

The Electrochemistry of Thiol Self-Assembled Monolayers (SAMs) on a Hanging Mercury Drop Electrode (HMDE)

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The electrochemistry of functionalized self-assembled monolayers on Hg is studied by cyclic voltammetry and AC voltammetry. The results suggest that thiols can be adsorbed either chemically or physically depending on the Hg potential. The transformation between these two states occurs via an oxidation-reduction process. While a multi-layer of short chemisorbed thiols is formed under positive potentials than the oxidation-reduction process, a dense monolayer is self-assembled under more negative potentials.

The result of adsorption of species onto surfaces followed by their spontaneous organization, the so-called self-assembled monolayers (SAMs), has been one of the major research fields which expands from biosensors to corrosion prevention and lubrication. SAMs are usually formed as a result of the spontaneous adsorption (from solution) of amphi-functional molecules possessing high affinity toward the surface. Probably the most investigated system comprises SAMs of alkanethiols, RSH and dialkyl-disulfides, RSSR, on gold (1). SAMs on solid surfaces have been extensively characterized due to the large variety of available surface techniques including spectroscopy (in ambient and UHV), microscopy and electrochemistry (2). However, as solid surfaces cannot be atomically flat over large areas, the resulting monolayers accommodate defects such as pinholes and grain boundaries.

Surprisingly, SAMs on **mercury** is a relatively new field of research (3-15) which encounters the unique-

ness and advantages of a mercury surface together with the self-assembly technique to obtain highly-organized, two-dimensional (2-D) arrays of adsorbed molecules. Moreover, while the lattice structure of the solid substrate, e.g. Au(111), governs the organization of the adsorbed molecules, the intermolecular interactions of the adsorbed molecule are likely to determine the 2-D organization on Hg. Finally, liquid mercury offers flat surface with good electric conductivity and high affinity toward many organic functional groups.

Alkanethiols are well known for their high affinity toward mercury surfaces (16-26). In fact, the term *mercaptan* originates from this affinity. Nonetheless, they exhibit rather complex electrochemical behavior on this metallic surface. It is the aim of this contribution to describe their potential-dependent adsorption using cyclic voltammetry (CV) and AC voltammetry (ACV). Our results indicate that thiols on mercury are adsorbed in two states. The transition

between the two states occurs via an oxidation-reduction process.

Experimental

Electrochemical measurements were performed with a hanging mercury drop electrode (HMDE, controlled growth mercury electrode, BAS, West Lafayette, Indiana) controlled by a 100B potentiostat (BAS). A HMDE with a surface area of 0.0229 and 0.0126 cm² was used for *in-situ* and *ex-situ* measurements respectively (see below). Experiments were conducted in a conventional three-electrode cell. A Pt counter electrode and a Hg/Hg₂SO₄ reference electrode were used and therefore, all potentials are quoted versus this reference electrode. All experiments were conducted (unless otherwise written) at 25°C.

6-Mercaptohexanoic acid, HS(CH₂)₅CO₂H, was synthesized according to a described procedure (27) and dissolved in the electrolyte solution, i.e. a sulfate buffer (0.1 M, pH=2.8) that was prepared from po-

tassium sulfate (BDH) and sulfuric acid (J. T. Baker). High purity water (EasyPure U.V., Barnstead, Dubuque, Iowa) was used for all solutions.

Solutions were de-aerated with nitrogen for ten minutes prior to each experiment. Thiols were adsorbed onto a fresh mercury drop from a stirred solution (10^{-6} - 10^{-3} M of thiol in 0.1 M sulfate buffer, pH=2.8) under different potentials for a measured period of time. *In-situ* is termed for those measurements, which were carried out in the thiol solution. On the other hand, *ex-situ* experiments describe measurements in which the modified electrode was transferred from the adsorption solution **under potential**, washed carefully with water and inserted into a thiol-free solution **under the initial potential** of the following electrochemical

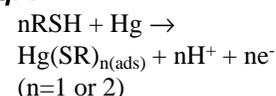
measurement. CV was acquired at $1 \text{ V}\cdot\text{s}^{-1}$. Phase selective AC voltammetry (PSACV) was recorded at a scan rate of $4 \text{ mV}\cdot\text{s}^{-1}$, frequency of 50 Hz and potential amplitude of 25 mV.

