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| Electrodeposition of Bilayers of Dithiols: A New Route to Complex Organic Interfaces |                                             |

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**ELECTRODEPOSITION of BILAYERS of DITHIOLS:  
A NEW ROUTE to COMPLEX ORGANIC INTERFACES**

**SANDRA RIFAI**

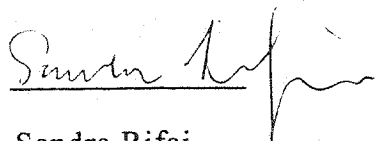
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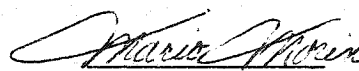
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***I dedicate this thesis to my parents and to 20  
years in Canada.***

## ABSTRACT

Organized organic films form a new class of nanomaterials, having potential applications in biosensing and molecular electronics. The development of such devices is impeded by the lack of simple and reliable methods for depositing molecular assemblies. An original electrodeposition scheme that allows for the formation of functionalized organic monolayers has been developed. With this method, it is possible to create organic interfaces that can be made to selectively react through application of an electric field. This electrochemical approach has been used to form reproducible monolayers and bilayers of aromatic and alkyl dithiols.

The mechanism guiding the adsorption of dithiols at the gold surface (from basic aqueous electrolyte solution) proceeds in two steps. First, a monolayer of vertically oriented dithiols (i.e. attached with a single S-Au bond) is formed via a nucleation and growth process. Next, the unreacted sulfur end groups dimerize with dithiolates in solution to form a bilayer. More specifically, bilayer formation occurs through the nucleophilic attack of an activated thiolate end group by a dithiolate from solution and follows a Langmuir process. The extent of bilayer formation depends on the accessibility of the unbound thiolate and its distance from the electrode surface. The interaction between the negatively charged thiolate and the aqueous electrolyte plays a major role in the assembly of these compounds. In addition, intermolecular interactions are influential in the packing of rigid (i.e. aromatic) and flexible (i.e. alkyl) dithiol films.

## RÉSUMÉ

Les films organiques organisés forment une nouvelle classe de nanomatériaux ayant des applications potentielles comme capteurs chimiques et en électronique moléculaire. Le développement de ces matériaux est ralenti par l'absence de méthodes simples et fiables pour déposer ces assemblages moléculaires. Une méthode originale d'électrodéposition permettant la formation de monocouches organiques fonctionnalisées a été développée. Avec cette méthode, il est possible de fabriquer des interfaces organiques pouvant réagir lors de l'application d'un champ électrique. Cette approche électrochimique a été utilisée pour former des monocouches et des bicouches de dithiols alkyles et aromatiques.

Le mécanisme d'adsorption des dithiols à la surface d'or (à partir de solutions aqueuses alcaline) procède en deux étapes. Premièrement, une monocouche de dithiols orientés verticalement (i.e. adsorbés par un seul lien S-Au) est formée par un processus de nucléation et croissance. Ensuite, les groupes terminaux soufrés dimérisent avec des dithiolates en solution de façon à former une bicouche. Plus spécifiquement, la formation d'une bicouche survient lors de l'attaque nucléophile d'un groupe terminal thiolate activé par un dithiolate en solution et procède selon un processus de Langmuir. Le degré de formation de la bicouche dépend de l'accessibilité du thiolate non-lié et de sa distance avec la surface de l'électrode. L'interaction entre les dithiolates chargés négativement et la solution électrolyte joue un rôle majeur dans l'assemblage de ces composés. En outre, les interactions moléculaires ont une influence sur l'arrangement des films de dithiols rigides (c.-à-d. aromatiques) et flexibles (c.-à-d. alkyles).

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## LIST of ABBREVIATIONS

|              |                                                   |
|--------------|---------------------------------------------------|
| AFM .....    | atomic force microscopy                           |
| BDMT .....   | benzenedimethanethiol                             |
| BDT .....    | butanedithiol                                     |
| BM .....     | benzylmercaptan                                   |
| CTR .....    | counter electrode                                 |
| CV .....     | cyclic voltammetry                                |
| EDT .....    | ethanedithiol                                     |
| EQCM .....   | electrochemical quartz crystal microbalance       |
| HDT .....    | hexanedithiol                                     |
| HF .....     | Hartree-Fock                                      |
| HREELS ..... | high-resolution electron energy-loss spectroscopy |
| IHP .....    | inner Helmholtz plane                             |
| IRAS .....   | infrared reflection-absorption spectroscopy       |
| ODT .....    | octanedithiol                                     |
| OHP .....    | outer Helmholtz plane                             |
| PDT .....    | propanedithiol                                    |
| PZC .....    | potential of zero charge                          |
| SCE .....    | saturated calomel electrode                       |
| SERS .....   | surface enhanced Raman spectroscopy               |
| SPM .....    | scanning probe microscopy                         |
| STM .....    | scanning tunneling microscopy                     |
| UHV .....    | ultrahigh vacuum                                  |

WKG .....working electrode

## LIST of SYMBOLS

|                     |                                   |
|---------------------|-----------------------------------|
| $E$                 | .....electrode potential          |
| $Q$                 | .....charge                       |
| $\Gamma$            | .....surface concentration        |
| $j$                 | .....current density              |
| $\eta$              | .....overpotential                |
| $C$                 | .....capacitance                  |
| $d$                 | .....thickness                    |
| $\epsilon_r$        | .....relative dielectric constant |
| $\epsilon_0$        | .....permittivity of free space   |
| $k$                 | .....rate constant                |
| $A$                 | .....pre-exponential factor       |
| $\Delta G^\ddagger$ | .....Gibbs energy of activation   |
| $\alpha$            | .....transfer coefficient         |
| $F$                 | .....Faraday's constant           |
| $n$                 | .....number of electrons          |
| $R$                 | .....gas constant                 |
| $T$                 | .....temperature                  |
| $A$                 | .....absorbance                   |
| $I$                 | .....intensity                    |
| $m$                 | .....mass                         |
| $t$                 | .....time                         |

## **Chapter 1: Introduction**

### **1.1 “Nano” World**

Whether it is used in nanometer, nanoscale, nanosecond, or nanotechnology, the prefix “nano” has made its way into newspapers, magazines, journal articles, and television. A lot of the excitement revolves around using organic molecules (that can be switched between conducting and nonconducting states) to make nanomaterials having applications in sensing, electronics, and other areas. Specifically, the emerging field of molecular electronics is attracting plenty of attention. It responds to the demand for miniaturization of electronic circuit elements, and focuses on the electrical behavior of molecules as alternative materials to silicon-based circuitry.

Molecules are nanometer-scale objects having well defined structures and electronic properties. The electronic energy levels in molecules can be fine-tuned by, e.g. changing substituents on an aromatic ring [1]. Simple changes in molecular structure may be useful for an electronic application. Aside from their advantageous size and synthetic adaptability, other enticing properties of molecules include their light weight, nontoxicity, and low cost [2].

### **1.2 Chemical Design of Molecular Wire**

The simplest component of an integrated organic electronic system is a molecular wire, which transports either electron or hole charge. To construct a molecular wire, some type of highly conjugated backbone must be designed to allow for the easy flow of electrons. Electrons, in atoms or molecules, have energy levels that are quantized and can only be any one of a number of discrete values. The shape of the electronic orbitals is determined by the molecule’s specific characteristics. The overlap of orbitals may be perturbed to achieve a

switching, whereby the electronic flow may be turned on or off [3-6]. One of the first simple electronic devices was a molecular rectifier proposed by Aviram and Ratner in 1974. It consisted of a donor and an acceptor  $\pi$  electron system, separated by a sigma bonded (insulator) tunneling bridge [7].

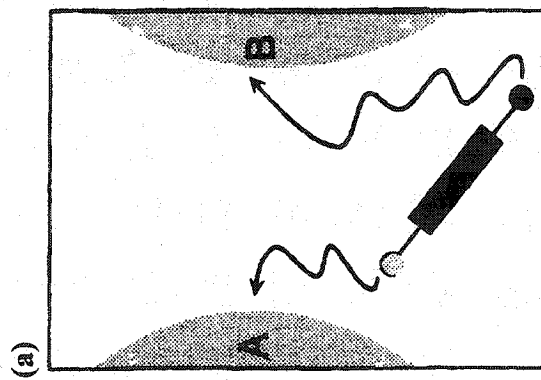
### 1.3 “Hooking up” Electronically Active Molecules to Nanometer-scale Contacts

Molecules exhibiting the appropriate bridging characteristics for a molecular wire also require terminal functional groups that can become directly attached to metal contacts. This poses a problem for bifunctional molecules, because both ends may react with a single surface. Since any potential molecular wire must bridge two electrodes, how does one go about positioning a single molecule in a gap between two metal surfaces?

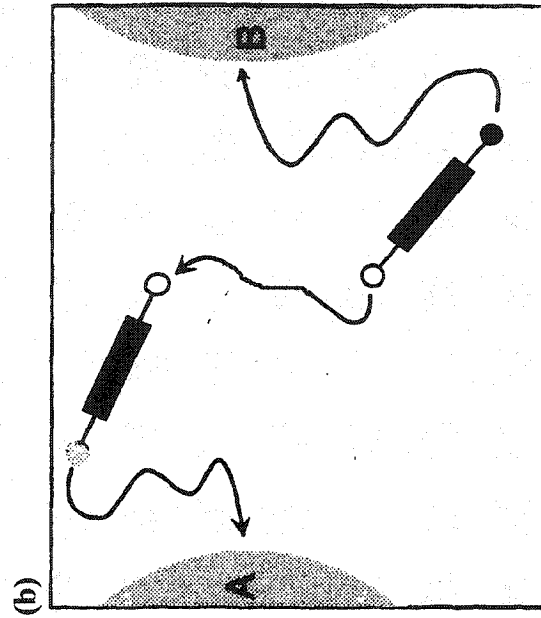
So far, there are two basic approaches involving either single molecule manipulation or statistical assembly [1]. The first approach utilizes a molecular resolution tool such as the tip of a scanning tunneling microscope (STM) or an atomic force microscope (AFM) to transfer each molecule to its appropriate location. This approach is obviously impractical for engineering applications. The second approach is similar to the way nature assembles living systems. It involves a combination of contacts, molecules, and containing environment, e.g. a solution. The molecules self-assemble into place spontaneously as shown in Figure 1.1a. This approach may be extended to layer by layer growth (Figure 1.1b) or to form a hybrid device with a self-assembled array of molecules contacted by a deposited top metal electrode (Figure 1.1c) [1].

Several fundamental design challenges must be met in order for molecules to self-assemble as part of a device and are summarized in Figure 1.2 [1]. Molecular orientation effects must be taken into consideration with such compounds. The molecules have to be

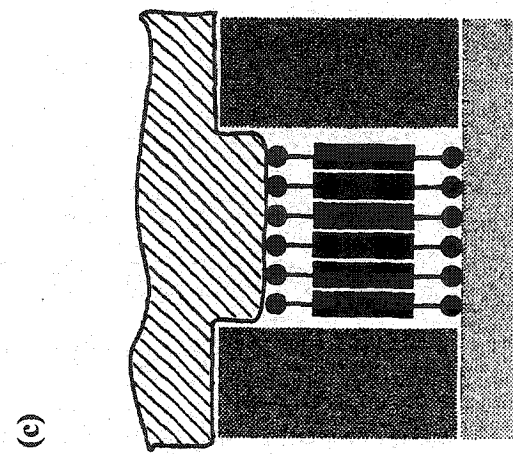




**Molecular  
Self-Assembly**

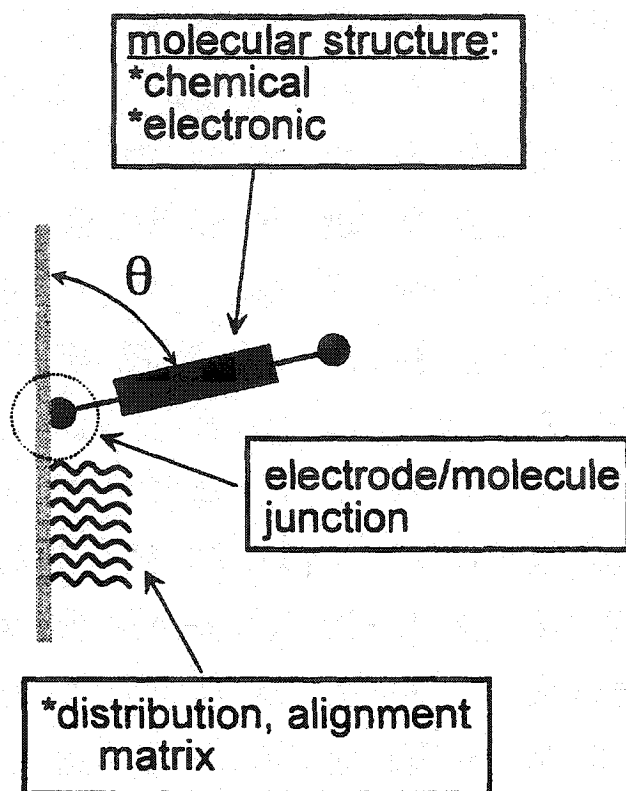


**Self-Assembly and Layer Growth**



**Hybrid:  
Self-Assembly +  
Conventional Fabrication**

**Figure 1.1:** Illustration of a two metal contact, molecule-based device: (a) self-assembly of a single organic molecule; (b) self-assembly involving multilayer growth; (c) self-assembled array of molecules contacted by a deposited top metal electrode. Modified from reference 1.



**Figure 1.2:** Schematic of a bifunctional molecule connected to a metal surface with one terminal group, which details the critical chemical-based aspects of its structure. Copied from reference 1.

driven to orient outwardly so that their second functional end group is available for reactivity. Highly conjugated molecules tend to have extremely polarizable electron clouds, which induce attractive dispersion forces towards polarizable metal surfaces. These interactions may cause the molecule to lie flat, and this problem will only magnify as the length of the molecule increases. Mixed monolayer compositions have been explored in order to try and overcome this latter problem [3,8].

The gold thiolate (R-S-Au) system is the most extensively studied self-assembled monolayer (SAM) [9]. Gold electrodes are used primarily because of the metal's high conductivity and inertness. Thiols form strong S-Au bonds (bond strength of  $\sim 120 \text{ kJ mol}^{-1}$  [1]), which readily establish stable thiol-gold junctions. The specific interaction of gold with sulfur and other "soft" nucleophiles, and its low reactivity towards "hard" acids and bases, makes it possible to vary the structure of the terminal group. In this way monolayers can be formed having functional groups at the organic/solution interface that may be used as different contacts.

#### **1.4 Functionalized Thiol Monolayers**

For instance, carboxylic acid terminated alkanethiols form monolayers with preferential adsorption to the gold surface through the thiol end group. They have received special interest because of their hydrophilic properties [10-20]. Specifically, properties such as acid/base equilibria can be controlled by the electrode potential in solution [12,15]. In addition, these molecules can serve as adhesion layers for biomolecules and cells [13,18-20]. For example, mercaptopropionic acid SAMs have been used as biosensors to selectively interact with the lysine groups of Cytochrome *c* [18,19]. They have also been used for the

electrochemical detection of dopamine [20]. These topics have been extended to other hydrophilic molecules as well, such as hydroxyl terminated thiols [10,16,21-23].

Recently, SAMs of aromatic thiols having different substituents and terminal groups have been extensively studied [22-34]. Beyond their rigidity, the advantage of functionalized aromatic thiols is in their potential as molecular wires. Conjugated molecules are useful for molecular electronics applications because they are electrically conducting. Their conjugation affects the acidity of the thiol proton, and can therefore make the thiolate a softer or a harder ligand [27]. Since the thiolate is an electron-donating group, an electron-attracting substituent will result in a significant molecular dipole moment. These properties can change the conductivity of the molecule from an off to on state [33,34]. For example, one such wire (specifically a molecule containing a nitroamine redox center) was reported to exhibit an unusual switching behavior known as negative differential resistance (NDR) [33]. The “negative resistance” is characteristic of a decrease in the current with an increase in the applied voltage. This study was further extended to explore the molecule’s potential as a memory storage device. The ability to write, read, and erase the initial state of this molecular device accomplished random access memory (RAM) [34].

### **1.5 Dithiols**

A considerable part of the literature on functionalized monolayers deals with dithiols [10,35-69]. The majority of it is focused on the potential applications of dithiol reactivity in molecular electronics. If dithiols can form SAMs in which only one thiol group is attached to the metal surface, then the other end group may be available to form a chemical bond with a second metal electrode [46-49,51,55,63-65]. Several groups have used dithiols for covalently attaching gold nanoparticles [48,49,51,55], while others are using dithiols as

bridging compounds between metal surfaces and semiconductor nanocrystals [46,47]. The thiol groups of 1,4-benzenedithiol have been used as contacts between two gold electrodes of a mechanically controllable break junction [63-65]. This study provided a quantitative measure of the charge transport in a single organic molecule, which is an essential step in the development of molecular-scale electronics. Organo-metallic films have also been made using the reducing properties of thiols in reactions involving  $\text{Cu}^{2+}$  [38,56] and  $\text{Ag}^+$  [39]. A gold surface modified with a dithiol monolayer was used to grow microcrystalline zirconia [57]. The electrodeposition of copper on a gold electrode coated with a dithiol layer has been reported [52]. Another prospect is applications of aromatic dithiol SAMs as molecular wires [50,54,64,67].

The oxidative chemistry of the unreacted sulfur of the vertically adsorbed dithiols has been exploited to form multilayers [40,41]. A method involving immersing a gold substrate into a dithiol solution, followed by oxidation of the sulfur to sulfoxo species through exposure to air was used to form a second layer [40]. The bond between the first and second dithiol layer was suggested to be a S-S bond between sulfoxo species. Up to seven layers were deposited by this method. The unreacted thiol was photo-oxidized with UV light and sulfoxo species were identified with XPS measurements [41]. Less extensive oxidation of the unreacted thiol has also been observed. In this case, bilayers and multilayers were formed by the oxidative formation of a S-S bond between dithiols [42,50,54,59,60,67]. However, these reactions depend on the presence of trace oxidants such as oxygen (and on the type of solvent, the dithiol concentration, and the duration of the self-assembly) [40-42,59,60]. Poor control of the oxidant concentration leads to the slow formation of disordered and incomplete multilayers. It was possible to prevent the formation of

multilayers by adding tri-n-butylphosphine, which reduced the disulfides as they formed [67]. In this case, a monolayer with a surface of unreacted thiols was obtained. This surface could be used in well-controlled reactions to form a second layer.

While previous studies have focused on the electronic and photophysical properties of the nanodevices, the structural characterization of the dithiol films is incomplete. To exploit the full potential of molecular electronics devices, the structure of the monolayers used to make them needs to be controlled. There are some reports on the characterization of dithiol monolayers, most of which are spectroscopic in nature [38,41,42,50,54,56,59-61,66-68]. Using ellipsometry and X-ray photoelectron spectroscopy (XPS), Tour et al. studied conjugated dithiol monolayers and multilayers spontaneously adsorbed on gold [54]. Since multilayer formation was observed, it was inferred that one thiol end adsorbed to the surface, while the other end projected away from it. This vertical configuration has also been reported for other conjugated dithiols [50,56,59-60] and alkanedithiol films [42] based on a similar argument. More recently, Rieley et al. employed XPS to study monolayers of 1,8-octanedithiol from ethanolic solution on gold [41]. The data were found to be consistent with an “upright” alignment of the hydrocarbon chains, similar to that suggested by Brust et al. for 1,6-hexanedithiol [38].

Using scanning tunneling microscopy (STM) under ultrahigh vacuum, Kobayashi et al. reported a different structure for 1,8-octanedithiol on gold, in which the molecules were aligned parallel to the metal surface [43,44]. This is also the case for 1,6-hexanedithiol deposited from the gas phase [10,35]. In addition, this orientation has been proposed for low coverages of alkanedithiols adsorbed from organic solution onto gold [10,35]. The binding of both sulfurs to the gold surface was observed for chelating alkyl dithiols as well [36,37].

Various aromatic molecules having thiol groups in the *ortho* position were used to improve the stability and order of organic layers by adsorbing through two metal-sulfur bonds [61,62,66,68]. Additionally, it is reported that most dithiols adsorb to the silver surface by both sulfurs [60,68,69]. A recent STM study obtained information on 1,8-octanedithiol adsorbing from solution onto Ag(111) [69]. The resulting SAMs were close-packed, with the molecules lying flat on the electrode surface. An important effect of the substrate on the adsorption geometry of the isomers of benzenedimethanethiol has been reported [56-62,68]. On a silver substrate the *para*, *meta* and *ortho* isomers adsorbed via their two sulfurs [60,68]. On a gold substrate, the *para* and *meta* isomers adsorbed via one sulfur [56-60], whereas the *ortho* isomer was found to adsorb via both sulfurs [61,62].

All of these data [10,35-69] indicate that the adsorption characteristics of dithiols onto metal electrodes are very dependent on the substrate and the phase from which they are deposited (i.e. vapor or solution). Most of the literature concentrates on the self-assembly of dithiols onto gold from organic solution [10,35-42,45-57,59-66]. These studies show that various structures and coverages can be formed by dithiols at the gold surface. The conditions of deposition, including the kind of solvent, the dithiol concentration, and the incubation time, all have a strong effect on the assembly of the dithiols. These parameters are more prevalent when the functionalized thiol is a dithiol, since both end groups will have an equally strong affinity to the gold electrode.

