for $\Delta\gamma$ as a function of electrode potential in fluoride is indicative of the behavior of a nonadsorbing or very weakly adsorbing anion, we have already noted that these measurements appear to be less sensitive to the nature of the anion than the surface stress measurements. Presently, we cannot entirely rule out this possibility.

Summary and Conclusions

We present measurements for changes in the surface free energy and surface stress of a Au(111) electrode as a function of electrode potential in an electrolyte containing

fluoride, which is the prototypical nonadsorbing anion, and a sulfate electrolyte. These measurements are compared to predictions of a thermodynamic analysis. In the case of a nonadsorbing anion, the analysis predicts a value for the quantity $(\partial \Delta f / \partial V)_\epsilon$ in the range of -0.2 to -0.4 C m^{-2} while the experiment yields a value of -0.91 C m^{-2} .

There are two likely sources that could be responsible for this disagreement. First, because the surface stress measurements were performed on a textured Au(111) surface (as opposed to a single crystal) it is possible that our estimate of the double-layer capacitance of $0.2\text{--}0.4 \text{ F m}^{-2}$ is too low. A value of $\sim 0.9 \text{ F m}^{-2}$ would bring the measured value of $(\partial \Delta f / \partial V)_\epsilon$ in line with the thermodynamic prediction. Alternatively, it seems possible that adsorption of the fluoride anion could also be responsible for the disagreement, although there was no hint of fluoride adsorption in our data for interfacial free energy change as a function of electrode potential. Nevertheless, this possibility is consistent with our data in that our results demonstrate that the surface stress is more sensitive to electrode potential/adsorption than the interfacial free energy.

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