Results and Discussion

F1 shows the *in-situ* CV of a HMDE in the background electrolyte and in a solution of 0.1 mM 6-mercaptohexanoic acid, $\text{HS}(\text{CH}_2)_5\text{CO}_2\text{H}$. The shape of the CV is characteristic of the electrochemistry of thiols on mercury and is well documented (16-26). Thiols adsorbed on mercury via a fast, irreversible oxidation reaction to form mercurous- or mercuric-thiolate adducts. This reaction occurs spontaneously under open circuit potential or upon applying a sufficiently positive potential to the

mercury interface. It is generally accepted that the adsorption of thiols on metallic mercury can be described by an oxidation process (**Eq. 1**) that is similar to the self-assembly process of thiol monolayers on gold surfaces. Nevertheless, there is still a controversy concerning the final oxidation state of the mercury in the adduct, the organization and orientation of the adsorbed molecules and, in particular, the different adsorption phases and phase transitions these layers undergo under a wide potential window.

Eq. 1



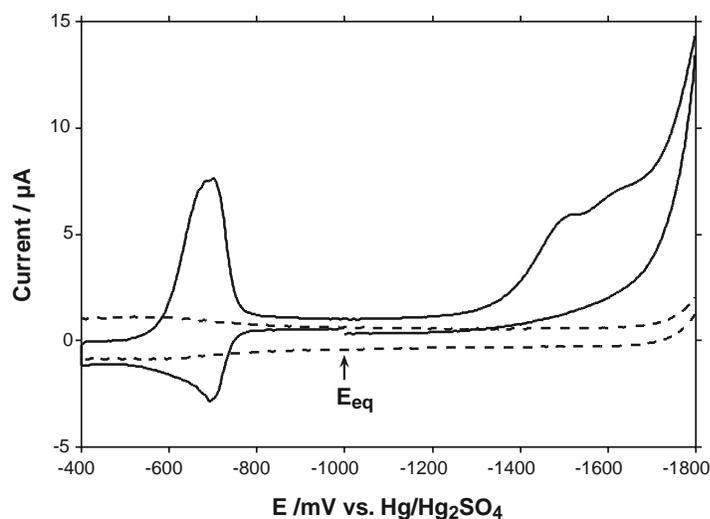
Hence, the diffusion-controlled oxidation wave in **F1** corresponds to the oxidation of mercury followed by the formation of a mercury-thiol adduct (**Eq. 1**). The anodic current does not diminish to the charging current, as would have been expected if the mercury surface had been covered with a blocking layer. This suggests that the thiol continuously reacts with the mercury surface as long as the potential is kept more positive than -0.7 V.

The symmetrical cathodic wave (**F1**) is attributed to the reduction of the adsorbed mercury-thiol adduct (reverse of **Eq. 1**). Measuring the charge under the cathodic wave allows determining the excess of surface coverage of the adsorbed thiol and therefore is expected to depend on the thiol and its intermolecular interactions.

We studied the effect of the initial potential and the scan rate on the cathodic wave, and concluded that a multi-layer is adsorbed under potentials that are more positive than the oxidation-reduction waves. The amount of adsorbed thiol, i.e. the thickness of the multi-layer, depends on the time the electrode is subjected to positive potentials ($E > -0.7 \text{ V}$). Evidently, the continuous reaction under positive potentials which results in the formation of a thick film

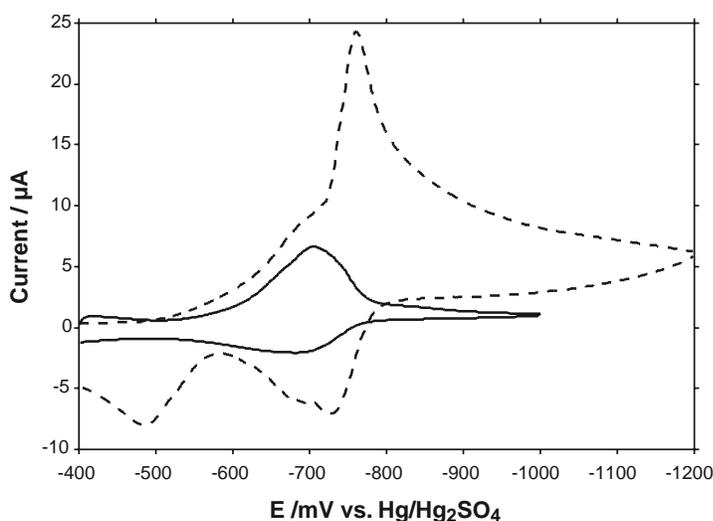
F1

Cyclic voltammetry of a HMDE recorded in 0.1 M sulfate buffer pH 2.8 (dashed line); in 0.1 mM 6-Mercaptohexanoic acid in sulfate buffer (solid line). Scan rate $1 \text{ V}\cdot\text{sec}^{-1}$, initial potential -1.0 V and equilibrium time 60 sec.