## 1.6 Goal of Our Research

Preparing well defined, stable, easily controlled, and reproducible self-assembled monolayers onto metallic electrodes is of utmost importance in the development of the field of molecular electronics. If one thiol end group is used to anchor the molecule to a substrate,

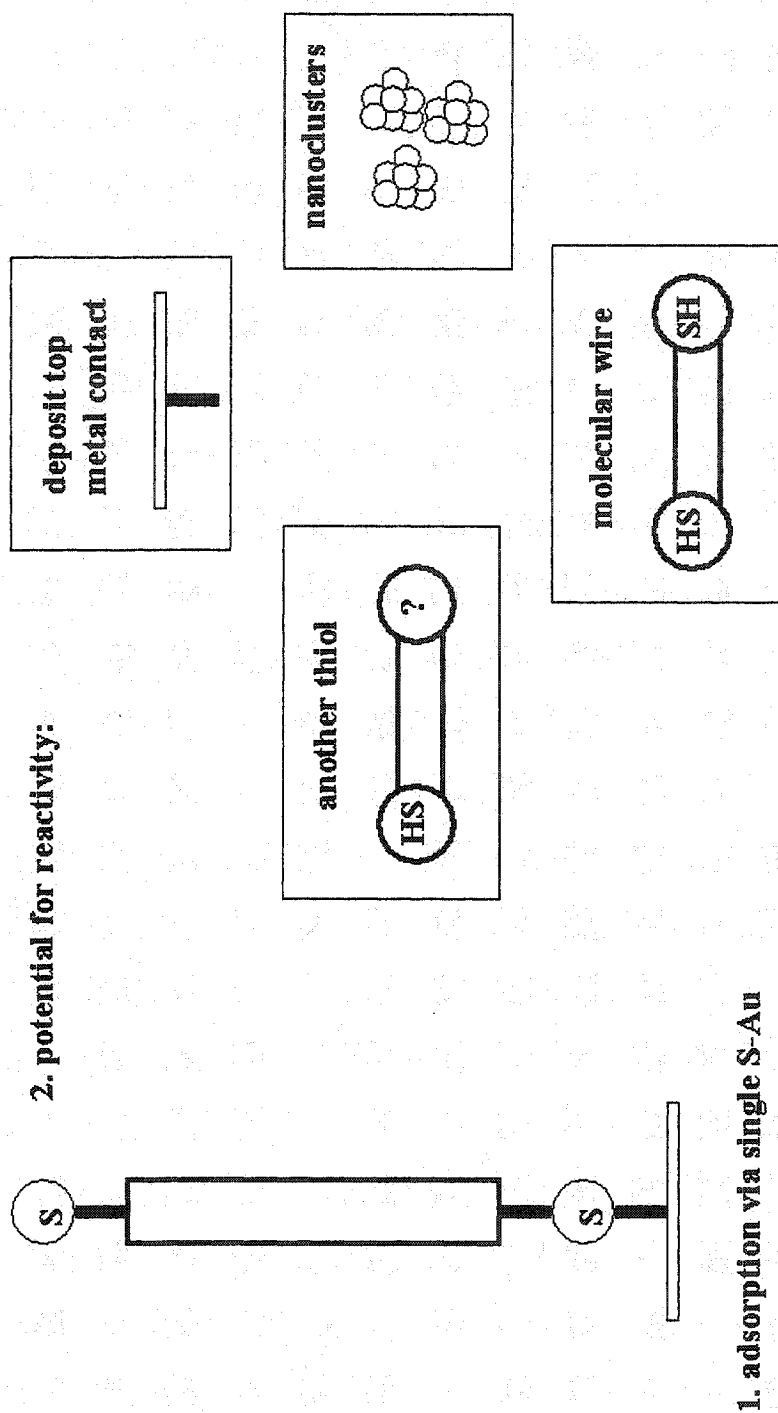
the other end can act as a template for a variety of chemical reactions (Figure 1.3). For example, a second layer of conducting or insulating molecules can be deposited. In this reaction either thiols or dithiols could be used. This involves the formation of a disulfide bond through the oxidative dimerization of the thiol groups. Methods involving chemical oxidants or exposure to UV light have been used to form bilayers [40,41,60]. The unbound thiol group could also be reacted with metal colloids or contacts [46-49,51,55,63-65]. In this case, it is the strong exothermic adsorption reaction of the sulfur that drives the reaction.

The goal of our research is to develop a set of deposition conditions, whereby we can first form a complete monolayer of dithiols adsorbed to the gold surface via a single sulfur (with the unreacted thiol group at the organic/solution interface). The second sulfur is then available for reactions, such as those illustrated in Figure 1.3. Specifically, we focus on reacting the unbound sulfur with other thiols and dithiols to obtain complex multilayered structures. This layer by layer growth of organic films is a simple synthetic approach and could lead to new organized nanomaterials.

### **1.7 An Electrochemical Approach Towards Depositing Dithiols onto Au(111)**

An alternate approach to spontaneous adsorption (i.e. under open circuit conditions), which is most commonly used in the formation of thiol self-assembled monolayers, is electrodeposition [70-80]. By applying a sufficiently positive potential to the metallic substrate in contact with a thiol solution, monolayers can be made. The coverage and properties of the electrodeposited monolayers have been shown to be identical to those deposited chemically, i.e. by immersing a clean metal into a dilute solution of thiols [71,72]. The electrochemical route provides a better control of the deposition conditions. This allows for the formation of partial layers, which is extremely difficult by conventional methods.





**Figure 1.3:** Scheme for the use of a dithiol monolayer to form complex organic layers. If the dithiol is deposited via a single sulfur (with its molecular axis aligned perpendicular to the gold surface), the second sulfur is then available for reactivity with, e.g. another

This method also allows for the selective adsorption/desorption of adsorbates [80] and is therefore useful in the formation of mixed monolayers. These adlayers are stable over a wide potential range (e.g.  $\sim 1$  V for alkanethiols deposited onto gold). This allows for the possibility to exploit the electrochemical properties of modified electrodes that incorporate specific functionalities [12,15,20,52,81,82].

An electrochemical approach to the formation of thin organic films has already been employed in the synthesis of conducting polymers [83]. In electro-organic reactions, the active species is generated at the electrode surface through electron transfer. Often, a radical cation is formed, which couples with other radicals through a combination reaction to build a polymer chain. This is also the case with chemical oxidative polymerization, with the difference being that a chemical oxidant initiates the polymer formation. However, it has been observed that better ordered polymers are formed through electrochemical methods than through chemical synthesis [83]. This growth of films through application of an electric field may be extended to dithiol systems, since sulfur radicals can be generated electrochemically and are known to dimerize in solution [84-88].

## **1.8 Outline of Thesis**

This thesis reports on the study of the electrodeposition of aromatic and alkyl dithiols at the Au(111) surface. Chapter 2 describes the theory and experimental setup of the techniques employed in the electrodeposition of the dithiol films on gold and their subsequent characterization. Chapter 3 reports on the oxidative deposition of monolayers and bilayers of 1,4-benzenedimethanethiol (1,4-BDMT) onto a Au(111) single crystal. Bilayer formation was verified through cyclic voltammetry, differential capacitance measurements, chronocoulometry, quartz crystal microbalance experiments, and high-

resolution electron energy-loss spectroscopy. The orientation and the order of the electrodeposited films were explored using infrared reflection-absorption spectroscopy and scanning probe microscopy respectively. A mechanism for bilayer formation is proposed. In Chapter 4, the isomeric effect on the oxidative deposition of bilayers of the three isomers of BDMT is examined electrochemically and spectroscopically. The bilayer electrodeposition protocol is extended to alkanedithiols of varying chain lengths in Chapter 5. The activation of the S<sup>-</sup> was examined as a function of its separation from the gold surface. Finally, Chapter 6 compares the bilayer formation of a rigid (e.g. 1,4-BDMT) and a flexible (e.g. 1,6-hexanedithiol [1,6-HDT]) dithiol. In addition, mixed layers of 1,4-BDMT and 1,6-HDT are formed. Throughout the thesis, the different interactions involved in the self-assembly process of the monolayers and bilayers are examined. A brief conclusion is presented in Chapter 7.

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## Chapter 2: Theory and Experimental

### 2.1 Introduction

The goal of our research is to define a set of deposition conditions whereby we can control the growth of dithiol films at the Au(111) surface. An electrochemical approach was used to explore the deposition of various dithiol compounds on a gold single crystal. The organic films were electrodeposited using cyclic voltammetry (CV), and characterized with several techniques. A surface concentration of dithiols was calculated after integration of the oxidative adsorption peaks, and from chronocoulometric measurements. The ion blocking properties of the films were investigated through differential capacitance experiments. In addition, the changes in mass (occurring simultaneously with the oxidative deposition/reductive desorption) were monitored using an electrochemical quartz crystal microbalance (EQCM).

The orientation and organization of the electrodeposited dithiol films was studied on a macroscopic scale using infrared reflection-absorption spectroscopy (IRAS). *Gaussian*<sup>®</sup> vibrational calculations [1] were performed to aid in the assignment of the bands present in the spectra obtained. The intensities of the bands in the IR spectra were used to determine the orientation of the adsorbed molecules. Both the IRAS and high-resolution electron energy-loss spectroscopy (HREELS) results were used to qualitatively describe the films deposited at the gold surface. These spectroscopic techniques allowed us to investigate the organization of the dithiol molecules within the layers. Scanning probe microscopy was employed to evaluate the order of the dithiol films at the molecular level. Both atomic force microscopy (AFM) and scanning tunneling microscopy (STM) were used as probes to obtain information on the order of the dithiols at the gold electrode from the topography.

Each technical section in this chapter consists of two parts. The first part discusses the theory pertaining to the particular method used to investigate the electrodeposited dithiols on Au(111). The second part describes the experimental setup, i.e. procedures, instrumentation, and chemicals used in the respective studies. In addition, details on the data analysis are presented.

## **2.2 Formation of Thiol Self-Assembled Monolayers (SAMs) on Gold**

The interactions involved in the self-assembly process of alkanethiols at the Au(111) surface are described in this section. Adsorption occurs upon desolvation of the thiol end group, which requires more energy in the case of a charged species, e.g. thiolates from basic aqueous electrolyte (section 2.2.2). Simultaneously, the expulsion of solvent molecules and electrolyte near the electrode surface takes place. This results in significant changes of the double layer region (section 2.3.3). The energetics of the deposition of an organic monolayer and its ordering are complex due to the various interactions that influence the adsorption process. These include metal-adsorbate, adsorbate-adsorbate, adsorbate-solution, and solute-electrolyte solution interactions and are detailed in the following sections.

### **2.2.1 Interactions Involved in Chemisorption**

Self-assembled monolayers (SAMs) on metal substrates have been extensively studied. One of the most widely investigated and well-characterized systems involves alkanethiols on gold surfaces [2, p237]. Previous work has demonstrated that there are several interactions present in such alkanethiol SAMs that influence the assembly process. These include strong sulfur headgroup-substrate interactions, interadsorbate interactions, and endgroup/solution interactions. The balance of these three main interactions governs the structure and growth of the organic film.

The adsorption of alkanethiols onto a Au(111) substrate from solution is a rapid exothermic process of about  $170 \text{ kJ mol}^{-1}$  [2-4]. The sulfurs adsorb preferentially to the three-fold hollow sites separated by  $5 \text{ \AA}$  [5-7]. This close-packed arrangement allows for Van der Waals interactions between the alkyl chains. These intermolecular interactions are estimated to be about  $-2 \text{ kJ mol}^{-1}$  per methylene group [2,3,8]. In addition to these Van der Waals interactions, the aromatic dithiols will involve  $\pi$ - $\pi$  interactions between the benzene rings. Sufficient time must be allowed for the assembly of the molecules, such that the interadsorbate interactions may be maximized. There is also a weak endothermic process due to the interactions between the terminal methyl groups and the solution interface, which is dependent on the solvent. This interaction might be more significant for dithiols, since a sulfur atom is much more electron rich than a carbon atom. For example, a charged thiolate group is solvated in basic aqueous electrolyte.

### 2.2.2 Interactions Governing the Electroformation of a S-Au bond

The electroformation of a S-Au bond is an activated process whose rate constant ( $k$ ) may be expressed in terms of the transition state theory as

$$k = A \exp(-\Delta G^\ddagger / RT). \quad (2.1)$$

$A$  is the pre-exponential factor,  $\Delta G^\ddagger$  is the Gibbs energy of activation,  $R$  is the gas constant, and  $T$  is the absolute temperature. To obtain a more accurate kinetic picture of electrode processes, it requires that the theory explain the observed dependence of current on potential. Assuming a Nerstian behavior, equation 2.1 becomes

$$k = A' \exp(-\alpha n F \eta), \quad (2.2)$$

where  $A'$  involves all of the terms independent of potential,  $\alpha$  is the transfer coefficient and lies in the range from 0 to 1,  $n$  is the number of electrons transferred,  $F$  is Faraday's constant,

and  $\eta$  represents the overpotential. The overpotential ( $\eta = E - E^0$ ) is typically defined as the applied potential ( $E$ ) relative to the reversible potential ( $E^0$ ).  $E^0$  represents the average value of the potentials of a reversible electron transfer process.  $\alpha$  gives information on where the activation barrier for electron transfer is. For a solution redox process,  $\alpha = 0$  represents an early transition state, while  $\alpha = 1$  represents a late transition state.

When a small positive overpotential is applied to the gold electrode, its Fermi-level energy decreases. Electrons are then transferred from the thiol headgroups to the metal surface upon adsorption. According to equation 2.2, the more positive the  $\eta$  is, the faster the oxidative adsorption. In addition to being dependent on  $\eta$ , the rate of deposition is also strongly dependent on the nature of the electrolyte solution. For instance, the solvation energies of the same compound in different media will vary greatly. For example, the solvation energy for ethanethiol is  $-5.5 \text{ kJ mol}^{-1}$  in pH neutral aqueous solution [9,10]. This value increases significantly to between  $-293$  and  $-335 \text{ kJ mol}^{-1}$  for ethanethiolate in alkaline aqueous solution of pH higher than the  $pK_a$  of the thiol group [11]. Another factor influencing the electrodeposition process is the activation energy for S-H bond dissociation. Of course, this does not play a role in alkaline solution.

One recent chronoamperometric study reported that the rate of deposition is dependent on the potential in basic solution, and almost independent in neutral solution [12]. The rate constant was plotted as a function of deposition potential for each electrolyte solution and a value for  $\alpha$  was obtained. An  $\alpha = \frac{1}{2}$  was obtained for the adsorption of alkanethiolates onto gold [13]. Such an intermediate value for  $\alpha$  is characteristic of a transition state that occurs close to the electrode surface [14, p523]. On the other hand, if  $\alpha$  is very small, the rate-limiting step for oxidative adsorption (transition state) is at the

electrode surface [14, p523]. This is the case for deposition of alkanethiols onto the gold electrode, where the S-H dissociation is rate-limiting [12].

### **2.2.3 Interactions at the Organic/Solution Interface**

#### **2.2.3a pH Effect**

The terminal group interactions are most prevalent for ionizable functionalized alkanethiols [15-22] and will be highly dependent on the pH of the electrolyte solution [18-22]. Specifically, there is likely to be significant electrostatic interaction between the negatively charged thiolate end groups for our dithiols in basic aqueous electrolyte (0.5 M KOH). In addition to the role of solvation discussed in the previous section, other factors at the organic/solution interface will be influential in the dithiol assembly from basic solutions. For example, interfacial ion-association is another stabilizing interaction that may minimize the repulsion between the terminal groups [19,22-24]. It has been shown that the terminal carboxylate groups of a monolayer experience an increase in repulsive electrostatic interactions, as the concentration of KOH decreases [19]. The ionic strength is obviously a factor to consider. A decrease in the ionic strength from 0.5 M KOH, should result in stronger repulsion between thiolate end groups, because of the lesser degree of screening. A recent EQCM study reported that self-assembled thiol monolayers with carboxylic acid functionality undergo pH-dependent phase transitions [22]. The monolayer was stabilized in the acid form by hydrogen-bonding and through metal-ion complexation in the carboxylate form [22]. Other studies have shown that a thiol monolayer modified with immobilized redox centers can be stabilized through ion-pairing [23,24].

#### **2.2.3b Charge Effect on Electroactive Self-Assembled Monolayers**

There is a potential drop ( $\phi^M - \phi^S$ ) that occurs across the metal surface (M) and bulk solution (S). A schematic representation is shown in Figure 2.1 [25]. The upper potential profile corresponds to the drop at the bare surface, while the lower one represents the drop across an organic film. Typically, this is used to describe the reductive desorption of a thiol monolayer [25]. Since thiols can only desorb in their reduced form, a large negative external potential is required to induce electrochemical desorption due to the low ion permittivity of the monolayer. This corresponds with a shift in the reductive peak potential to more negative values, as the alkanethiol chain length increases [25].

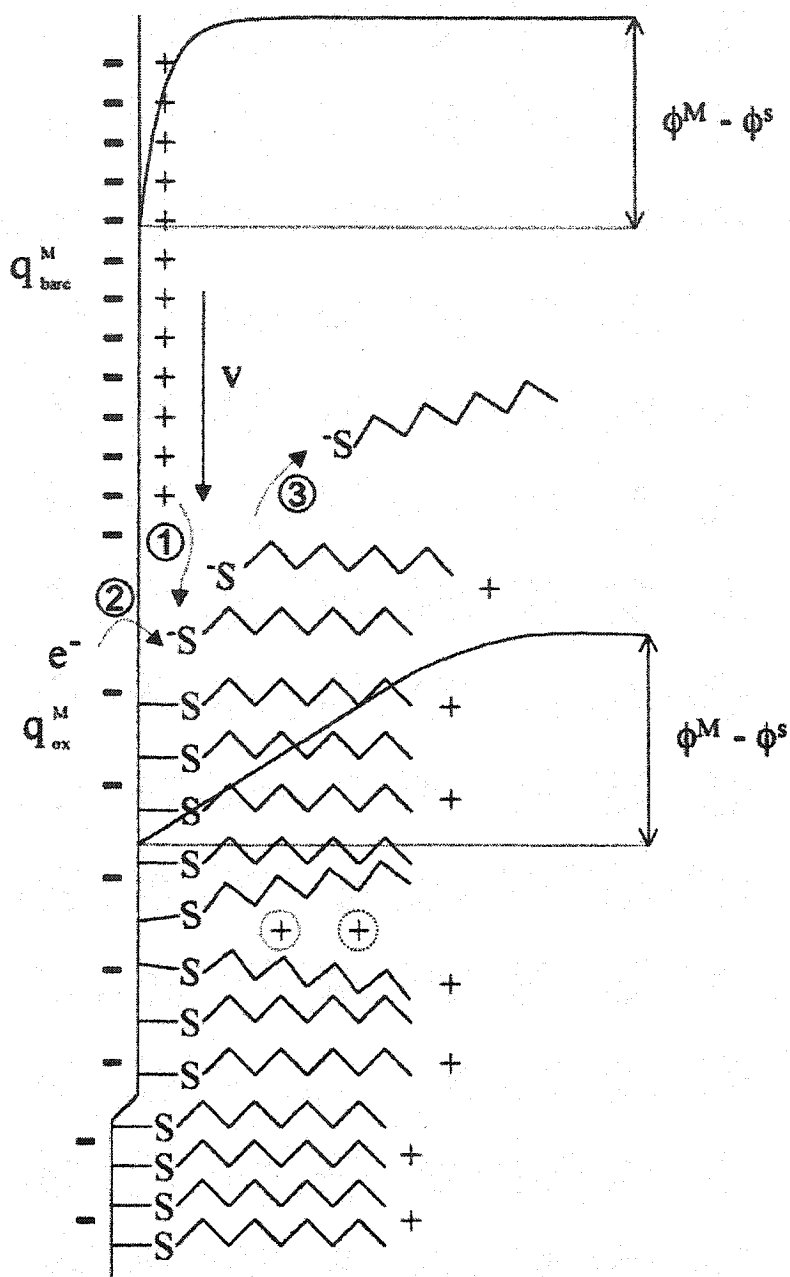
Intuitively, the reverse should be applicable to electrochemically oxidize the unbound thiolate end group in a dithiol monolayer. That is, a large positive potential is required to activate the terminal sulfur group at the organic/solution interface. As the dithiol length increases, an even more positive potential will be necessary. Of course, the potential experienced by the thiolate group depends on the interfacial region, the charge on the electrode, and the ionic strength [15-25].

## **2.3 Electrochemical Techniques**

### **2.3.1 Cyclic Voltammetry (CV)**

#### ***Theory***

Electrode processes are often studied by cyclic voltammetry (CV), which involves application of a linear potential sweep cycle to an electrode and simultaneously measuring the resulting current [14, p215]. The measured current has two components (faradaic and capacitive), which are normally coupled and difficult to separate. This is especially the case for species that undergo rapid mass transfer from the bulk solution to the electrode surface upon their oxidation/reduction (e.g. organic layer).



**Figure 2.1:** Representation of the reduction of a thiol monolayer at a fixed potential drop  $\phi^M - \phi^S$ . Desorption occurs in three steps: (1) surface redistribution of electrolyte ions, (2) electron transfer, and (3) detachment of the reduced thiol molecules. Copied from reference 25.



The faradaic current results from an electron transfer process at the electrode/solution interface. The nonfaradaic current, i.e. capacitive current, is due to the accumulation/depletion of charged entities at the electrode/solution interface without actual charge transfer. The latter of the two currents results in a transient current, which accounts for variations in the double layer capacitance as a function of potential when a species is adsorbed/desorbed. For instance, if a negative potential is applied to the electrode, it is balanced by an excess of positively charged entities at the metal surface. The applied potential is relative to the potential of zero charge (PZC), which will be discussed in detail in section 2.3.3. When the potential is scanned to values where e.g. a species is oxidatively deposited, it will displace the cations. This displacement results in a current, which is also known as an image current. We were able to correct for the capacitive current through our integration method during data analysis.

We can obtain valuable information from the current-potential (I-E) curve, i.e. cyclic voltammogram. The potential axis is also a time scale. CV may be used to check the quality of the Au(111) single crystal and the purity of the electrolyte solution. The voltammogram indicates the potentials at which oxidative and reductive processes occur. CV can therefore be used to qualitatively investigate the mechanistic properties of an organic film. In a typical preliminary study, the voltammograms are recorded over a wide array of potential scan rates and for various potential ranges. By observing how the peaks appear and disappear upon changing the potential scan rate and potential limits (window-opening experiment), it is possible to determine how the processes represented by the peaks are related to one another. In addition, from the scan-rate dependence of the peak amplitudes, peak positions, and peak

shapes, the role of adsorption and diffusion in the electrochemical process under study can be identified [26, p223].