F2

Cyclic voltammetry of a HMDE in a thiol-free solution. Scan rate $1 \text{ V}\cdot\text{sec}^{-1}$, initial potential -0.4 V and equilibrium time 2 sec. Adsorption was performed in a 0.1 mM solution of 6-Mercaptohexanoic acid at -1.0 V (solid line) and -0.4 V (dashed line) for 5 minutes.



prevents determining the excess surface coverage (of a monolayer) for short thiols, from *in-situ* CV.

Therefore, we conducted a series of *ex-situ* experiments in which adsorption was performed in a 0.1 mM solution of HS(CH₂)₅CO₂H under different potentials for 5 minutes. The electrode was then transferred **under the adsorption potential** from the thiol solution, washed with water under open circuit potential and immersed into a thiol-free solution (0.1 M sulfate buffer, pH=2.8) **under the initial potential of the electrochemical measurement (-0.4 V)**. Such measurements make it possible to step the potential more positive than the oxidation wave without continuously depositing thiols on the Hg drop interface.

F2 shows the CV in a thiol-free solution after adsorbing HS(CH₂)₅CO₂H under two different potentials, i.e. -1.0 and -0.4 V. The cathodic wave that is observed in both cases suggests that thiols are adsorbed at potentials that are either more negative or positive than the oxidation-reduction wave. Difference in the shape and the size of this wave hints at the existence of more than a single adsorbing state. When adsorbing thiols under potentials that are more negative than the cathodic wave, i.e. $E_{\text{ads}} < -0.8$ V, the charge of the *ex-situ* cathodic wave is constant and its current varies linearly with scan rate. The excess surface coverage ($E_{\text{ads}} = -1.0$ V) reaches a constant value that corresponds to a full monolayer coverage ($83 \mu\text{C}\cdot\text{cm}^{-2}$) after approximately 60 seconds. On the contrary, when adsorbing under positive potentials, $E_{\text{ads}} > -0.7$ V, the charge of the cathodic wave increases with the adsorbing time, implying that a multilayer is formed.

The above results allude to the existence of two adsorbing states for thiols on mercury. Under potential that is more positive than the reduction wave ($E > -0.7$ V), thiols are **chemisorbed** as a result of an oxidation reaction to form a mercury-thiol adduct (**Eq. 1**). The layer is not suffi-

ciently thick to prevent further oxidation and deposition of a multilayer. **Physisorption** is obtained under a more negative potential ($E < -0.8$ V). In this potential window ($-1.4 \text{ V} < E_{\text{ads}} < -0.8 \text{ V}$) the adsorption is reversible and a dense monolayer is formed. When a physisorbed monolayer is inserted into a thiol-free solution under positive potential, an **instantaneous chemisorption** occurs and the resulting layer can be reduced during the following CV scan. While scanning or stepping from positive to negative potential, the chemisorbed thiols undergo physisorption. Therefore, the surface concentration of the thiol in a thiol-free solution decreases as a function of time that the HMDE is left at the physisorption potential window, i.e. $E < -0.8$ V.

This approach of equilibrating the HMDE under potential to assure the formation of a monolayer followed by its transfer (under potential) into a thiol-free solution for measuring the excess surface coverage, has been used for determining the adsorption isotherm of HS(CH₂)₅CO₂H. The isotherm reaches saturation which indicates the formation of a dense monolayer as the thiol concentration exceeds $5 \cdot 10^{-5}$ M. Under saturation conditions, the excess surface coverage is $(8.7 \pm 0.2) \cdot 10^{-10} \text{ mol}\cdot\text{cm}^{-2}$ which corresponds to $19 \pm 1 \text{ \AA}^2$ per thiol molecule. These values are in good agreement with previous reports (8, 10, 18).

Better insight into the organization of a 2-D system on a conducting interface can be obtained by measuring the differential capacity of the double layer. The classical way to obtain the differential capacity is by measuring the alternating current. In the absence of a faradaic current, and under conditions where the resistance of the solution is low (i.e. high ionic strength of the supporting electrolyte), the differential capacity is proportional to the amplitude of the alternating current (ΔI_{ac} , **Eq. 2**). (ΔE is the amplitude of the alternating

potential, f is the frequency and C is the differential capacity.)

Eq. 2

$$\Delta I_{\text{ac}} = 2\pi f \Delta E C$$

The 100B potentiostat of BAS enables measuring the alternating current in a digital way on the basis of the original digital AC voltammetry (ACV) developed by Bond and Anderson (28). A short but excellent introductory was published recently by Bott in this journal (29). In digital AC measurements, a small-amplitude sinusoidal alternating voltage is applied to the electrochemical cell and the resulting alternating current is measured. The sinusoidal current is rectified and averaged. The average value is then represented as the alternating current. As a consequence of averaging a sinusoidal wave, the value that is represented for the alternating current ($I_{\text{ac,meas}}$) is 0.637 of the amplitude value (ΔI_{ac}), i.e. $I_{\text{ac,meas}} = 0.637 \Delta I_{\text{ac}}$. In order to perform a digital AC voltammetry measurement, namely to measure the AC while scanning the potential, the small-amplitude alternating voltage is superimposed on a slowly varying linear DC potential. The capacity can be calculated from the digital ACV using **Eq. 3**.

Eq. 3

$$C = I_{\text{ac,meas}} / (0.637 \cdot 2\pi f \Delta E)$$

In ACV measurements the frequency of the alternating current and the applied voltage are identical, but their phase angle is usually different. The phase angle between the applied voltage and the measured current (ϕ) depends on the electronic components (resistors, capacitors, etc.) that are the equivalent of the impedance of the system. An in-phase ($\phi = 0^\circ$) alternating current indicates that the current is dominated by resistive components, i.e. by faradaic processes. On the other hand, an out-of-phase ($\phi = 90^\circ$) alternating current is indicative of capacitive elements, usually caused by non-faradaic proc-

esses such as phase transition. Any combination of two or more components results in an alternating current with a phase angle $0^\circ < \phi < 90^\circ$ (vector summation).

In order to investigate the complicated system comprised of thiols

on mercury where faradaic and non-faradaic processes appear throughout the same potential window, it is useless to measure the total ACV. An alternative approach is to disassemble the two components. Thus, we use the so-called phase selective AC

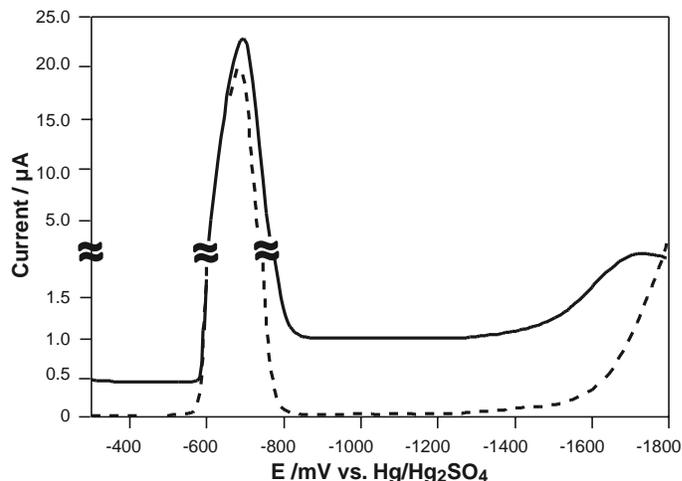
voltammetry (PSACV) technique. This technique measures digitally the projection of the alternating current at a specific phase angle.

F3 shows the in-phase and out-of-phase components of the PSACV, which were recorded in a 0.1 mM HS(CH₂)₅CO₂H solution. Small out-of-phase capacitive currents are observed at potentials positive and negative to the electrochemical reaction. At potentials more negative than the faradaic wave, the capacity matches that of a monolayer (6.8 $\mu\text{F}\cdot\text{cm}^{-2}$), while substantially lower values measured at the positive range indicate the formation of a thicker multi-layer film (ca. 0.4 $\mu\text{F}\cdot\text{cm}^{-2}$). To assure the type of current in each region of the potential window, the phase angle in each region was measured. PSACV was recorded at different phase angles and the obtained alternating current, at specific potential values, was plotted as a function of the phase angle (**F4**). Notice that the phase angle defined in the BAS 100B software is 360 minus the actual phase angle. Because the PSACV gives the projection of the alternating current on the requested angle, the highest PSACV value will be obtained at the phase angle of the system. It can be seen that at potentials more positive (-0.3 V) and negative (-1.0 V) than the electrochemical reaction (**F4B**), the PSACV attains a maximum value at 90° which supports a capacitive component. On the other hand, the phase angle at the faradaic wave (**F4A**) is approximately 45°, indicating the high resistive component of this process.