Through electrodeposition, it is possible to integrate the current peaks to obtain charges. If the number of electrons transferred per adsorbed molecule ( $n$ ) is known, these charges ( $Q$ ) can then be converted to surface concentrations ( $\Gamma$ ) from the following expression

$$\Gamma = \frac{Q}{nFA}, \quad (2.3)$$

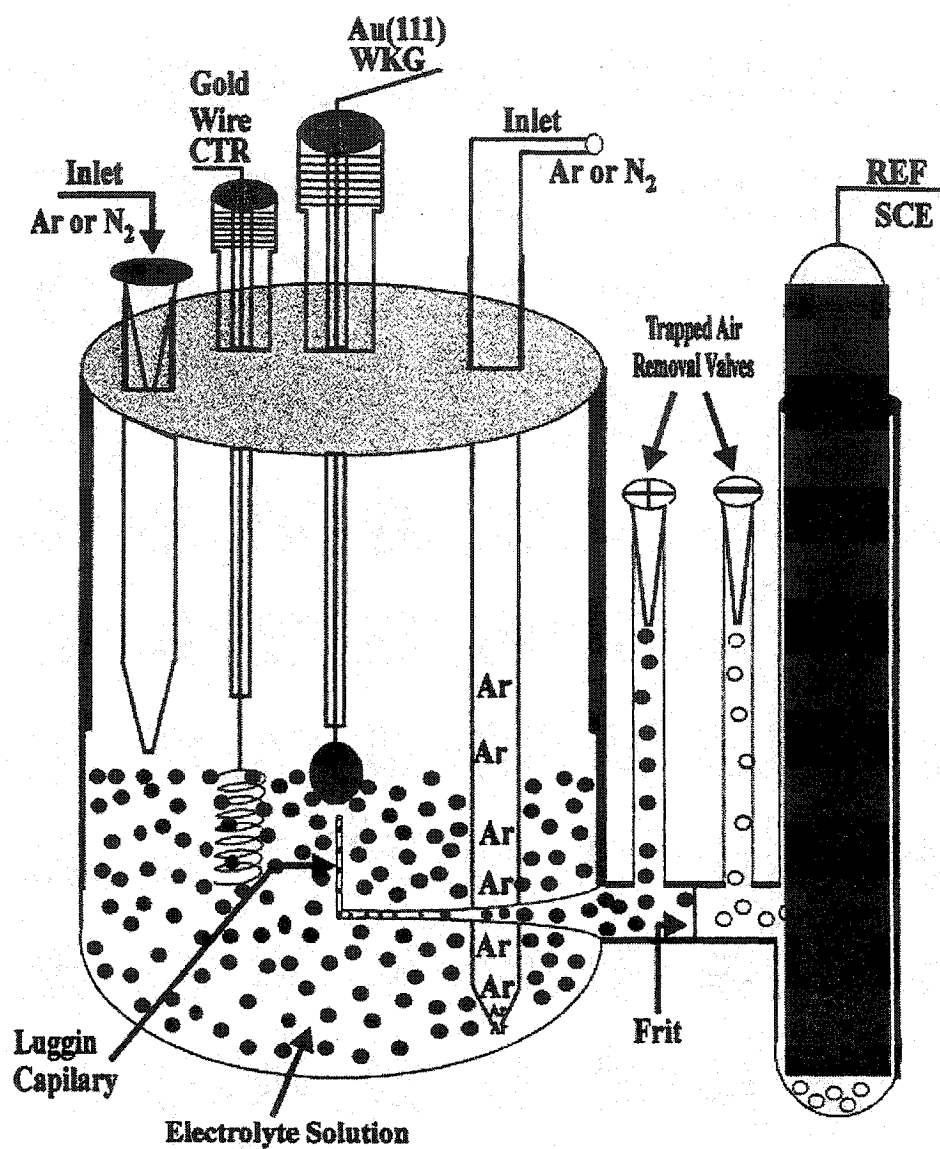
where  $F$  is Faraday's constant and  $A$  is the area of the electrode surface. This provides direct information on the molecular coverage at the gold surface. It also gives an implication as to how well the molecules are packed at the surface.

### ***Experimental***

Cyclic voltammetry was performed in a conventional three-electrode cell [27], shown in Figure 2.2 [28]. The working (WKG) electrode was a Au(111) single crystal (99.999%, Engelhard). The counter (CTR) electrode was a gold wire, 0.5 mm in diameter, and coiled to maximize the surface area (99.999%, Engelhard). All of the potentials given in this thesis are relative to a saturated calomel electrode (SCE) (Fischer Scientific). The current was measured between the working electrode and the counter electrode. The potential applied to the working electrode was set relative to the reference electrode. The potentiostat used was a Solartron, model number 1287 and the cyclic voltammograms were recorded with CorrWare software (Scribner Associates Inc.).

### ***Solution Preparation, Electrochemical Cell, and Current Peak Integration***

Benzylmercaptan (BM) (99% purity) and the isomers of benzenedimethanethiol (BDMT) (1,4-BDMT 98% purity and 1,2 and 1,3-BDMT 95% purity) were purchased from



**Figure 2.2:** Three-Electrode Electrochemical Cell Schematic. Copied from reference 28.

Aldrich. The alkanethiols and dithiols, including hexanethiol (95%), heptanethiol (95%), hexadecanethiol (92%), 1,2-ethanedithiol (1,2-EDT 90+%), 1,3-propanedithiol (1,3-PDT 99%), 1,4-butanedithiol (1,4-BDT 97%), 1,6-hexanedithiol (1,6-HDT 96%), 1,8-octanedithiol (1,8-ODT 97+%), and 1,9-nonanedithiol (1,9-NDT 95%) were also purchased from Aldrich. Organic films were electrodeposited from 1 mM solutions of BM and the alkanethiols and dithiols, whereas saturated solutions of the BDMT isomers were used in their electrodeposition. All measurements were taken in either 0.5 M KOH (Aldrich, 99.99 % semiconductor grade) or 0.1 M NaF (Merck, suprapur) electrolyte solutions made with deionized and distilled water (Milli-Q Plus, Millipore Corp.). Monolayers of the thiols and dithiols were also chemically deposited through incubation of the Au(111) electrode in a 10 mM ethanolic solution (Omnisolv, spectroscopic grade) for periods ranging from 1 hour to several days. All chemicals were used as received.

The electrochemical cell was placed in a faraday cage to minimize electrical noise and magnetic interferences. All glassware was cleaned in hot concentrated sulfuric acid (BDH) for about 40 minutes to destroy any organic impurities. The cell was then rinsed with Milli-Q water and filled with the electrolyte. The solutions were degassed with Ultra Pure Carrier argon gas (Air Products Canada) or nitrogen (departmental line filtered to remove O<sub>2</sub> and H<sub>2</sub>O). A hanging meniscus was made with the single crystal, to ensure exposure of only the (111) face to the electrolyte solution. Cyclic voltammograms were then recorded and analyzed.

The potentials and surface concentrations reported here are the average of at least three measurements. Charge densities were obtained by integration of the oxidative and reductive peaks using CorrView software (Scribner Associates Inc.). The initial and final

points of the baseline were chosen before and after the current peak. Through this “baseline correction”, we were able to correct for the capacitive current. This method of integration was not possible for processes that were slow, resulting in a broad oxidative peak. In these cases, chronocoulometry was used to evaluate (and correct) the charge corresponding to the particular oxidative process.

### 2.3.2 Chronocoulometry

#### *Theory*

Chronocoulometry is a potential-step experiment that is the integral analog of the corresponding chronoamperometric approach [14, p140]. In this method, the potential of the working electrode is changed instantaneously to a value that causes an electrochemical reaction, and the charge-time response is monitored. A potential-time profile is applied to the working electrode, once the electrochemistry of the system is well understood. In our case, the potential ( $E_1$ ) is first set to a value (-1.00 V) where no electron transfer is occurring and an uncoated Au(111) surface is observed. At time  $t = 0$ , the potential is stepped to a new value ( $E_2$ ) where an electrochemical process occurs and the charge-time response is recorded (i.e. chronoamperogram). The potential may be stepped again to monitor another electrochemical reaction at the gold electrode.

In order to obtain an accurate estimate of the amount of molecules electrodeposited from the charge measured ( $Q_{TOT}$ ), the faradaic charge ( $Q_{ORG}$ ) and capacitive charge ( $\Delta Q$ ) must be deconvoluted [29]. The  $\Delta Q$  results from the difference between the double layer charge of the coated gold electrode ( $Q_1$ ), and the double layer charge of the uncoated electrode ( $Q_2$ ).

$$\Delta Q = Q_2 - Q_1 \quad (2.4)$$

A value for  $\Delta Q$  can be estimated by first assuming that the thiol coated gold electrode is a perfect capacitor. The charge  $Q_1$  accumulated by a capacitor is obtained from the following expression

$$Q_1 = C_1(E_1 - E_{1,PZC}), \quad (2.5)$$

where  $C_1$  represents the electrode capacitance (section 2.3.3) at a potential  $E_1$ .  $E_{1,PZC}$  is the potential of zero charge of the coated Au(111) surface. It is assumed to have a value of  $-0.45$  V in  $0.1$  M KOH, which is the maximum of the electrocapillary curve of a thiol-coated gold electrode [30].

The uncoated electrode is not a perfect capacitor, and  $Q_2$  must therefore be obtained from chronocoulometric measurements. A potential jump of  $-1.00$  to  $-0.75$  V on a clean gold surface in  $0.5$  M KOH, resulted in a value of  $6 \mu\text{C cm}^{-2}$  for  $Q_2$ . This number was used in correcting the oxidative charge for monolayer formation. A similar potential jump experiment from  $-1.00$  to  $-0.10$  V resulted in a value of  $34 \mu\text{C cm}^{-2}$  for  $Q_2$ . Therefore,  $28 \mu\text{C cm}^{-2}$  was the value for  $Q_2$  used in correcting for the oxidative charge for bilayer formation.

### ***Experimental***

The chronocoulometric experiments were performed using the cell setup described above for CV, and were carried out with an EG&G potentiostat, model 263A (Power Suite software). The value for the charge transferred was obtained from the plateau of the charge-time curves. The plateau was reached at a time sufficiently long for complete deposition. The faradaic charges  $Q_{\text{ORG}}$  reported are the average of at least three measurements and were calculated using

$$Q_{\text{ORG}} = Q_{\text{TOT}} - \Delta Q. \quad (2.6)$$

### **2.3.3 Differential Capacitance**

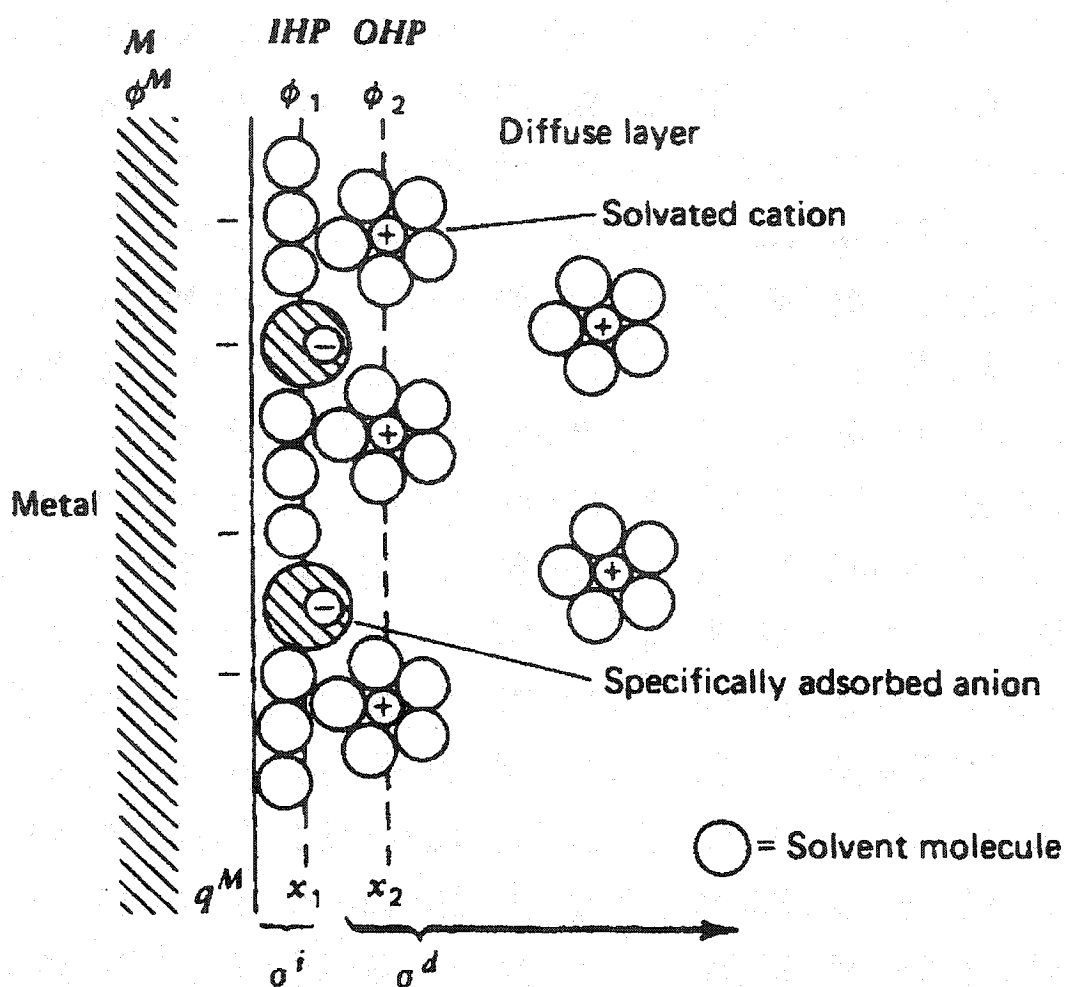
## Theory

The formation of an electrical double layer at the metal/solution interface is dictated by several factors including, e.g. the electrolyte, the electrode composition, and the potential applied to the metal surface. Figure 2.3 shows a model for the interface, which consists of three main parts: (1) the inner Helmholtz plane (IHP), (2) the outer Helmholtz plane (OHP), and (3) the diffuse layer [14, p9]. The inner layer contains solvent molecules and sometimes other species that are specifically adsorbed. The locus of the specifically adsorbed ions represents the IHP and is at a distance  $x_1$  from the metal surface. The charge density in this inner layer is given by  $\sigma^i$  ( $\mu\text{C cm}^{-2}$ ). Solvated ions can only approach the metal by a distance  $x_2$ ; the locus of centers of the nearest solvated ions represents the OHP. The interaction between these solvated ions and the charged metal involves only long-range electrostatic forces. Due to thermal agitation, the solvated ions are also distributed in the diffuse layer, which extends from the OHP to the bulk solution. The structure of the double layer can affect the rates of electrode processes. The method most widely used to characterize this double layer region is differential capacitance.

The modified gold electrode/solution interface can be represented as an ideal capacitor consisting of two parallel plates separated by an organic material. The Helmholtz theory models the differential double layer capacitance ( $C_{\text{DL}}$ ) through the expression

$$C_{\text{DL}} = \frac{dQ}{dE} = \frac{\epsilon_r \epsilon_0}{d}, \quad (2.7)$$

where  $Q$  is the charge on the plates,  $E$  is the potential difference across the plates,  $\epsilon_r$  is the relative dielectric constant of the separation medium,  $\epsilon_0$  is the permittivity of free space, and  $d$  is the distance between the electrode surface and plane of closest approach for ionic charge. The potential of minimum differential capacitance in pure electrolyte solution, which is not



**Figure 2.3:** Model of the double layer region at the electrode/solution interface. The ionic charge density in the inner Helmholtz plane (IHP) is represented by  $\sigma^i$ , while the ionic charge density in the outer Helmholtz plane (OHP) and diffuse layer is represented by  $\sigma^d$ . Copied from reference 14.



specifically adsorbed on the electrode, is defined as the PZC. At potentials more negative than the PZC, there is an excess of cations at the surface, while at more positive potentials there is an excess of anions at the surface. At the PZC, there is no excess charge of the surface and no excess of anions or cations in solution at the surface [14, p495].

If the organic layer at the metal surface does not undergo faradaic reactions in the potential range being probed, capacitance measurements provide information on the thickness of the deposited layer (from equation 2.7, the thicker the film the lower the capacitance) as well as its permeability to water and anions [31-33]. From the latter we can extract information on the type of layer formed. For instance, a disordered layer with defects might incorporate water molecules having a high dielectric constant or allow ions to approach the metal surface more closely. This, in turn, would result in a higher capacity. However, defects are not always characteristic of a disorganized film. The molecules could adsorb in such a way that the entire surface is covered (with an overall disorganization), resulting in a low capacity. In the same respect, a highly organized film might have a couple of holes resulting in a high capacity. The above discussion illustrates the importance of combining capacitance results with other surface techniques.

The Helmholtz theory is limited in that the model assumes ideal conductors on both sides of a dielectric material (i.e. organic film). Although the gold electrode is nearly ideal, such an assumption cannot be made for the electrolyte solution. A more adequate description for the capacitive behavior of the electrical double layer is three capacitors in series given by

$$C_{TOT}^{-1} = C_{MS}^{-1} + C_{ORG}^{-1} + C_{DL}^{-1}, \quad (2.8)$$

where  $C_{MS}$  is determined from the Au-S bond length and  $\epsilon_r$  of the thiol headgroup (i.e. the sulfur bound to the gold surface),  $C_{ORG}$  is determined from  $d$  and  $\epsilon_r$  of the organic backbone,

and  $C_{DL}$  is determined from  $d$  and  $\epsilon_r$  of the endgroup/solution interface [31,32]. For the dithiol systems,  $C_{DL}$  will play more or less of a significant role in its contribution to  $C_{TOT}$ , depending on the pH of the electrolyte from which it is deposited. For example, a negatively charged thiolate group (alkaline solution) will result in a higher  $\epsilon_r$  than a thiol group (acidic solution). This, in turn, would result in an overall higher  $C_{TOT}$ .

### ***Experimental***

The differential capacitance measurements were done with a Solartron system (potentiostat model 1287, impedance analyzer model 1260), using a similar cell setup as that described above for CV. To obtain a measure of how the capacity changes as a function of potential, the electrode potential was cycled at  $5 \text{ mV s}^{-1}$  in a region of interest. A 20 Hz AC signal of 5 mV RMS amplitude was superposed onto the DC potential.

The AC current output was fed into the impedance analyzer and separated into two components, in-phase (the phase angle is zero as compared with the original AC signal) and out of phase components (the phase angle is  $90^\circ$  relative to the original AC signal). The differential capacitance of the double layer was determined using the following expression

$$C_{DL} = (I_{re}^2 + I_{im}^2) / V_{ac}\omega I_{im} , \quad (2.9)$$

where  $I_{re}$  and  $I_{im}$  are the real and imaginary components of the current respectively.  $V_{ac}$  represents the root mean square value of the AC potential and  $\omega$  is the circular frequency. All capacity values reported are an average of at least three measurements.

#### **2.3.4 Electrochemical Quartz Crystal Microbalance (EQCM)**

##### ***Theory***

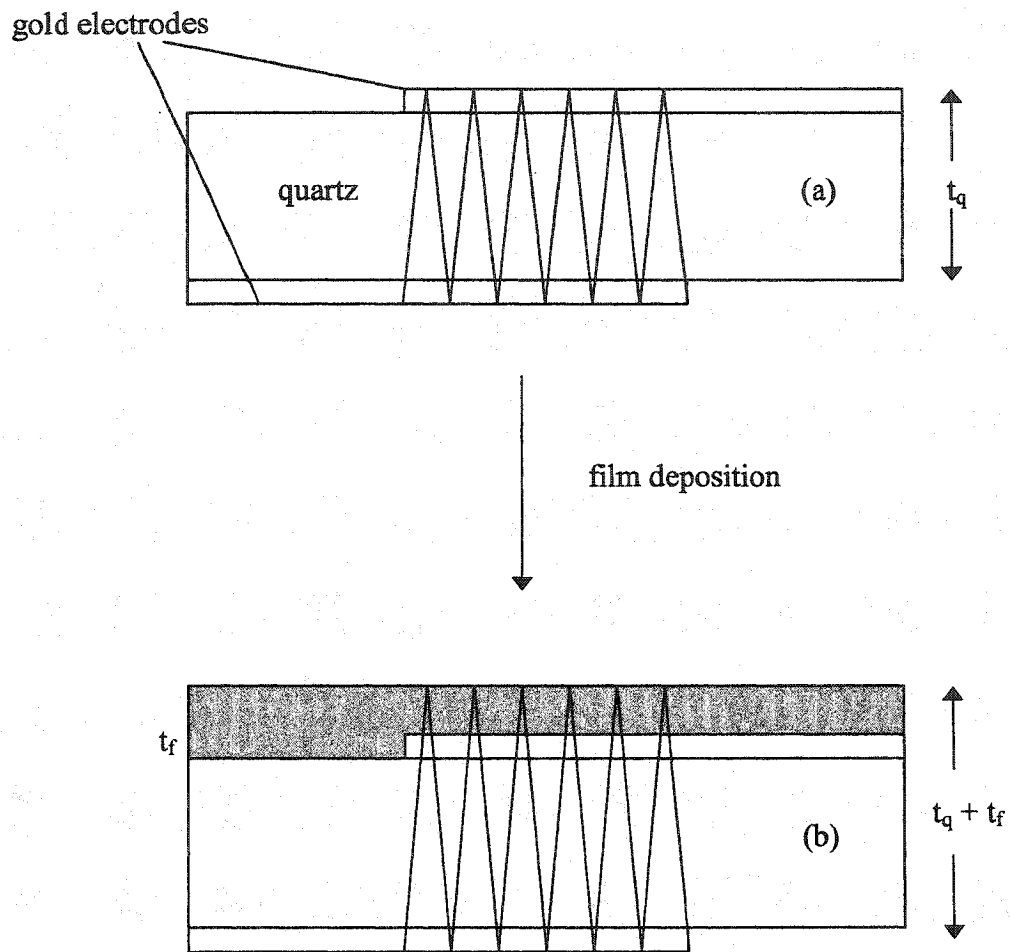
The electrochemical quartz crystal microbalance (EQCM) measures the mass change at an electrode, while simultaneously monitoring the electrochemical parameters of the

system [34,35, p599]. The principle upon which EQCM is based, is the piezoelectric behavior of quartz. When an AC voltage is applied across the quartz crystal (a piezoelectric material), it induces a corresponding mechanical stress. The resulting stress is dependent on the crystal symmetry, the electric field, and the angle of cut of the crystal substrate with respect to its crystallographic axes (which is a resonant frequency). The vibrational motion of the crystal results in a transverse acoustic wave that propagates across the thickness of the crystal ( $t_q$ ), reflecting back and forth at the surfaces as shown in Figure 2.4a [34]. When a layer of a foreign material ( $t_f$ ) is deposited onto the quartz crystal, the generated wave will travel through that layer as well (Figure 2.4b [34]). This assumes that the particle displacement and shear stress are continuous across the crystal/film interface. If the assumption is made that the acoustic properties of the film are similar to those of the quartz, then the thickness due to the film can be directly treated as a change in the thickness ( $\Delta t$ ) of the quartz crystal.