The dependence of the current on ω ($\omega=2\pi f$) shows that the peak current varies linearly with $\omega^{1/2}$, as expected for a faradaic process. At the same time, the current at potentials that are positive and negative to the electrochemical reaction varies linearly with ω as expected for a capacitive current (**Eq. 2**). In essence, these results support the existence of two adsorption phases at potentials negative and positive to the faradaic wave.

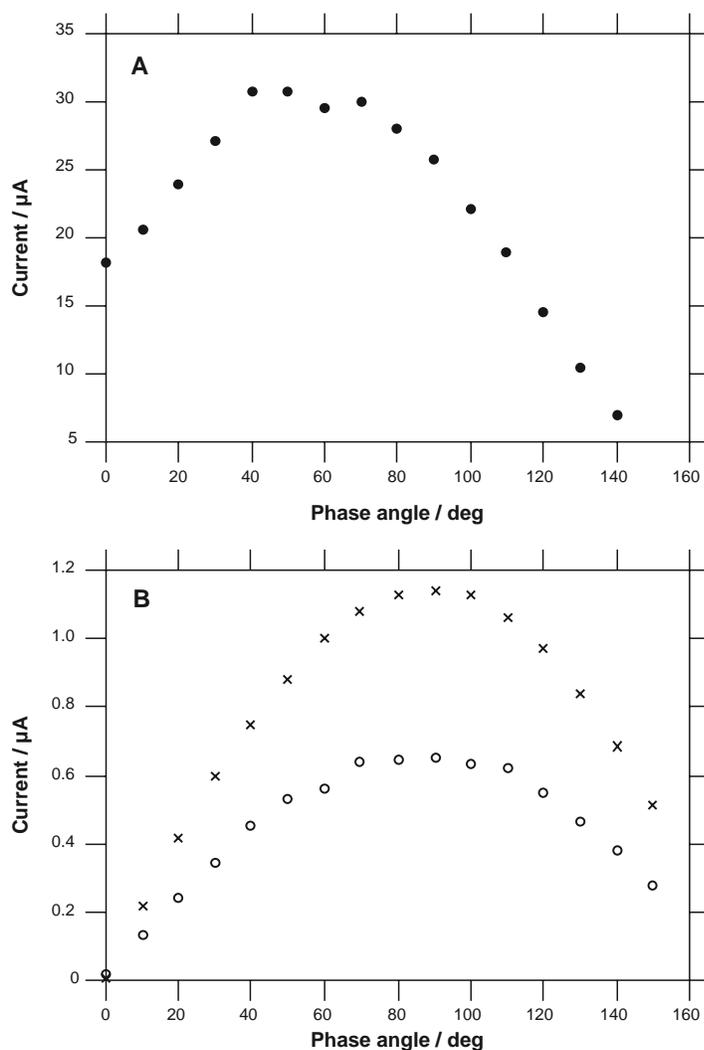
F3

In-phase (dashed line) and out-of-phase (solid line) PSACV of a HMDE in 0.1 mM solution of 6-Mercaptohexanoic acid. Scan rate 4 mV sec⁻¹, frequency 50 Hz, potential amplitude 0.025 V, equilibrium time 60 sec and initial potential -0.3 V.



F4

PSACV current as a function of the phase angle, measured at (A) -0.7 V (at the peak current) and (B) 0 -0.3 V and x -1.0 V (positive and negative of the peak current) in solution of 1 mM 6-Mercaptohexanoic acid. Scan rate 4 mV sec⁻¹, frequency 50 Hz, potential amplitude 0.025 V, equilibrium time 60 sec and initial potential -1.2 V.



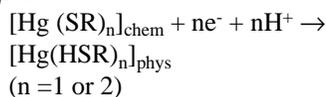
Another observation resulting from the AC voltammetry is the increase of capacity at negative potential (commencing at -1.6 V). The increase of capacity indicates a phase change, such as desorption or change in the organization of the layer. The reductive desorption is likely to be excluded because our *ex-situ* experiments clearly showed that water-soluble thiols are adsorbed under these negative potentials. **F5** shows that the negative edge potential is shifted positively as the temperature increases. This indicates that the process which the monolayer undergoes at these potentials must be exoergic. Nevertheless, we cannot determine whether it involves partial desorption or reorganization.

The dependence of the potential of adsorption (pit potential) on temperature is well documented and modeled for many systems, e.g. thymine and uracil and their derivatives (30-33). Unfortunately, these models cannot be applied for the adsorption of thiols on mercury due to the slight dependence of potential on temperature as compared with other systems. This is likely to be a consequence of the relatively small adsorption cross section of the thiols. In other words, the thiols are adsorbed through the -SH group and therefore, any phase change or reorganization (which does not involve complete desorption) is not expected to involve significant energy changes.

Finally, the dependence of the capacity on thiol concentration was also examined. The results point out that the potential range of the capacity minimum increases with thiol concentration, as expected for a reversible adsorption. Nonetheless, due to the small changes in capacity originating from the same reason as mentioned above, extraction of the thermodynamic parameters with a certain degree of accuracy is impossible.

To conclude, the above results strongly indicate that two adsorption states of ω -functionalized alkanethiols (regardless of the functional group) can be observed on mercury. The transformation between the two states is potential driven and occurs upon an oxidation-reduction process (**Eq. 4**).

Eq. 4



Our measurements cannot provide the value of n, and therefore the oxidation state of the mercury. Nevertheless, it is evident that one electron is transferred per each thiol (10). The formation of a chemisorbed monolayer at potentials that are more positive than the oxidation wave (ca. $E > -0.7$ V) is followed by the growth of a multi-layer, as is clearly indicated by the low double-layer capacity. The growth of a multi-layer

depends on the nature of the thiol, i.e. on the monolayer ability to block electron transfer between the Hg and thiols in solution. On the other hand, a compact monolayer is physisorbed upon applying a potential that is more negative than the oxidation-reduction wave. Transferring the coated HMDE to a thiol-free solution and immersing the drop under a positive potential ($E > -0.7$ V) leads to an oxidation process and an instantaneous chemisorption of the physisorbed thiols.

The potential range through which the thiols are physisorbed resembles a true reversible specific adsorption, such as exhibited by various molecules with other functional groups. Such adsorption is characterized by a capacity pit that is sensitive to temperature and concentration of the adsorbate in the electrolyte solution. It is evident from our capacitance measurements that the physisorbed thiols undergo a state/phase transition at more negative potential (ca. -1.6 V). This transition has the characteristics of a phase transition, however to a lesser extent. We attribute this behavior to the nature of the thiol adsorption via a small part of the molecule. Therefore, transitions or reorganizations of the alkyl chains which do not interact with the Hg are not likely to have significant impact on the pit characteristics. One should realize that the adsorption of thiols on Hg is not a true two-dimensional adsorption and thus cannot be theoretically treated by the same well-developed models.

Acknowledgment

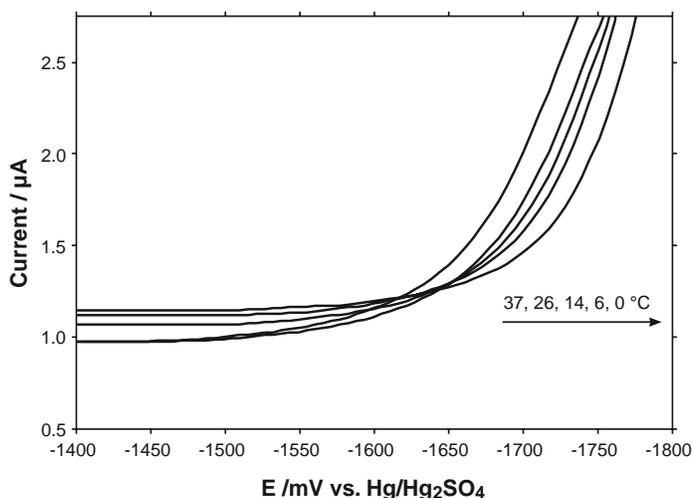
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F5

Out-of-phase component of PSACV recorded under different temperatures in a solution of 5 mM 6-Mercaptohexanoic acid. Scan rate 4 mV sec^{-1} , frequency 50 Hz, potential amplitude 0.025 V, equilibrium time 60 sec and initial potential -1 V.



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