This change in thickness results in a change in the resonant frequency ( $\Delta f$ ), and is described by the Sauerbrey equation [36]

$$\Delta f = -2f_0^2 \Delta m / A(\mu_q \rho_q)^{1/2}, \quad (2.10)$$

where  $f_0$  is the frequency of the uncoated quartz crystal,  $\Delta m$  is the mass change,  $A$  is the piezoelectrically active area,  $\rho_q$  is the density of quartz, and  $\mu_q$  is the shear modulus. The change in thickness is represented in equation 2.10 by  $\Delta t = \Delta m / \rho_q A$ . This assumes that the density and transverse velocity of the two materials are identical. If all of the constants in the above expression are combined, the relationship between mass and frequency reduces to  $\Delta m = -\Delta f \times S$ , where  $S$  in our case is  $5.608 \text{ ng cm}^{-2} \text{ Hz}^{-1}$  [37].



**Figure 2.4:** Schematic representation of (a) the transverse shear wave in a quartz crystal and (b) a composite resonator including the quartz crystal and a layer of foreign material. See text for description of symbols.

The Sauerbrey relationship also assumes that the frequency shift, resulting from the mass deposited at some radial distance from the crystal center, will be the same regardless of that distance. It therefore requires that the deposited film be rigid and thin, having a uniform thickness across the entire active region. Often, this is not the case, and interferences can result in non-ideal behavior. To name a few, viscoelastic effects, high mass loadings and non-uniform mass distribution, surface roughness, surface stress, and interfacial slippage can all cause changes in the resonant frequency [34,35].

### ***Experimental***

The EQCM measurements were taken with an EG&G system (potentiostat model 263A and QCA-917 quartz crystal analyzer) and controlled with Power Suite software (Princeton Applied Research, Perkin Elmer Instruments Inc.). Although the basic setup was the same as that described for CV, a slight modification to the three-electrode cell shown in Figure 2.2 was used, and is presented in Figure 2.5 [38]. In this case, the working electrode was a 9 MHz AT-cut quartz crystal, with gold sputtered on a Ti layer (Seiko). Prior to addition of the dithiol, an EQCM response was measured in pure electrolyte. The frequency was constant ( $\pm 0.1$  Hz) within the region of interest (i.e. monolayer and bilayer formation). All masses reported are the average of at least three measurements.

## **2.4 Spectroscopic Techniques**

### **2.4.1 Infrared Reflection-Absorption Spectroscopy (IRAS)**

#### ***Theory***

The surface vibrations of adsorbates on metals may be studied with a variety of spectroscopic techniques [39]. In IRAS, the absorption of infrared radiation due to the excitation of surface vibrations of adsorbates is detected after reflection of the incident IR

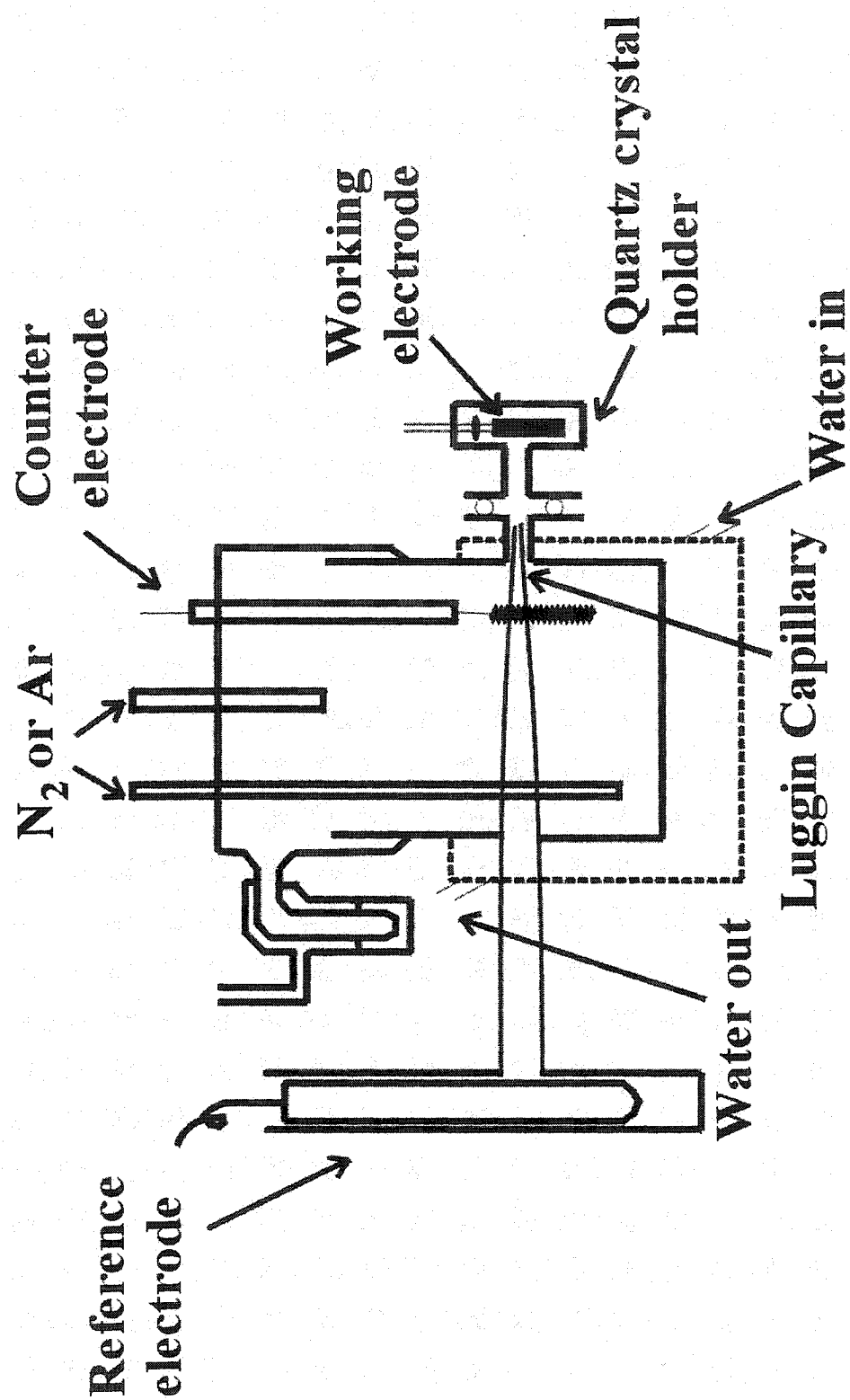


Figure 2.5: Electrochemical cell for EQCM experiments. Copied from reference 38.

beam from a substrate. The absorption phenomenon is governed by the IR selection rule pertaining specifically to metal surfaces, which states that only vibrational modes whose transition dipole moment derivatives possess a component normal to the surface will be observed [39-41]. The absorption of IR radiation is enhanced when the angle between the incident beam and surface normal is maximized and is limited to *p*-polarized radiation (the electric field is polarized parallel to the plane of incidence). This can be understood by consideration of the electric fields generated by radiation at the uncoated metal surface. Figure 2.6 is a schematic of the incident (i) and reflected (r) vectors of *s*- (the electric field is polarized perpendicular to the plane of incidence and parallel to the plane of the metal surface) and *p*-polarized radiation [39, p414].

At all angles of incidence at a metal interface, the *s*-polarized component undergoes a 180° phase shift. Hence, the resultant of the incident and reflected vectors is approximately zero at the metal surface. Obviously, the *s*-component does not interact to a great extent with the surface dipoles. In contrast, the *p*-polarized component undergoes a phase change that varies strongly with the angle of incidence. At a grazing angle of incidence, the *p*-component is enhanced and a nearly doubled resultant vector occurs perpendicular to the surface. This *p*-component can then interact strongly with the vibrational modes of the adsorbates having a dipole derivative perpendicular to the metal surface. It is these excited modes that are observed in the IR spectra [39-41].

A comparison of the IR spectra obtained in transmission mode of the solid can be made with the IRAS spectra for the self-assembled layers. The variation in the relative intensities of the vibrational bands, gives some indication of the orientation of the adsorbates

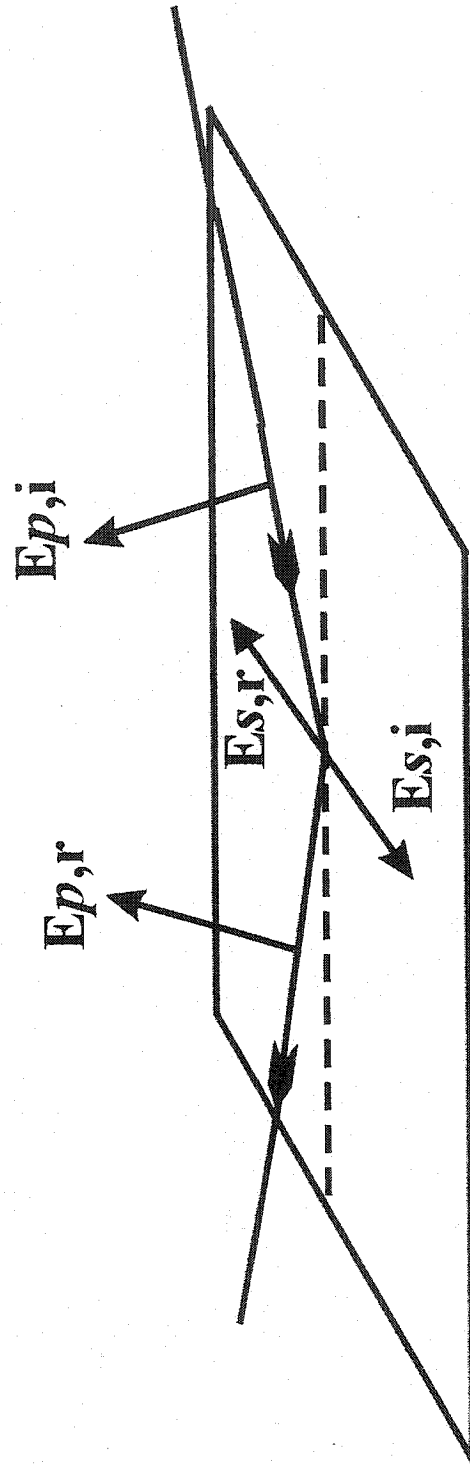


Figure 2.6: The incident (i) and reflected (r) electric vectors (E) of the *p*- and *s*-polarized radiation at the metal surface.

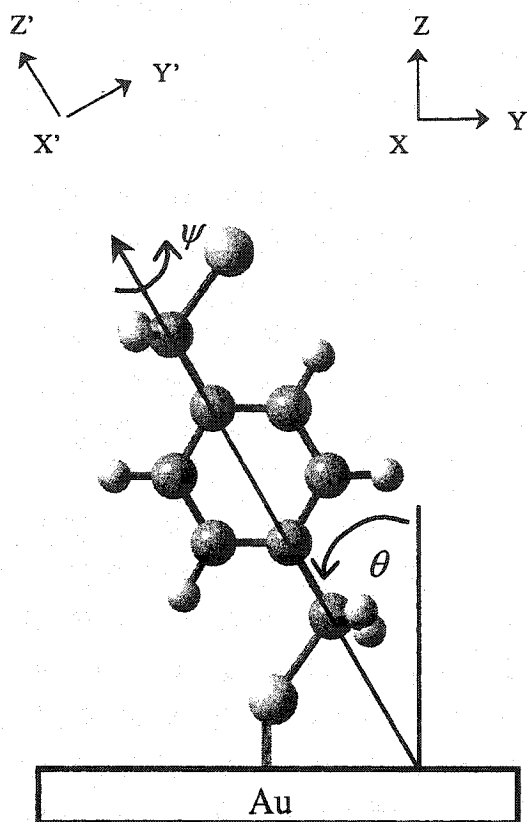


at the metal surface. With this in mind, a method for determining the geometry of the adsorbed molecules is presented [42-45].

Two sets of Cartesian coordinates are used to express the dipole direction in these calculations. One set is relative to the metal surface, and the other represents the molecule. In the metal surface system, X and Y are assigned to the surface plane, while Z corresponds to the surface normal. The X', Y', and Z' coordinates define the molecular system.

In our case, we are interested in the orientation of the aromatic ring. Figure 2.7 presents a schematic of a single 1,4-BDMT molecule adsorbed onto a gold surface. The molecular coordinates represent the following: Z' is the molecular axis, Y' is perpendicular to Z' and in-plane, while X' is perpendicular to Z' and out-of-plane. The aromatic ring is free to move relative to the metal surface through a tilt ( $\theta$ ) and twist ( $\psi$ ) angle. The tilt angle ( $\theta$ ) is the angle between the molecular axis and the surface normal. The twist angle ( $\psi$ ) is defined as the angle between the plane of the benzene ring relative to the plane formed by the molecular axis and the surface normal. The configuration of adsorbed 1,4-BDMT shown is of Cs symmetry, with the sulfur atom assuming an  $sp^3$  hybridization. This C-S-Au bond angle of  $109.5^\circ$  has been reported for compounds having a methylenethiol substituent on a benzene ring [46-49]. A molecular dynamics simulation predicted that benzylmercaptan (BM) deposits onto Au(111) in a nearly perfect herringbone structure, through  $sp^3$  hybridization of the sulfur end group [49].

We are interested in the projection of the vectors of the X' and Y' direction onto the Z-axis (active mode). The matrix for the transformation from the molecular coordinates to the surface coordinates is given by



**Figure 2.7:** Euler's angles for 1,4-BDMT adsorbed to the gold surface.  $X'$ ,  $Y'$ , and  $Z'$  represent the molecular coordinates, while  $X$ ,  $Y$ , and  $Z$  represent the surface coordinates.  $\theta$  is the tilt angle and  $\psi$  is the twist angle.

$$\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} \cos\psi & -\sin\psi & 0 \\ \sin\psi\cos\theta & \cos\psi\cos\theta & -\sin\theta \\ \sin\psi\sin\theta & \cos\psi\sin\theta & \cos\theta \end{pmatrix} \begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} \quad (2.11)$$

where  $x'$ ,  $y'$ , and  $z'$  are unit vectors in the  $X'$ ,  $Y'$ , and  $Z'$  axes respectively [42]. Solving the matrix for  $z$ , we get  $z = (\sin\psi\sin\theta)x' + (\cos\psi\sin\theta)y' + (\cos\theta)z'$ . We can now derive expressions for the absorbance  $A$  in  $x'$ ,  $y'$ , and  $z'$  as a function of the intensity of the electric field ( $E$ ), the transition moment ( $M$ ), as well as the tilt ( $\theta$ ) and twist ( $\psi$ ) angles from the surface normal.

$$A_{x'} = M^2 E_{x'}^2 \sin^2\psi \sin^2\theta \quad (2.12)$$

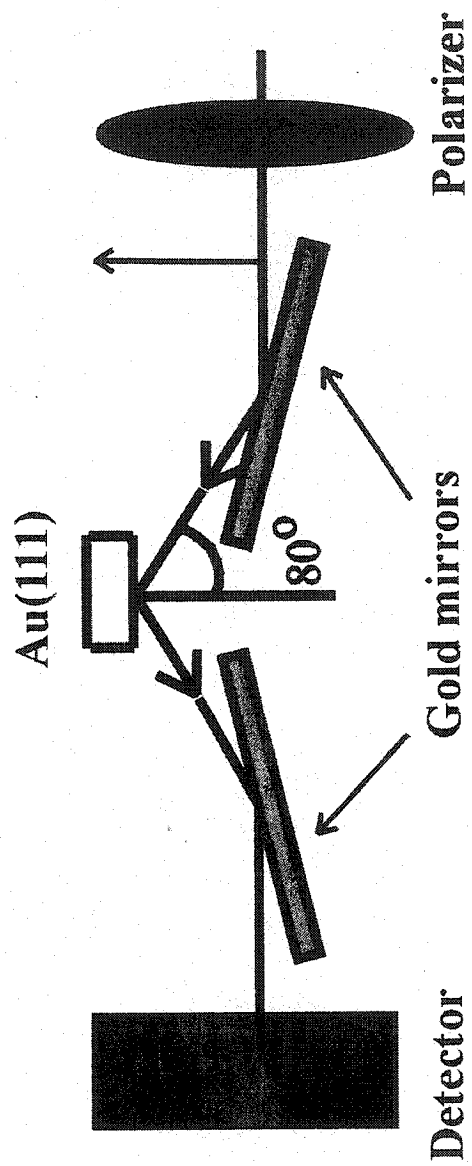
$$A_{y'} = M^2 E_{y'}^2 \cos^2\psi \sin^2\theta \quad (2.13)$$

$$A_{z'} = M^2 E_{z'}^2 \cos^2\theta \quad (2.14)$$

The proposed method uses the relative intensities of two vibrational modes whose transition dipole moment vectors are orthogonal (or not collinear) to one another. If the molecular axis is perpendicular to the metal surface, we do not have to account for rotation about the axis. In this configuration, the vibrations that are perpendicular to the molecular axis are parallel with the surface and therefore are not visible in IR. Rotation must be considered only when the adsorbed molecules are tilted from the surface normal. In this case, Euler's angles may be used to calculate the molecular orientation at the surface.

### ***Experimental***

The IRAS experiments were carried out with both a Nicolet Magna-IR 550 and a Nexus 670 spectrometer under a dry air atmosphere and the experimental setup is shown in Figure 2.8. A ZnSe wire grid polarizer was used to polarize the IR radiation of the incident beam perpendicular (i.e.  $p$ -polarized) to the sample surface. The gold mirrors were



**Figure 2.8:** IRAS experimental setup.

positioned to form a grazing angle of incidence of  $80^\circ$  between the surface normal and beam direction.

The intensity of the spectra is expressed in absorbance (A) and calculated using the following expression

$$A = -\log(I/I_0), \quad (2.15)$$

where I and  $I_0$  are the reflected intensities of the organic modified gold surface and clean gold surface respectively. The absorbance spectra presented here are an average of at least 1500 scans taken at a resolution of  $2\text{ cm}^{-1}$ .

The spectra in the high frequency region were generated using equation 2.15 directly. However, further manipulation of the low frequency spectra was required due to the presence of water bands. An absorbance spectrum was first generated for the modified sample. A second absorbance spectrum was generated for the clean sample alone, using a slight modification of equation 2.15, where now  $A = -\log(I_{oi}/I_{of})$ . In this case,  $I_{oi}$  represents a reference IR spectrum (i.e. clean gold surface) taken at an initial time and  $I_{of}$  represents a reference IR spectrum taken after a few hours of purging the sample. This absorbance spectrum was then subtracted from that of the modified surface to eliminate the bands due to water.

#### **2.4.2 High-Resolution Electron Energy-Loss Spectroscopy (HREELS)**

##### ***Theory***

HREELS is a very useful spectroscopic probe of both physical and chemical properties of surfaces [50]. It involves a monoenergetic beam of electrons, which is scattered from the surface under investigation. The energy lost by the electrons is then analyzed, and corresponds to vibrational or electronic excitations. HREELS has a high surface sensitivity

and can be used to probe all surface species, including hydrogen, which is difficult to detect with IR spectroscopy. Under optimal conditions, the instrumentation is capable of detecting surface adsorbate concentrations below 0.001 monolayer [39].

There are two main scattering regimes typically employed in HREELS. The dipole scattering mechanism is characterized by small scattering angles about the specular direction and low incident energies. The vibrational excitations result from the long range interactions between the electron beam and the dipole of the adsorbates. This selection rule is similar to the one described for IRAS, since the incident electrons interact mainly with the long range fields created by the oscillating dipole [39,50]. The spectra generated show electron energy losses arising from the vibrational excitation of modes of the adsorbate that possess a net change in dipole moment perpendicular to the metal surface.

A second scattering regime, characterized by large scattering angles (off-specular scattering) and higher incident energies is known as impact scattering. This component results from the short range interaction between the electron and molecule. In impact scattering, the electron does not “see” the electric field until it is very close to the metal surface, approximately a distance of 1 Å. It then penetrates the metal surface to a depth of around 10 Å, which implies that the inelastic event is initiated while the electron is within the metal and not above it, i.e. in vacuum. The selection rules are less restrictive for impact scattering than dipole scattering; both adsorbate modes vibrating parallel and perpendicular to the surface may be probed [39,50].

Data obtained from HREELS can be interpreted on several levels [50]. For our purposes, we used the energy loss peaks to characterize the surface composition of our adsorbate. Vibrational signatures were assigned to obtain a description of the molecular

species present at the surface. The main advantage of HREELS over IRAS is that it can readily scan the entire infrared region; in IRAS, the MCT-A detector cuts off near  $700\text{ cm}^{-1}$ . As a result, we have access to bands such as the S-S stretch located around  $500\text{ cm}^{-1}$  that we cannot probe with IRAS [4,51]. However, the resolution does not match that of IRAS; the resolution of HREELS is usually not better than  $50\text{ cm}^{-1}$ , while for IRAS it can be smaller than  $1\text{ cm}^{-1}$  [39, p414].

### ***Experimental***

In order to perform experiments involving the scattering of low energy electrons from surfaces, it is necessary to use spectrometers with an overall resolution greater than 30 meV [39]. This type of resolution is achieved by the spectrometer shown in Figure 2.9, which consists of two main parts. The first is a source producing a beam of highly monoenergetic electrons. The beam is directed towards the surface at a certain incident energy  $E_0$  (depending on the scattering regime) and is reflected at an energy  $E_0 - h\nu_{\text{vib}}$ , which is detected by the analyzer. The overall resolution of this combination can be varied between 7 and 150 meV independently of the primary electron energy (1 to 70 eV). The angular resolution is  $1.5^\circ$  [39]. 1,4-BDMT samples were introduced into the ultrahigh vacuum chamber via a load lock system. HREEL spectra were obtained using the LK3000 spectrometer (LK Technologies, Bloomington, IN) in specular mode at an incident energy of 4.0 eV. Spectral resolution was on the order of  $55\text{ cm}^{-1}$  (full width at half maximum of the elastic peak) at a count rate on the order of  $10^3$  cps.

### **2.5 Scanning Probe Microscopy (SPM)**

Scanning probe microscopes are a family of instruments used to study surfaces from the atomic to the micron level. All SPMs function on similar principles, and contain the

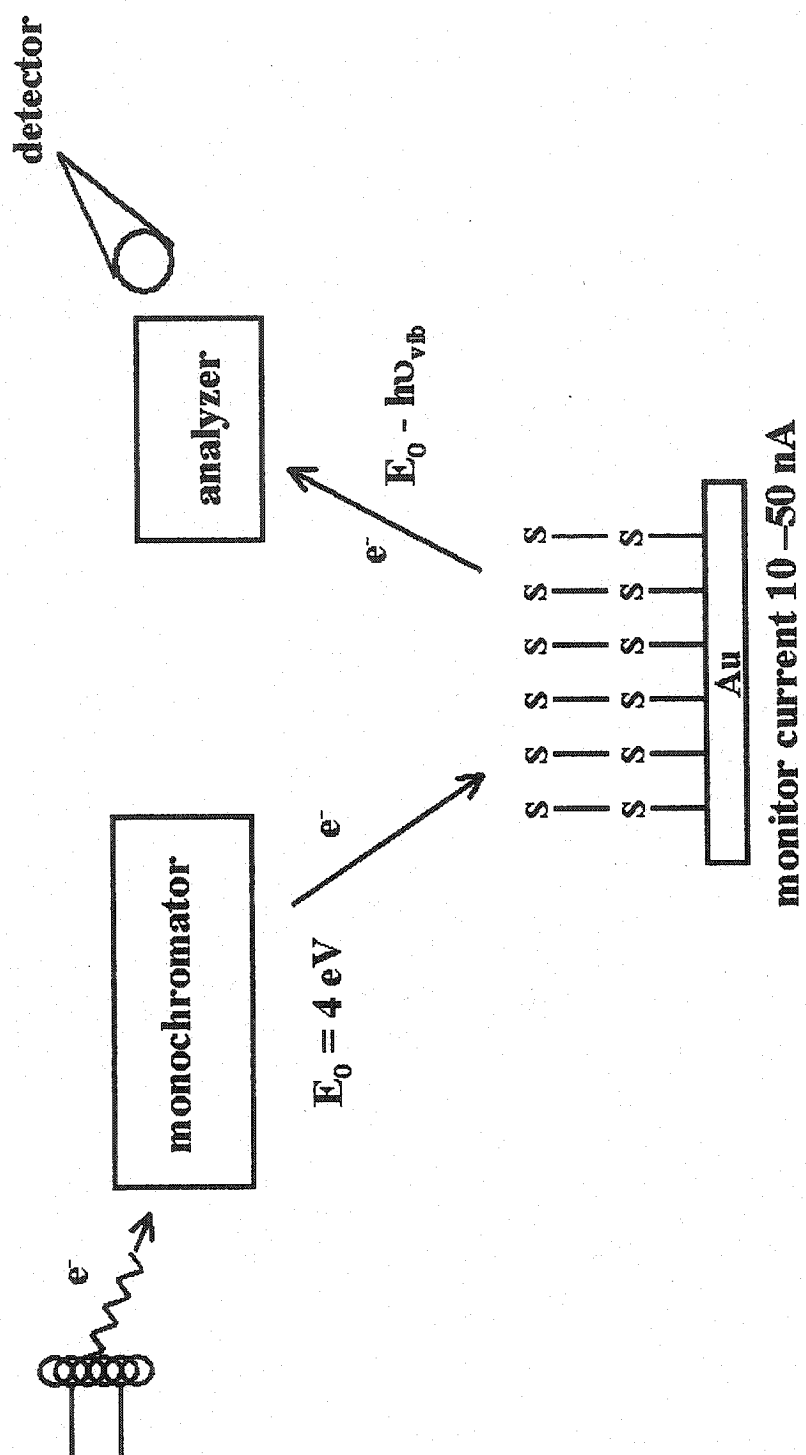


Figure 2.9: Schematic of a HREELS spectrometer .



components depicted in Figure 2.10 [52]. A course tuner is used to bring the probing tip into the vicinity of the sample. A feedback system is used to control the vertical position of the tip. A piezoelectric scanner rasters the tip over the sample (or the sample under the tip). A computer system drives the scanner, measures the data, and converts it into an image.

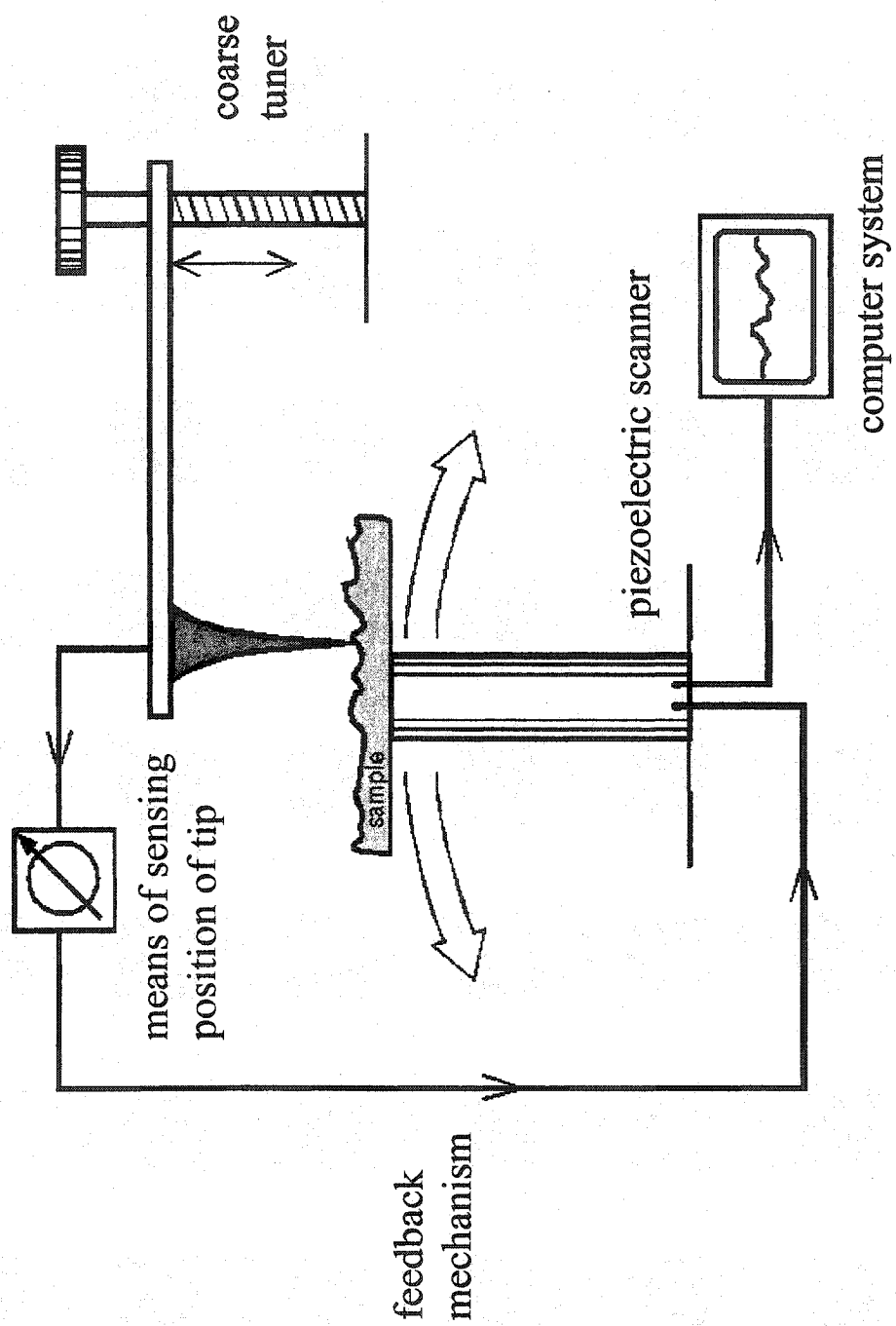
### 2.5.1 Atomic Force Microscopy (AFM)

#### *Theory*

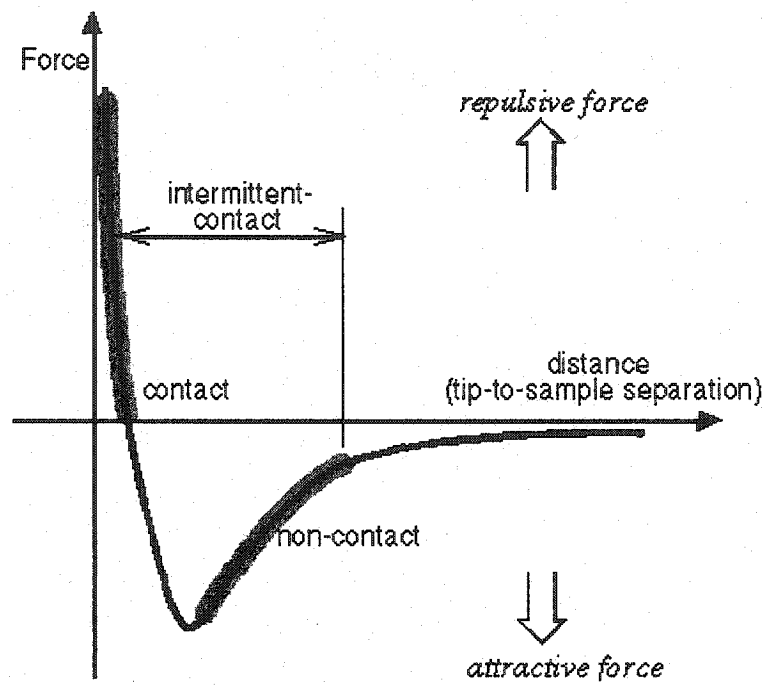
The atomic force microscope can be used to probe the surface of such samples as insulators, semiconductors, and electrical conductors with a sharp tip. Forces between the tip and sample cause the cantilever to bend, or deflect. A laser beam that is reflected from the back of the tip quantifies the deflection. A set of four photodetectors measures the cantilever deflection as the tip is scanned over the surface under study, and a computer then generates a map of the surface topography.

Several forces are involved in the deflection of the cantilever, but the one most commonly associated with AFM is the Van der Waals force, which is a weak interatomic force. Figure 2.11 plots the interatomic force versus the distance between the tip and sample [52]. Two distance regimes are shown, labeled as contact and non-contact. In the contact regime, the tip is held a few angstroms away from the sample surface, and the interatomic force between the cantilever and sample is a repulsive one. In the non-contact regime, the tip is held tens to hundreds of angstroms from the sample surface, and the interatomic force felt between the cantilever and sample is an attractive one. This attraction is as a result of the long range Van der Waals interactions.

The images presented in this thesis were obtained in contact AFM mode, also known as the repulsive mode, where the tip makes soft “physical contact” with the sample surface.



**Figure 2.10:** Schematic of a generalized scanning probe microscope (SPM). Copied from reference 52.



**Figure 2.11:** Interatomic force versus tip-sample distance curve. Copied from reference 52.

Examining the force curve in Figure 2.11 in more detail will illustrate better how such AFM images are obtained. Starting from the right side of the curve, the atoms of the tip and sample are far apart. As the atoms are brought closer together, they weakly attract. This attraction increases as the atoms are brought even closer, until they are so close that their electron clouds begin to repel. As the interatomic separation continues to decrease, this electrostatic repulsion weakens the attractive force. When the distance between the atoms reaches that of a chemical bond (a few angstroms in length), the force goes to zero. The atoms are in contact when the Van der Waals force is positive (repulsive).

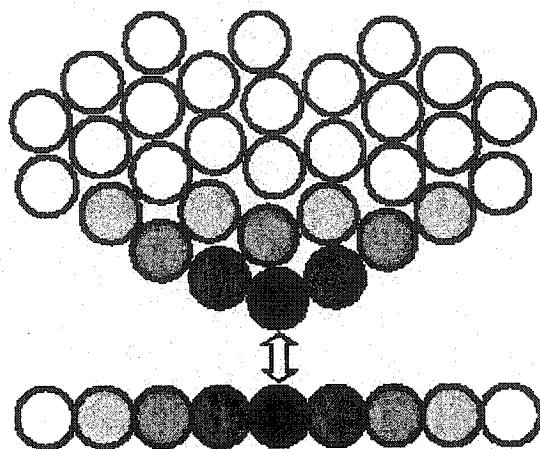
In addition to the repulsive Van der Waals force, two other forces are associated with contact AFM, namely a capillary force and the force exerted by the cantilever itself. The capillary force results from a thin water layer, which is often present under ambient conditions. The water wraps around the tip, applying a strong attractive force ( $10^{-8}$  N) that holds the tip in contact with the surface. The magnitude of the capillary force is dependent on the tip-to-sample separation. The force exerted by the cantilever is very similar to that of a compressed spring, and its magnitude and sign depend upon its deflection and spring constant.

As long as there is contact between the sample and tip, the capillary force remains essentially constant because it is assumed that the water layer is homogeneous and that the tip-to-sample distance is incompressible. The varying force is the one exerted by the cantilever, and therefore it is the determining factor of the overall force exerted by the tip. This total force on the tip must be balanced by the Van der Waals force in order to image in contact AFM mode. The magnitude of the total force exerted on the sample is typically in the range of  $10^{-7}$  to  $10^{-6}$  N.

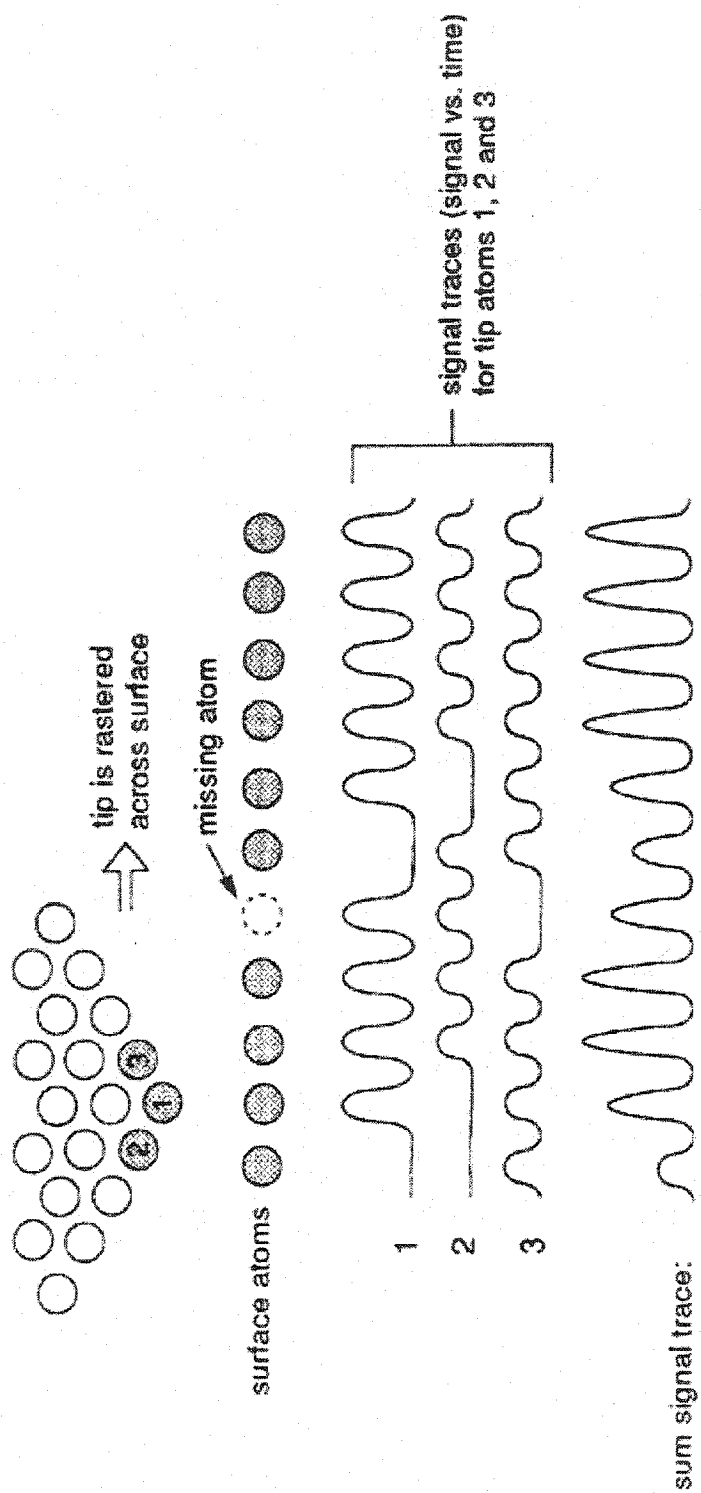
Once the AFM has detected the cantilever deflection, a topographic image is obtained in either constant-height or constant-force mode. In constant-height mode, the height of the scanner is fixed and the topograph displayed is a measure of the deflection of the cantilever. In contrast, constant-force mode requires the cantilever deflection to be maintained, while the scanner responds by moving in the  $z$  direction. In this case, the topograph is obtained from the scanner's motion.

For AFMs, the dependence of the cantilever deflection on the tip-to-sample separation is weak, and as a result, several atoms on the tip can interact simultaneously with several atoms on the sample (Figure 2.12) [52]. A perfect example of how this multiple interaction of AFM tip atoms and sample atoms can affect the image is provided in Figure 2.13 [52]. Three tip atoms are assumed to interact with the surface and their respective signal traces are shown as a function of time, where the signal reflects the interatomic force between the given tip atom and the surface atom beneath it. Time zero is defined when tip atom 3 comes into contact with the first surface atom, some signal is registered at this point and is shown in trace 3 of Figure 2.13. At the next instant in time, atom 1 detects the first surface atom, atom 3 detects the second surface atom, and atom 2 has not yet contacted any atoms. At the third instant in time, all three tip atoms detect a surface atom and the signals vary in intensity according to their distance from the surface.

Since the tip atoms are displaced laterally, they produce signal traces that are offset from one another, and the resulting image is a combination of the contribution of the interacting tip atoms. As a result, in the given example, no atomic vacancy is detected. This is a simple case whereby only three tip atoms are interacting with the surface. In reality, several tip atoms are interacting with several surface atoms at a time. Therefore, features



**Figure 2.12:** Interatomic interaction between the tip and sample in AFM. The shading shows the strength of the interaction, where the darkest coloring represents the strongest interaction. Copied from reference 52.



**Figure 2.13:** AFM scan of an atomic-scale periodic lattice, showing the sum signal trace of three tip atoms interacting with the surface atoms. The atomic vacancy is shifted in the summed trace and not well resolved. Copied from reference 52.

such as atomic vacancies would be even less well defined and shifted even further. Although the periodicity of the lattice is reproduced, true atomic resolution is not achieved.

### ***Experimental***

All AFM images were taken in constant-force mode (i.e. height mode) and under ambient conditions using a Digital Instrument Nanoscope II (Santa Barbara, CA). Various scanners are available for use with the MultiMode™ SPM. Each scanner exhibits its own unique piezo properties, and has a certain range of capabilities. The “E” scanner was used to obtain molecular resolution, having a scan size of 10  $\mu\text{m}$  x 10  $\mu\text{m}$  and a vertical range of 2.5  $\mu\text{m}$ . After a sample was loaded, the instrument was allowed to come to thermal equilibrium, which required about 30 minutes. Oxide-sharpened silicon nitride cantilevers with square pyramidal tips (Digital Instruments, Veeco) were used. The horizontal displacement of the tip was calibrated using hexadecanethiol modified gold films.

### **2.5.2 Scanning Tunneling Microscopy (STM)**

#### ***Theory***

Unlike in AFM, insulating materials cannot be imaged with STM. The principle behind STM is that a bias voltage is applied between the conducting tip and sample [53-55]. When the tip is brought into close proximity of the sample ( $\sim 10$  Å), electrons from the sample “tunnel” through the gap into the tip or vice versa, depending on the sign of the applied bias voltage. The resulting tunneling current ( $I_t$ ), which varies with the tip-to-sample separation, is the signal used to create the STM image. In order for tunneling to take place, both the tip and sample must either be a conductor or semi-conductor.

STMs can scan a sample in one of two modes, constant-height or constant-current mode. In constant-height mode, the tip is rastered over the sample and the tunneling current



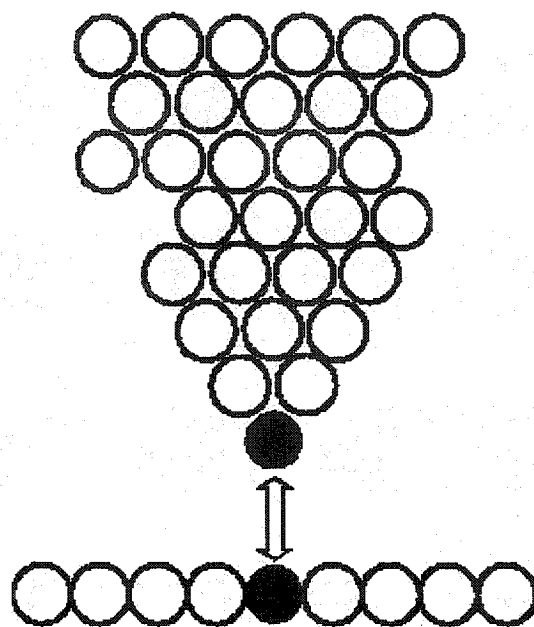
varies depending on the local electronic properties of the sample. It is this tunneling current, which constitutes the data set, i.e. image obtained. In constant-current mode, a feedback mechanism keeps the current constant by adjusting the height of the scanner at each point of measurement. For instance, if the tunneling current were to decrease, the system adjusts the voltage applied to the piezoelectric scanner to decrease the tip-to-sample separation. In this case, the motion of the scanner determines the data set. All of the STM images to be presented were imaged in constant-current mode.

An image obtained in constant-current mode maps the topography of the sample. The tunneling current imaged corresponds more accurately to the electronic density of states at the surface. STMs can sense the number of filled or unfilled electronic states near the Fermi surface within the energy range determined by the bias voltage. Rather than imaging the physical topography of the sample, STMs image a surface of constant tunneling probability. STMs can therefore be used as a surface analysis tool that can probe the electronic properties of the surface with true atomic resolution. AFMs, on the other hand, have a lateral resolution of about 10-20 Å with the sharpest tips commercially available. The distinction between imaging *atomic-scale features* (AFMs) versus *true atomic resolution* (STMs) lies in the respective tips' shape. Because the tunneling current has an exponential dependence on the tip-to-sample separation, only the closest atom on the STM tip interacts with the closest atom on the sample surface, as illustrated in Figure 2.14 [52]. This contrasts the multiple interaction of AFM tip atoms and sample atoms shown in Figures 2.12 and 2.13.

### ***Experimental***

All STM images were taken in constant-current mode and under ambient conditions using a Digital Instrument Nanoscope II (Santa Barbara, CA). The "E" scanner head was

used to obtain atomic resolution. Mechanically cut platinum/iridium tips were used, having a length of 6.35 mm and a base width of 250  $\mu\text{m}$  (Digital Instruments, Veeco). After a tip was loaded into the SPM head, sufficient time (1 hour) was provided for it to “relax” into place before imaging. The horizontal displacement of the tip was calibrated using a freshly cleaved sample of graphite.



**Figure 2.14:** Interatomic interaction between the tip and sample in STM. The shading shows the strength of the interaction, where the darkest coloring represents the strongest interaction. Copied from reference 52.

## 2.6 Gaussian<sup>®</sup> Calculations [1]

### Theory

Computational chemistry simulates chemical structures and reactions, either through molecular mechanics or electronic structure theory. Both areas perform the same basic types

of calculations: 1. computing the electronic energy of a molecular structure, 2. performing geometry optimizations to locate ground states, transition states, and excited states, and 3. computing the vibrational frequencies of molecules and other properties such as NMR [56, p3].

Molecular mechanics calculations use the laws of classical physics and perform computations based upon nuclear interactions. They do not explicitly treat the electrons in a molecular system. This makes them ideal for calculations of very large systems, because they are computationally inexpensive. On the other hand, this also limits their potential for application on chemical problems where electronic effects are important. For example, they cannot be used to describe bond dissociation/formation.

Electronic structure methods are useful in these cases. They use the quantum mechanical Schrödinger equation as the basis for their computations:

$$H\Psi = E\Psi, \tag{2.16}$$

where  $H$  is the Hamiltonian operator,  $\Psi$  is the wavefunction of the positions of the particles (i.e. electrons and nuclei) within the molecule, and  $E$  the energy of the particles. For most systems, exact solutions to the Schrödinger equation are not practical or known. Electronic structure methods are characterized by their approximations to its solution.

There are two major classes of electronic structure methods, semi-empirical and *ab initio* calculations. The main difference between the two is the trade-off between computational cost and accuracy of results. Semi-empirical methods are relatively inexpensive, but do not provide as high quality predictions for as broad a range of systems as do *ab initio* computations. A suitable method and basis set must be selected for a given chemical problem. A basis set is the mathematical description of the orbitals in the system

under investigation used to perform the calculation. Larger basis sets more closely approximate the orbitals by imposing fewer restrictions on the electrons' locations.

### ***Experimental***

*Gaussian*® 98 [1] was used to compute the vibrational spectra of molecules in their ground state. The structure was first optimized at a Hartree Fock (HF) level of theory with a 3-21G basis set. The coordinates of the geometry minimum were then used to run an optimization and frequency calculation using HF/6-31G\*. The predicted frequencies and intensities were used to assign the IRAS spectra. *Gaussview*® was utilized to visualize the unit dipole vector displacements corresponding to specific vibrational modes.

## **2.7 Gold Samples Preparation**

### ***Theory***

Surface processes are strongly influenced by the crystallographic orientation of the substrate. Different orientations could display different reactivities. This makes mechanistic studies of surface processes occurring at polycrystalline substrates difficult. Therefore, single crystal surfaces are used for such studies. The Au(111) orientation is the most readily used gold surface in the study of the oxidative and reductive processes of thiols. Furthermore, gold often crystallizes in this orientation, since the Au(111) face is the most stable and compact surface. For electrochemical studies, it has the most positive potential of zero charge, 0.28 V in 0.1 M KOH [57]. Gold is electrochemically inactive over a large range of potentials. This allows for a well resolved separation between the reductive desorption of the thiol, and the more negative potential for hydrogen evolution in aqueous solution [58]. Monolayers of thiols at the Au(111) also have the highest packing density when compared with the other orientations [29].

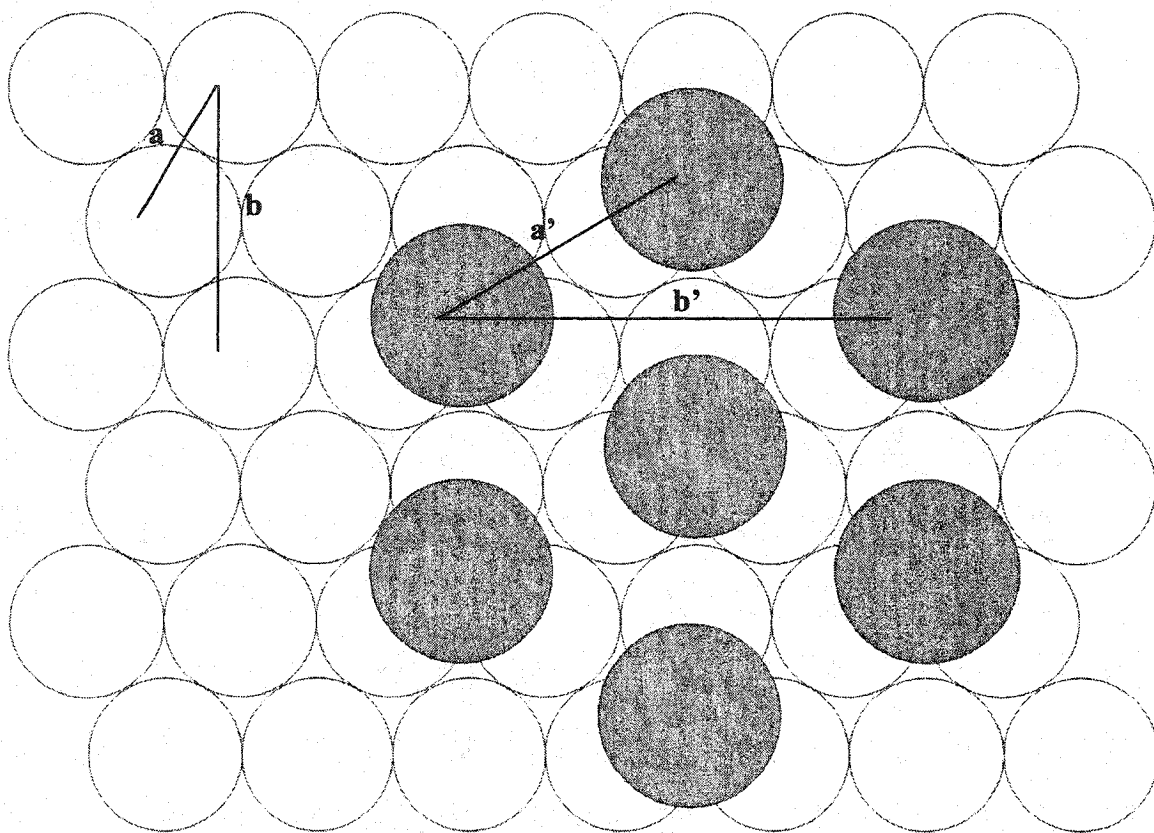
The Au(111) surface has a hexagonal symmetry and is shown in Figure 2.15. The white circles represent the gold atoms and the shaded ones represent the alkanethiol adlayer. The typical organization adopted by alkanethiols onto the gold surface is the well known commensurate  $(\sqrt{3} \times \sqrt{3})R30^\circ$  structure. This two-dimensional arrangement was previously determined for these types of monolayers using helium diffraction [59] and STM [7] techniques. The distances labeled in the drawing indicate the nearest- (a and a') and next-nearest-neighbor (b and b') spacings. The values of a and b for the gold lattice are 0.29 and 0.50 nm respectively [5]. The values of a' and b' for the  $(\sqrt{3} \times \sqrt{3})R30^\circ$  alkanethiol adlayer are 0.50 and 0.87 nm respectively [5]. This yields a surface concentration of  $7.6 \times 10^{-10}$  mol  $\text{cm}^{-2}$  for a complete monolayer of alkanethiols [58].

### 2.7.1 Au(111) Single Crystal

#### *Experimental*

The Au(111) single crystal electrode was melted using an induction furnace (Elma Engineering, California) from pure gold (99.999%, Engelhard). Laue X-ray back reflection was used to orient the crystal to within  $\pm 0.5^\circ$  of the (111) plane. The crystal was then mechanically polished using a high quality silicon carbide polishing paper (Tech-Met Canada and Struers) of three different grades, first the 1200 was used, then the 2400, and finally the 4000 grade. The polishing was continued on cloths (Technotorn cloth, Leco) having 6, 1, and 0.1  $\mu\text{m}$  diamond suspensions (Metadi, Buehler). The crystal was sonicated between polishing steps (Sonicator 2210, Branson) to remove any debris acquired during polishing.

The mechanical polishing was followed by electrochemical polishing to remove microscopic defects. The Au(111) was oxidized in a 0.1 M  $\text{HClO}_4$  (Seastar Chemicals) solution for about 10 minutes at a constant current density (galvanostatic) of  $100 \text{ mA cm}^{-2}$



**Figure 2.15:** Top view of a  $(\sqrt{3} \times \sqrt{3})R30^\circ$  alkanethiol adlayer (shaded circles) and the hexagonal Au(111) surface atoms (open circles). The distances labeled indicate the nearest- (a and a') and next-nearest-neighbor (b and b') spacings.

(Pine Model AFRDE5, potentiostat/galvanostat). It was then dipped into a 10-20% HCl (Fluka) solution for about 30 seconds to remove the gold oxide. Finally, it was rinsed with Milli-Q water and the process was repeated several times.

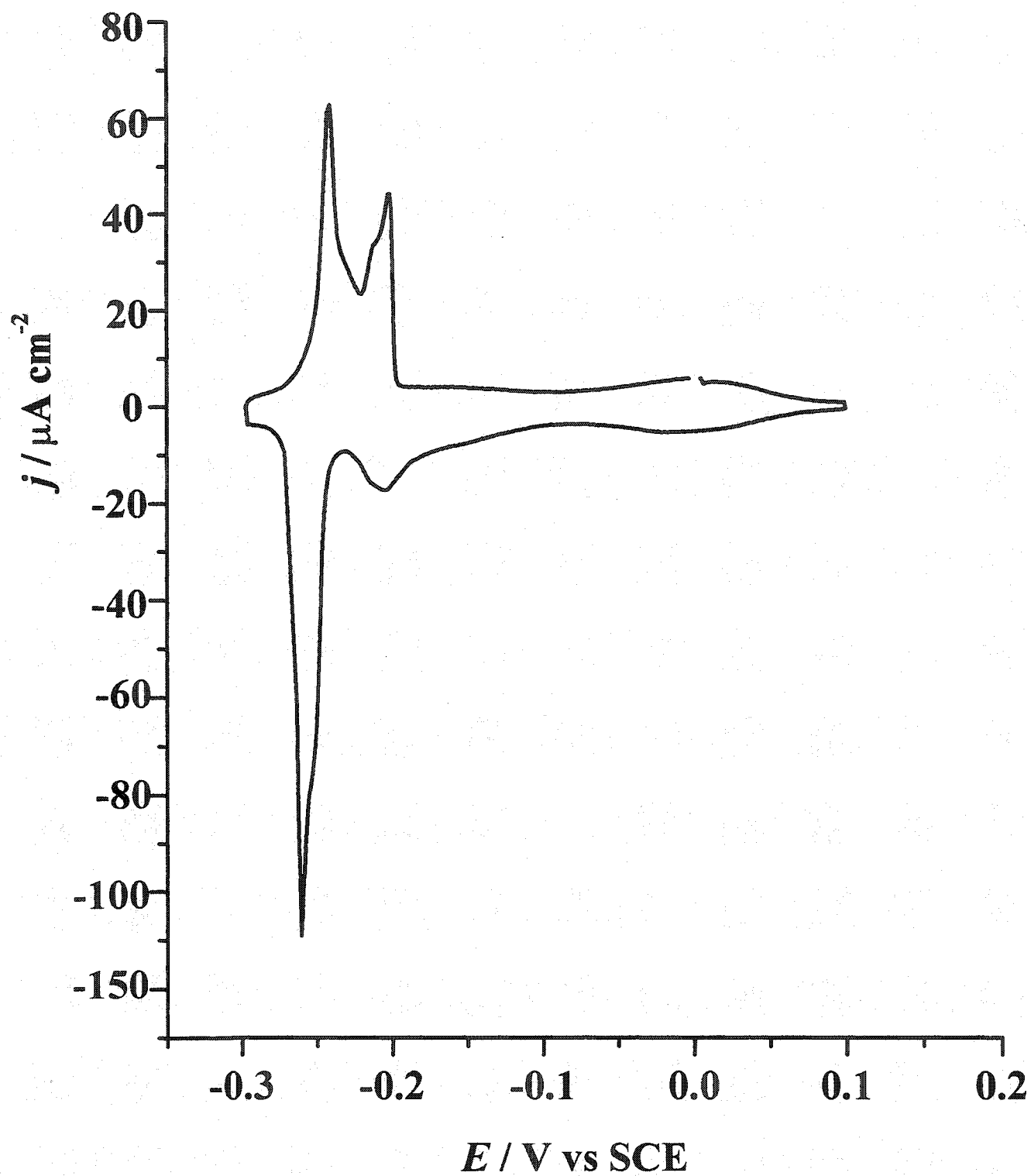
The gold single crystal was flame annealed (prior to every experiment) in natural gas to eliminate any surface stress and organic impurities. The quality and the cleanliness of the Au(111) working electrode and the rest of the electrochemical setup were tested by recording a cyclic voltammogram in 0.5 M KOH. Different gold oxide formation in the voltammetry is expected for varying crystallographic orientations. The “fingerprint” voltammogram for our Au(111) single crystal in 0.5 M KOH compares well with the literature [60].

The geometric area of the prepared single crystal was calculated to be  $0.19 \pm 0.01$  cm<sup>2</sup>. An electroactive area of  $0.18 \pm 0.01$  cm<sup>2</sup> was determined from lead underpotential deposition (UPD) experiments done in a 5 mM Pb(ClO<sub>4</sub>)<sub>2</sub> (Aldrich, 99.995+%) and 0.1 M HClO<sub>4</sub> solution and shown in Figure 2.16 [61]. A roughness factor of  $1.0 \pm 0.1$  was obtained from the above values. This single crystal was used as the working electrode in all of the electrochemical experiments.

## 2.7.2 EQCM Gold Quartz Crystal

### *Experimental*

The AT-cut quartz crystal, as well as the Teflon<sup>®</sup> crystal holder and Viton<sup>®</sup> o-rings were cleaned prior to running an EQCM experiment. The gold electrode was assembled into the teflon holder and covered with concentrated sulfuric acid for 5 minutes, followed by rinsing with Milli-Q water. It was then placed into ethanol for 10 minutes and rinsed again. A similar cleaning procedure was used on the holder and o-rings. All of the parts were stored in Milli-Q water until they were used.



**Figure 2.16:** Lead UPD on a Au(111) single crystal. Potential scan rate:  $20 \text{ mV s}^{-1}$ . See text for details.



A cyclic voltammogram was taken in 0.5 M KOH [60] and showed features atypical of a Au(111) surface, e.g. a broad oxidative peak right before the gold oxide formation for the (111) orientation, with its corresponding reductive peak. This implies that the gold-coated quartz crystal is in fact slightly polycrystalline in nature (i.e. it contains domains of different crystallographic orientations). This is reflected in the roughness factor, which has been previously reported to be about 1.3 to 1.5 for these particular electrodes [13].

### 2.7.3 Gold Films on Glass (Arrandee™)

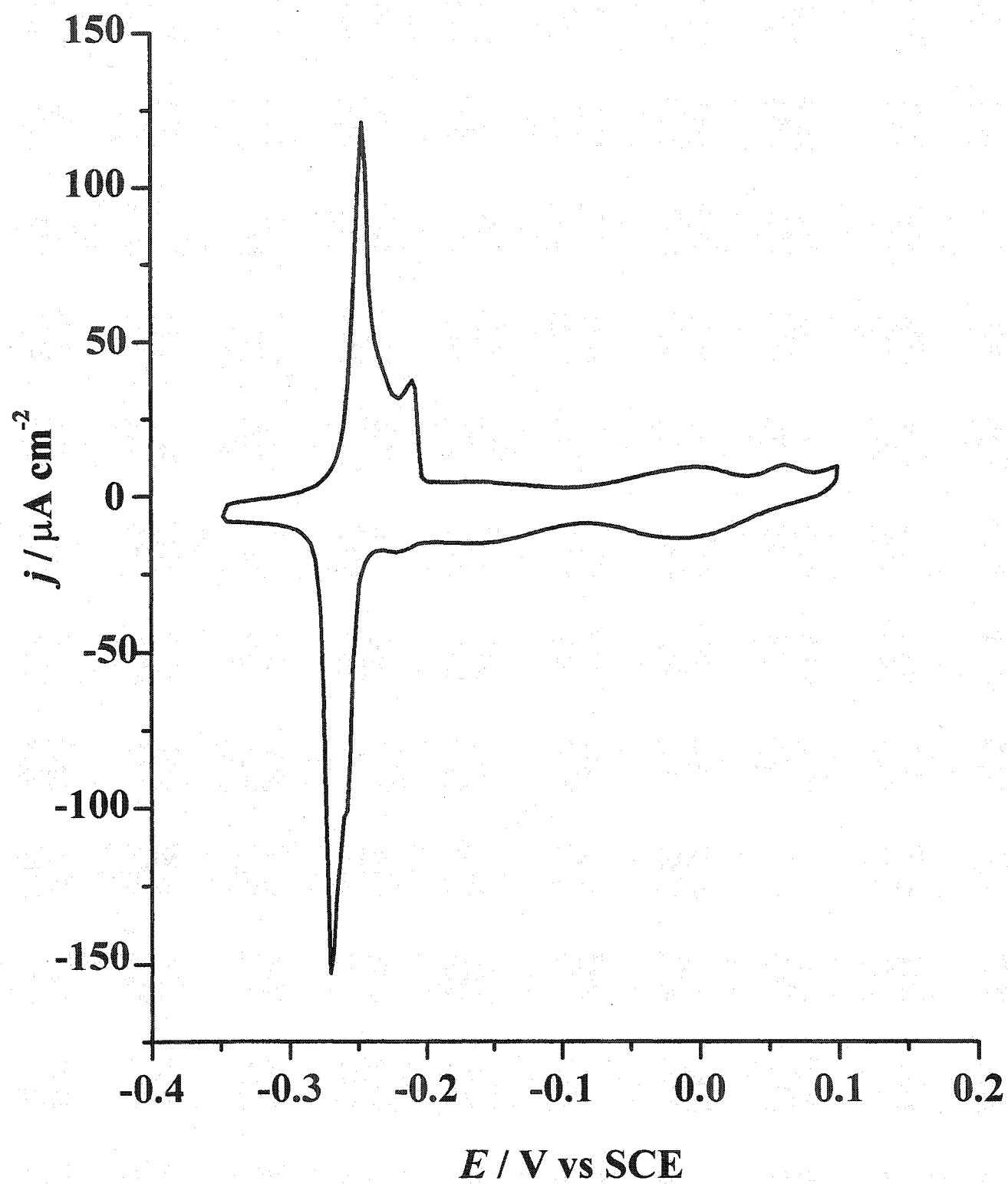
#### *Experimental*

The gold films (Arrandee™) used in the IRAS, HREELS, and SPM microscopy measurements were  $12 \times 12 \pm 0.2$  mm in dimension. They consisted of a gold layer of  $250 \pm 50$  nm deposited onto a  $1.1 \pm 0.1$  mm thick portion of borosilicate glass, with a  $2.5 \pm 1.5$  nm chromium adhesive layer. The gold sample was first rinsed with Milli-Q water and dried under a stream of nitrogen. It was next cleaned in a piranha solution (70% conc.  $\text{H}_2\text{SO}_4$  and 30%  $\text{H}_2\text{O}_2$ ) for 5 seconds, followed by rinsing with Milli-Q water and drying under nitrogen. A butane torch was used for annealing, which was performed in a dark room. When the sample glowed red, the flame was removed and the sample allowed to cool. This procedure was repeated two to three times. The sample was rinsed once more with Milli-Q water and dried prior to use.

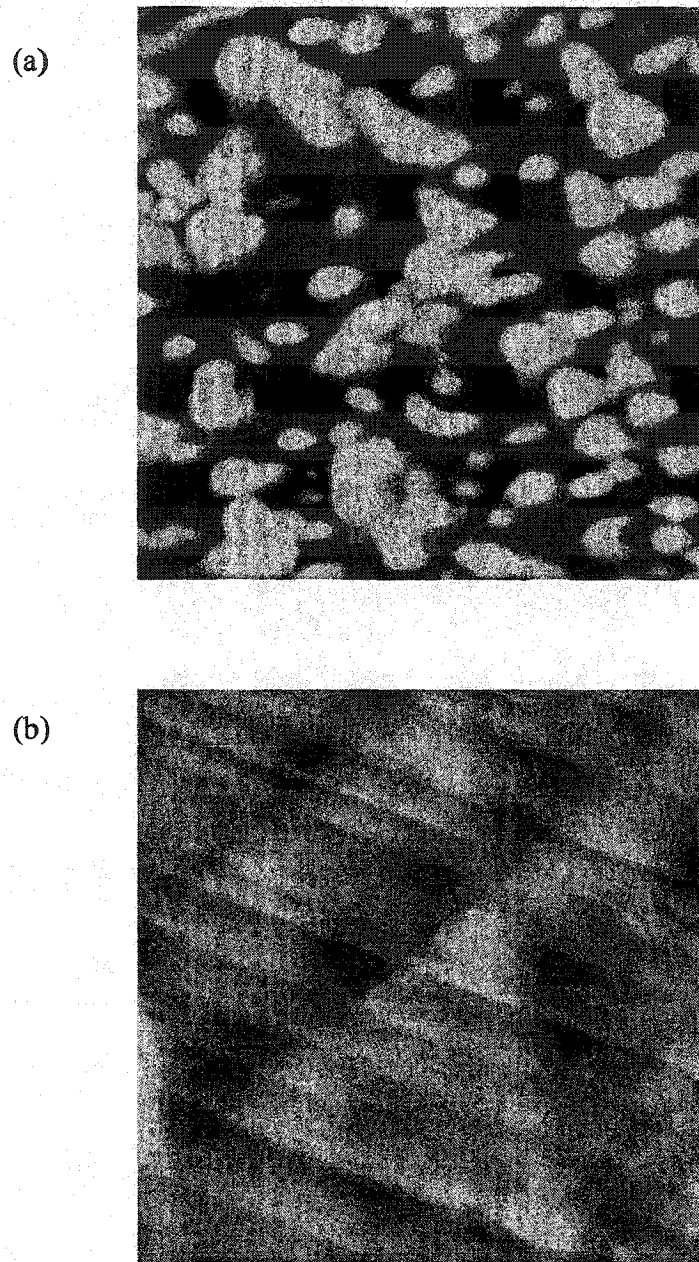
Cyclic voltammetry in 0.5 M KOH was used to test the quality of the flame-annealed surface using the three-electrode cell setup in Figure 2.2. The film was suspended (by one corner) in the electrolyte solution using an alligator clamp. Great effort was taken to ensure as much of the entire surface was inserted into the solution. Since we were unable to

quantify the exact area of the electrodeposited sample, we cannot comment on the absolute intensities between IR spectra obtained electrochemically, versus through incubation.

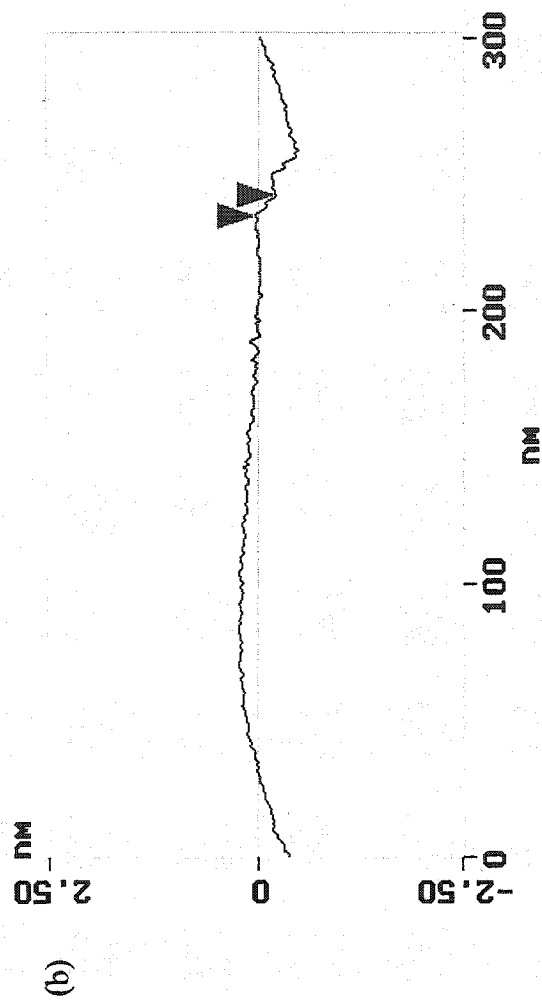
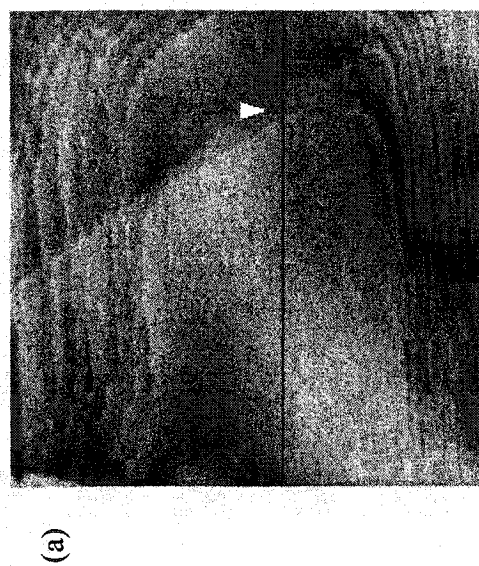
The typical “fingerprint” oxide formation was found in 0.5 M KOH and deemed to be comparable to that of a gold single crystal [60]. A roughness factor of  $1.2 \pm 0.1$  was determined from lead UPD experiments [61] using a slight modification of the crystal holder for EQCM measurements (geometric area:  $0.50 \text{ cm}^2$ ). The lead UPD voltammogram is presented in Figure 2.17 and compares well with the voltammetry in Figure 2.16. AFM and STM results presented in Figures 2.18 and 2.19 respectively, show large Au(111) terraces separated by monatomic steps.



**Figure 2.17:** Lead UPD on flame annealed gold films. Potential scan rate:  $20 \text{ mV s}^{-1}$ .  
See text for details.



**Figure 2.18:** AFM images covering 500 nm x 500 nm of (a) polycrystalline gold and (b) the 120/60 degree step edges that are typical of (111) domains after sample annealing.



**Figure 2.19:** (a) A 300 x 300 nm constant-current STM topograph of Au(111). (b) A cursor profile indicated in (a), which shows a 2.38 Å monatomic height separation between terraces. Imaging conditions: 20.0 mV and 1.0 nA.

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## Chapter 3: Electrodeposition of Bilayers of 1,4-Benzenedimethanethiol (1,4-BDMT) on

### Au(111)

#### 3.1 Introduction

Monolayer by monolayer growth of organic films is a synthetic approach that could lead to new materials. Dithiols are simple compounds that may be used for the step-wise growth of a bilayer, if one of the thiol end groups of the monolayer is available for reactivity. The bilayer would be formed via oxidative dimerization of an adsorbed dithiol and a dithiol in solution, which would chemically link the two molecules through a S-S bond.

Various adsorption mechanisms and reactivity of dithiol monolayers have been previously reported [1-36]. For instance, gaseous 1,6-hexanedithiol was found to adsorb flat onto a gold surface via its two sulfurs [1]. In contrast, when deposited onto Au(111) from organic solution, 1,6-hexanedithiol adopted an upright configuration [1,2]. Upon thermal treatment [1] or application of negative potentials [2], desorption was induced and a flat-lying configuration of 1,6-hexanedithiol was obtained. This binding of both sulfurs to gold has also been observed for chelating alkyl [3,4] and aromatic [5,6] dithiols.

On the other hand, several studies disagree with this flat orientation and suggest that the hydrocarbon [1,2,7-13,28-32] or aromatic [7,10,15-22,33-36] backbones in dithiol monolayers are positioned relatively vertical to the gold surface. Adsorption of the dithiol (from solution) through a single S-Au bond leaves the other sulfur accessible for a variety of chemical reactions through oxidation [7-22,28-36]. For example, it has been demonstrated that dithiols can be reacted with nanoclusters [7,15,17,29-32] or can be complexed with metal ions [8-10,18,19]. In other studies, the unreacted sulfur of the adsorbed dithiols has been oxidized to form inhomogeneous bilayers and multilayers [11-13,16,20-23,33].

These studies show that various structures and coverages can be formed by dithiols [1-36]. Obviously, the conditions of deposition have an effect on their adsorption geometry. It seems that the solvent type, the dithiol concentration, the incubation time, the purity of the dithiol solution, and the metal substrate preparation all influence monolayer growth. More specifically, it is likely that the lack of control of the oxidant concentration (e.g. oxygen), which is required for the formation of a S-S bond (i.e. bilayer), is responsible for the varying reactivities that have been observed.

Most previous studies on the adsorption of dithiols on Au (111) have been carried out under open circuit conditions, i.e. without application of an electric field [1-22,28-36]. Chemical incubation has several limitations, which makes it difficult to control monolayer formation: 1. the time scale required to form an organized layer is relatively long, 2. it is sensitive to contaminants, 3. it is difficult to control the thiol coverage, and 4. there is little selectivity, e.g. formation of hybrid systems in a reproducible way is difficult to achieve.

To better control the self-assembling process, electrodeposition of thiols on gold has been used [37-45]. This method of deposition only takes a few seconds and does not affect the quality of the films. Contaminants can easily be detected through cyclic voltammetry and thus a clean cyclic voltammogram is essential. By changing the potential limits, the number of moles of electrons transferred, i.e. the surface concentration, can be controlled. By varying the deposition potential, different molecules can be selectively adsorbed to form multi-component systems. To summarize, the electrodeposition of organic monolayers is time efficient, reproducible, easily controlled, and allows for selective adsorption.

The rate of the oxidative deposition of dithiolates, and their reactivity was controlled by applying a potential to the Au(111) electrode. In this chapter, we report on the

electrochemical formation of a complete monolayer of 1,4-benzenedimethanethiolate at the gold surface. The sulfur endgroup/solution interface then serves as a platform for oxidative reactivity; by scanning the potential towards more positive values, the adsorbed dithiolates are subsequently reacted with dithiolates in solution to form a bilayer.

1,4-BDMT was selected as the dithiol of interest because of its rigid structure due to the presence of the aromatic ring. When compared with an alkanedithiol of similar chain length, e.g. 1,6-hexanedithiol, it is expected that 1,4-BDMT is more likely to bind via a single sulfur to the gold surface than its more flexible alkyl-counterpart. In addition, aromatic rings have larger dimensions and can interact with each other through electrostatic forces, i.e.  $\pi$ - $\pi$  interactions. These  $\pi$ -electron systems also pose as pathways for electron transfer.

Recently, self-assembled monolayers (SAMs) of conjugated thiols have been extensively studied [16,46-63]. Conjugated molecules are useful for potential molecular electronics applications because they are electrically conducting. The electronic properties of these SAMs are greatly influenced by their molecular arrangement. Therefore, it is very important to control the molecular ordering and arrangement during the adsorption process. Even more so, when the molecule is bifunctional, as is the case with 1,4-BDMT.

## **Results and Discussion**

### **3.2 Electrochemical Deposition**

#### **3.2.1 Oxidative Deposition of Monolayers of 1,4-BDMT**

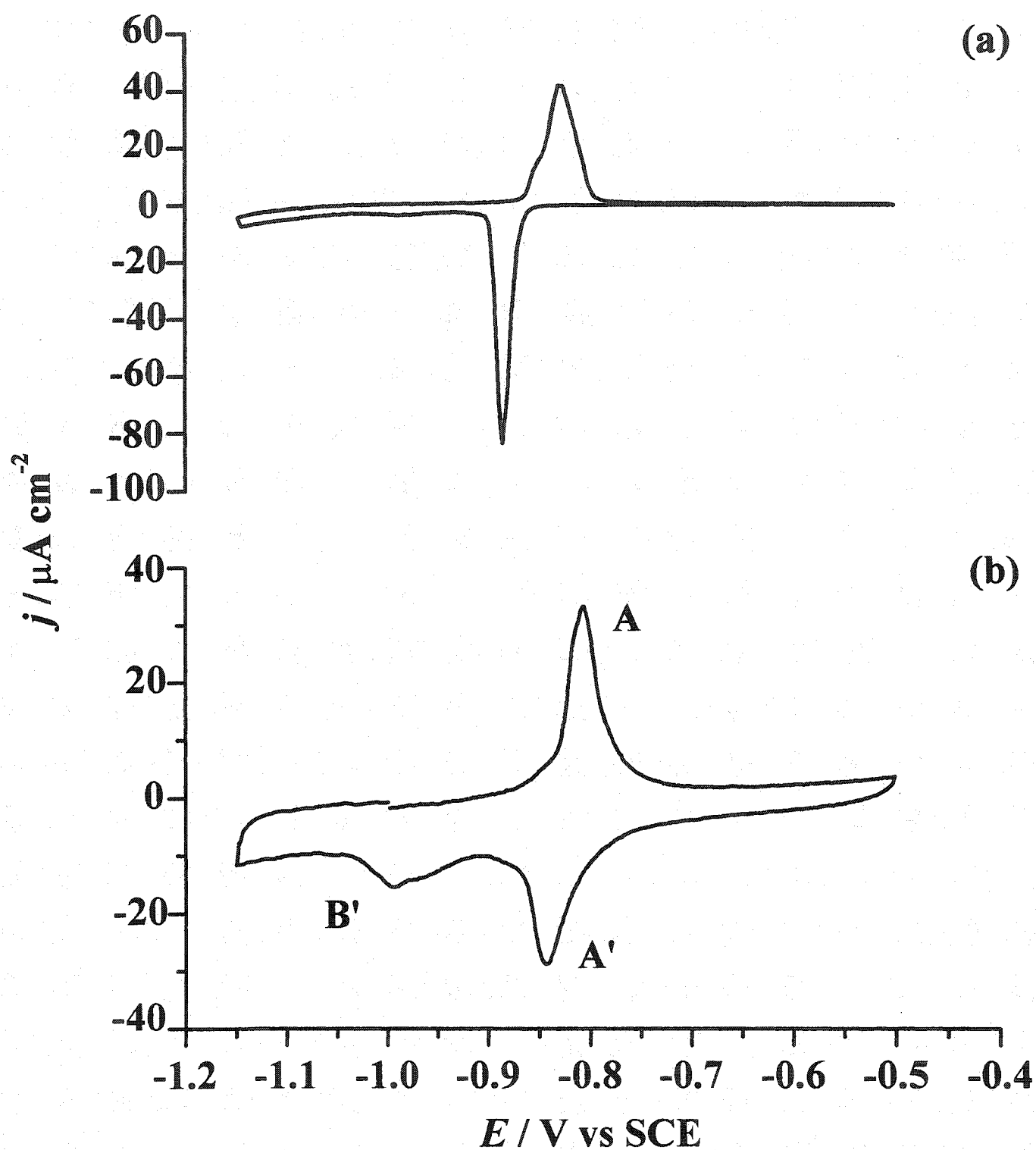
The oxidative electrodeposition of simple alkanethiols has been shown to yield ordered monolayers with properties identical to those of monolayers obtained without potential control [42,44]. However, this method has not been used to deposit more complex

thiols. We thus verified that a simple aromatic thiol, benzylmercaptan (BM), could be electrodeposited to form a monolayer with similar properties to those of a monolayer formed in the absence of applied potential [55].

The oxidative deposition of a BM monolayer onto a Au(111) single crystal from a 0.5 M KOH solution was examined and is shown in Figure 3.1a. The potential was initially held at  $-1.00$  V for 5 minutes in order to obtain an uncoated Au(111) surface. The potential was then scanned at  $20 \text{ mV s}^{-1}$  towards more positive values ( $-0.50$  V) to oxidatively deposit the aromatic thiolates. The subsequent negative potential scan going from  $-0.50$  V to  $-1.15$  V, corresponds to the reductive desorption of the BM monolayer. Narrow and symmetric oxidative and reductive current peaks are observed at  $-0.83$  V and  $-0.88$  V respectively. The small separation ( $\Delta E_p$ ) of  $50$  mV between the two implies that the electrochemistry of BM at the gold surface is a relatively reversible process.

The baseline corrected oxidative charge ( $Q$ ) is a measure of the surface concentration ( $\Gamma$ ) of the benzylmercaptans [41]. Assuming a one-electron adsorption process, a  $\Gamma$  of  $7.6(\pm 0.5) \times 10^{-10} \text{ mol cm}^{-2}$  was calculated. This value is identical to the one obtained by Tao et al. [55] from the reductive desorption current peak for a monolayer formed by the spontaneous adsorption of BM from an ethanol solution. This implies that the electrodeposited monolayers of BM are comparable to those obtained through chemical deposition.

Having established that we could reproduce the chemistry of BM at the gold electrode through application of an electric field, we decided to investigate the electrochemistry of 1,4-BDMT. This allowed us to explore the effect of a second methylenethiol group in the *para* position of the benzene ring on monolayer formation.



**Figure 3.1:** Cyclic voltammograms of the oxidative adsorption and reductive desorption of a monolayer of (a) BM in 0.1 M KOH and (b) 1,4-BDMT in 0.5 M KOH at a Au(111) surface. Potential scan rate: 20 mV s<sup>-1</sup>.

The cyclic voltammogram for the oxidative deposition of 1,4-BDMT from 0.5 M KOH is presented in Figure 3.1b and scans the same potential range as that applied to the BM system. The oxidative current peak A is narrow and fairly symmetric, which implies that the electrodeposition of 1,4-BDMT is a relatively homogeneous process [64, p521]. On the reverse scan, a symmetric cathodic peak A' at  $-0.84$  V is followed by a smaller peak B' at  $-0.99$  V. Peak A' is assigned to the reduction of a monolayer of 1,4-BDMT, and we attribute peak B' to inhomogeneous bilayer formation (details to follow). A small separation of 30 mV between the peaks A and A' ( $\Delta E_p$ ) suggests that the oxidative deposition/reductive desorption of a monolayer of 1,4-BDMT is a relatively reversible process.

Since the oxidative peak potentials of both molecules are comparable ( $-0.83$  V for BM and  $-0.81$  V for 1,4-BDMT), this suggests that they undergo the same binding mechanism to gold via one sulfur. Furthermore, integration of the anodic peak A of 1,4-BDMT revealed a similar charge to that of BM,  $73 \pm 4 \mu\text{C cm}^{-2}$  and  $74 \pm 4 \mu\text{C cm}^{-2}$  respectively. The corresponding surface concentration was then calculated to be  $7.5(\pm 0.4) \times 10^{-10} \text{ mol cm}^{-2}$  and  $7.6(\pm 0.5) \times 10^{-10} \text{ mol cm}^{-2}$ , assuming a one-electron process. Obviously, the presence of the second thiol end group in 1,4-BDMT does not significantly influence its coverage. The identical  $\Gamma$  implies that the 1,4-BDMT molecules adopt a vertical orientation similar to that of BM on Au(111) [55,65].

To eliminate the possibility that the charge of peak A corresponds to a two-electron process per adsorbate, we calculated values for the charge of A based on potential orientations that 1,4-BDMT could assume at the gold surface. The neutral structures were optimized at the HF/6-31G\* level of theory to obtain bond lengths and bond angles. The standard Van der Waals atomic radii were also incorporated in the calculations. Here, a few

possible geometries are presented with the aromatic moiety either parallel or perpendicular to the surface.

If 1,4-BDMT were to bind via both sulfurs ( $sp^3$  hybridization of the sulfur atoms, i.e. a  $109.5^\circ$  Au-S-C bond angle), with its benzene ring parallel to the gold surface, the area per adsorbate would be larger than  $73 \text{ \AA}^2$  ( $11 \times 6.6 \text{ \AA}$ ). This corresponds to a theoretical charge for A less than  $44 \text{ \mu C cm}^{-2}$ . On the other hand, if the benzene ring were perpendicular to the gold surface, the molecular area would be about  $41 \text{ \AA}^2$ , i.e.  $80 \text{ \mu C cm}^{-2}$  assuming a cross-sectional dimension of  $11 \text{ \AA}$  and a Van der Waals thickness of  $3.7 \text{ \AA}$ . In contrast, if the ring is oriented perpendicular to the gold surface via formation of a single S-Au bond, an area of  $24 \text{ \AA}^2$  ( $6.6 \text{ \AA} \times 3.7 \text{ \AA}$ ) is calculated, which corresponds to  $68 \text{ \mu C cm}^{-2}$ .

The last two orientations yield values for  $Q_A$  very similar to the experimentally obtained value of  $73 \pm 4 \text{ \mu C cm}^{-2}$ . However, if we reconsider the Au(111) surface (Figure 2.15) and its spacings, it is difficult to imagine how the 1,4-BDMT molecules could pack to form a full monolayer through adsorption of both sulfurs with the ring perpendicular to the surface. The vertical orientation proposed from the electrochemical comparison between 1,4-BDMT and BM is more likely, and is supported by further electrochemical experiments and the IRAS results to follow.

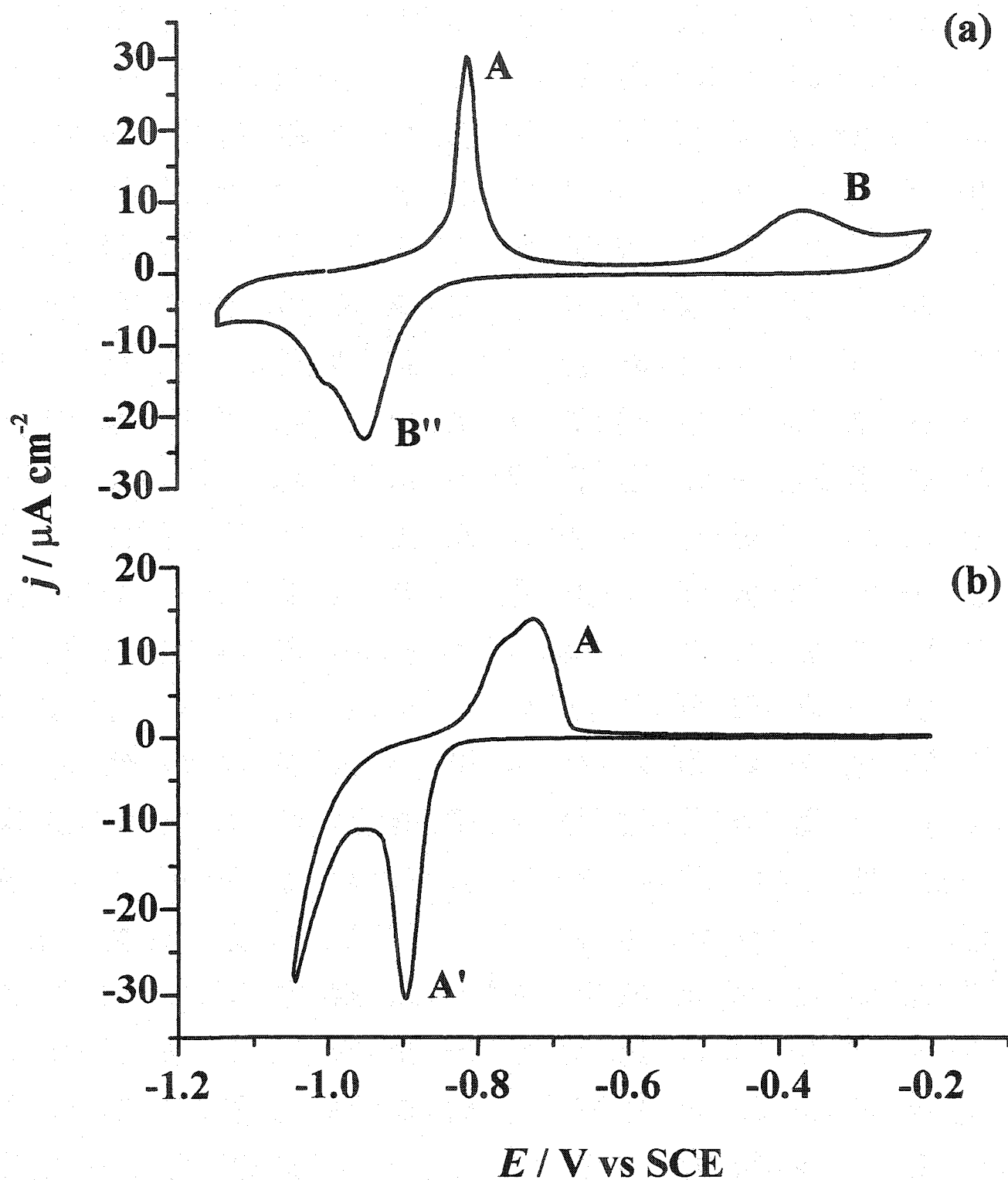
To compare the quality of the electrodeposited films of 1,4-BDMT and BM, differential capacitance measurements (between  $-0.30$  to  $-0.50 \text{ V}$  and in pure  $0.5 \text{ M KOH}$ ) were performed and the results are at first glance surprising. Our measurements indicate a change in capacity of  $20.0 \pm 2.0 \text{ \mu F cm}^{-2}$  for bare gold [10,19] to  $10.4 \pm 0.8 \text{ \mu F cm}^{-2}$  for the 1,4-BDMT monolayer. This value is almost double that of the BM monolayer ( $4.5 \pm 0.4 \text{ \mu F cm}^{-2}$ ). This may be attributed to the negatively charged sulfur end group of 1,4-BDMT,



which creates a charged interface responsible for the observed increase in capacitance. A recent study on the reductive desorption of a carboxylic-acid terminated alkanethiol, namely  $\text{HOOC}-(\text{CH}_2)_5\text{-SH}$  in 0.5 M KOH, reported a capacity of  $10.3 \mu\text{F cm}^{-2}$  [66]. This is identical to the capacity we measured for 1,4-BDMT, which is approximately similar in length to the  $\text{HOOC}-(\text{CH}_2)_5\text{-SH}$ .

To confirm that the large capacity was in fact due to the unreacted thiolate end group, 1,4-BDMT was electrodeposited in an aqueous electrolyte solution of 0.1 M NaF and the capacity was measured in pure 0.1 M NaF. In pH neutral solution, the thiol end group would be protonated and a significant decrease in the differential capacitance results is expected. Indeed, the capacity does decrease to  $3.8 \pm 0.3 \mu\text{F cm}^{-2}$ . This value is now comparable to the value reported by Kolb et al. for a monolayer of 1,6-hexanedithiol on Au(111) between 2.5-3.5  $\mu\text{F cm}^{-2}$  [2].

This pH dependence supports the suggestion that 1,4-BDMT adsorbs to the gold electrode through formation of a single S-Au bond and hints at a possible electroactive surface. To oxidize the sulfur at the organic/solution interface, the potential was scanned towards more positive values and the resulting cyclic voltammogram is shown in Figure 3.2a. Upon extending the anodic limit from -0.50 V to -0.20 V, a second oxidative peak B was observed at -0.36 V. The two anodic peaks A and B are separated by about 450 mV. This suggests that a second surface process involving the unbound sulfur occurs (see below). The shift of potential is probably related to the large distance [21] ( $\sim 10.4 \text{ \AA}$ ) between the thiolate terminal group and the gold electrode surface, which results in a screening of the applied electric field (section 2.2.3b). Also, in contrast to the two reductive peaks in Figure 1b, there is only one broad reductive peak labeled B' at -0.96 V.



**Figure 3.2:** Cyclic Voltammograms of the oxidative adsorption and reductive desorption of 1,4- BDMT from ( a) 0.5 M KOH and ( b) 0.1 M NaF at a Au( 111) surface. Potential scan rate: 20 mV s<sup>-1</sup>.

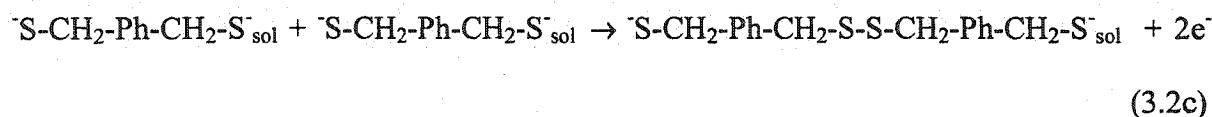
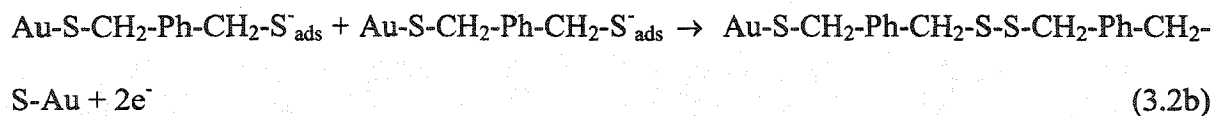
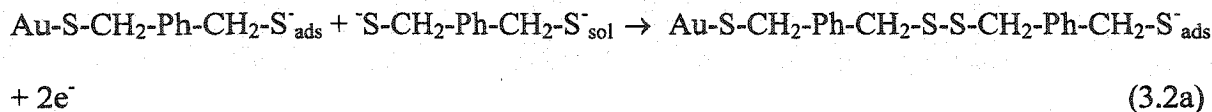
The pH of the solution changes the shape of the cyclic voltammogram as is shown in Figure 3.2b. In 0.1 M NaF, there is a broad oxidative current peak A at  $-0.74$  V when the potential is scanned from  $-1.05$  V to  $-0.20$  V at a rate of  $20 \text{ mV s}^{-1}$ . The  $\Gamma$  is similar to the one recorded in 0.5 M KOH and has a value of  $7.5(\pm 0.4) \times 10^{-10} \text{ mol cm}^{-2}$ . The deposition peak of 1,4-BDMT in NaF is broader and located at a more positive potential than the one in alkaline solution by 64 mV. This shift in potential indicates that more energy is required to deposit 1,4-BDMT onto gold at lower pH because of the additional difficulty of having to break the S-H bond. The absence of peak B in 0.1 M NaF suggests that this oxidative process is not occurring when the adsorbate is protonated.

On the reduction, we note that there is a single reductive peak of the protonated molecule in NaF. This peak is about 80 mV more negative than its de-protonated counterpart, peak A' (Figure 3.1b). The  $\Delta E_p$  is larger in NaF than in basic solution by about 150 mV. This is also related to protonation of the sulfur atoms. An electrochemical study of nonanethiol on Au(111) reported similar potential shifts, broadening of the anodic peak, and larger  $\Delta E_p$  values at decreased pH (i.e. below 8) [40]. In KOH, the 1,4-BDMT terminal group is a negatively charged and solvated S atom, which will repel its neighboring S<sup>-</sup> and is therefore easier to remove from the gold surface than the protonated form of the molecule. Similar behavior was observed for a carboxylate terminated thiol [66].

These electrochemical results suggest that the first anodic current peak A corresponds to the oxidative adsorption of vertically oriented dithiols described by the following equation:



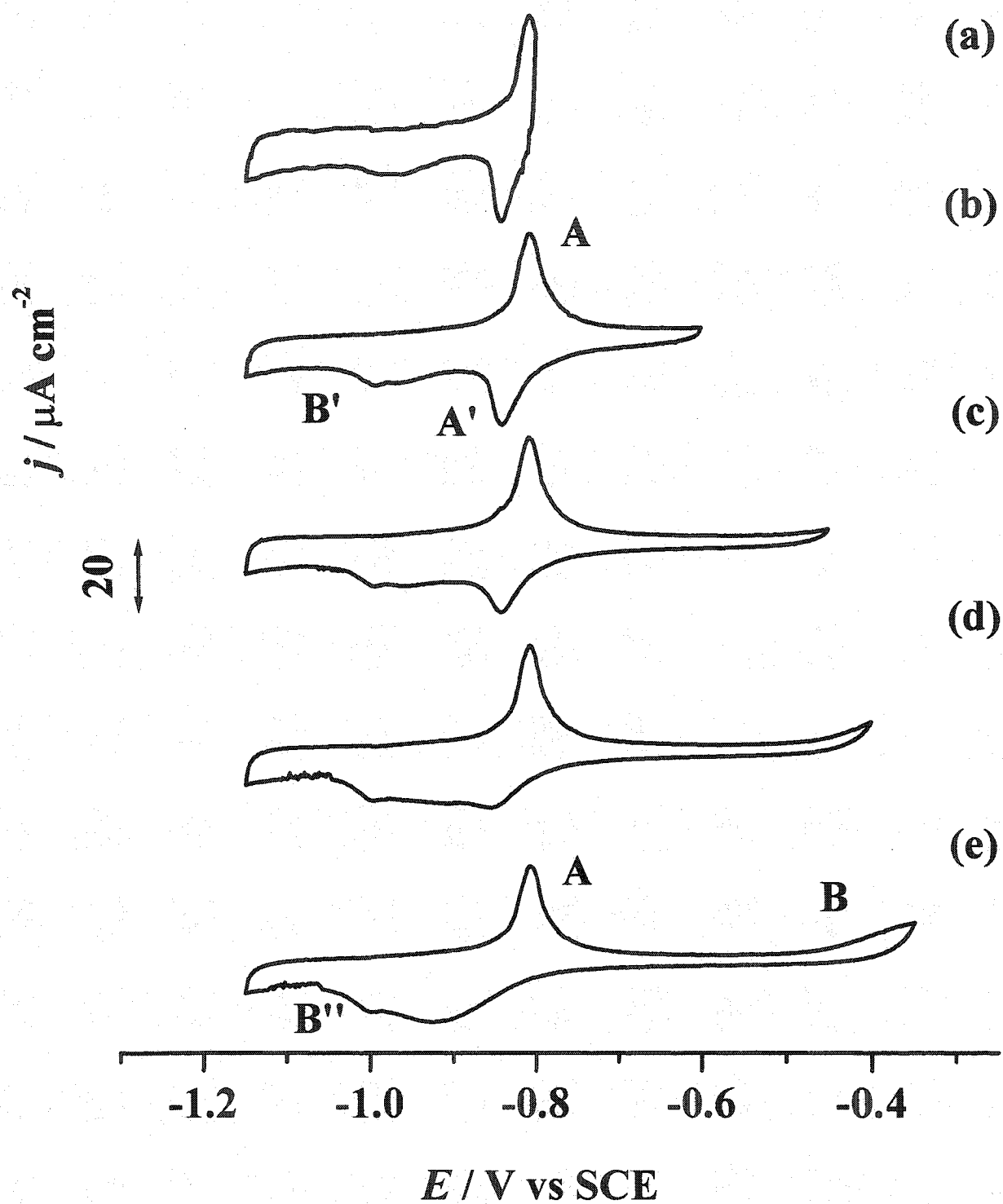
The second anodic peak B could originate through reaction of the unbound thiolate group formed in equation 3.1. Three likely oxidative reactions involving thiolates are summarized in the equations 3.2a, b, and c:



The first of these, equation 3.2a, describes the formation of a bilayer of 1,4-BDMT onto the gold electrode. Equation 3.2b corresponds to the dimerization of two neighboring 1,4-BDMT<sub>ads</sub>. Finally, equation 3.2c suggest that peak B results from the dimerization of two dithiols in solution. Several different experiments were performed to determine which of the proposed mechanisms is compatible with the electrochemical characteristics of the layer formed when peak B is observed.

### 3.2.2 Oxidative Deposition of Bilayers of 1,4-BDMT

In an effort to understand how the oxidative peaks A and B are related to A', B' and B'', window-opening experiments were performed (Figure 3.3). It is evident from scanning into peak A, that it is directly related to A'. As the potential is pushed to more positive



**Figure 3.3:** Cyclic Voltammograms of the oxidative adsorption and reductive desorption of 1,4-BDMT in 0.5 M KOH at anodic limits of (a) -0.80 V, (b) -0.60 V, (c) -0.45 V, (d) -0.40 V, and (e) -0.35 V at the Au(111) surface. Potential scan rate: 20  $\text{mV s}^{-1}$ .

values, A' and B' merge into one peak. This peak has been labeled B'', since it reflects the gradual growth of B' and the simultaneous decrease of A'. As the potential is scanned into peak B, at -0.35 V, the cathodic sweep is similar to the one in Figure 3.2a.

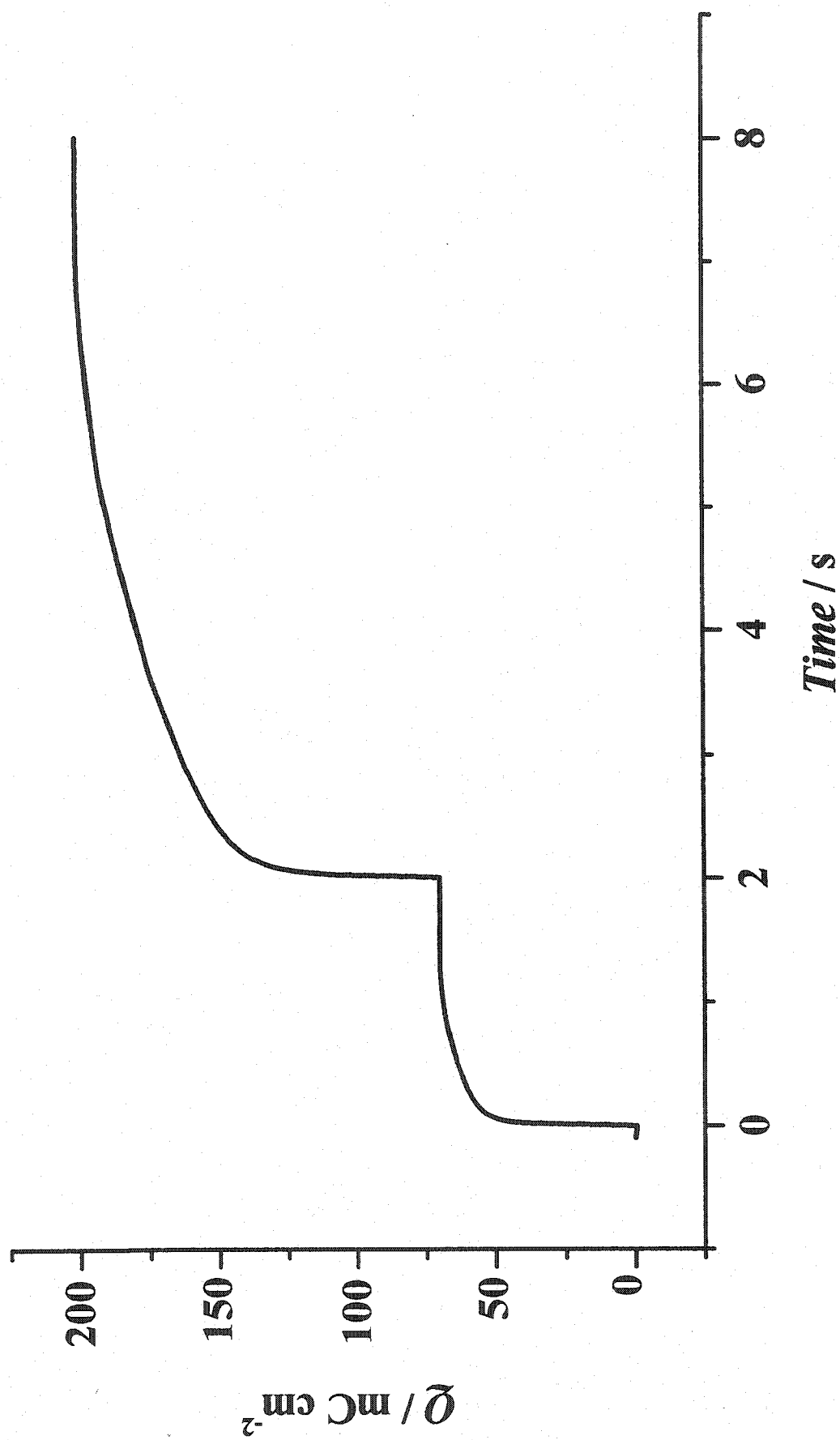
Upon scanning from peak A (monolayer formation) to peak B, a shift of 120 mV ( $E_{pB''} - E_{pA'}$ ) in the reduction potential is observed. The potential of the reductive current peak depends on the thickness of the organic film. The thicker the deposited organic layer, the more difficult it is for ion penetration through the film during reduction [40,55,67,68]. The shift of the reduction potential for B'' to more negative values is therefore consistent with an increase in the layer's thickness. This supports equation 3.2a since it is the only one out of the three possibilities for peak B that directly changes the film thickness. However, equation 3.2b cannot be ruled out, because dimer formation at the surface may also result in a better ion blocking film.

The above discussion presents a qualitative idea as to how peaks A and B are correlated. In order to quantify their relationship, we proceeded to obtain the charge ratio of peak B to peak A,  $Q_B/Q_A$ . It was not possible to directly integrate peak B from the voltammetry because of its broadness and large background current, which is indicative of a kinetically slow process. Chronocoulometric measurements were performed to obtain a more accurate value of the charges related to peaks A and B. In these experiments, the potential was first set at -1.00 V for five minutes to obtain an uncoated Au(111) surface. The potential was then stepped to -0.75 V, where the electrochemical reaction related to peak A occurs and the charge-time response was recorded for two seconds. Finally, the potential was stepped to -0.10 V, where the electrochemical reaction related to peak B occurs, and another charge-time response was recorded.

The charges for peaks A and B were obtained from these chronoamperograms (Figure 3.4) and corrected for capacitive charge (section 2.3.2) [40,41,69]. The ratio of the charges of B ( $133 \pm 8 \mu\text{C cm}^{-2}$ ) to A ( $70 \pm 7 \mu\text{C cm}^{-2}$ ) was determined to be  $1.9 \pm 0.2$ . The charge is a direct measure of the number of electrons transferred. Since peak A is representative of a one-electron adsorption process, peak B must represent a two-electron adsorption process in order for this charge ratio to be achieved. The only one of the equations for B that fits a theoretical value for  $Q_B/Q_A$  of two is bilayer formation (3.2a). Dimerization between adsorbates (3.2b) would require a charge ratio of one, while the solution process (3.2c) would result in a large, diffusion limited peak B.

The reductive charges of peaks A'+B' and B'' were obtained through integration of the cathodic current peaks in Figures 3.1b and 3.2a after a baseline correction. The absolute value of the reductive charge of peaks A'+B' ( $65 \pm 5 \mu\text{C cm}^{-2}$ ) is equal to (within error) the charge of peak A ( $70 \pm 7 \mu\text{C cm}^{-2}$ ). This is also the case for peak B'' ( $82 \pm 5 \mu\text{C cm}^{-2}$ ). The absolute values of the reductive charges are within errors identical to the oxidative charge of peak A, even if the total oxidative charge varies by almost a factor of three when the positive limit of the cyclic voltammogram is extended from  $-0.50\text{V}$  ( $70 \mu\text{C cm}^{-2}$ ) to  $-0.20\text{V}$  ( $203 \mu\text{C cm}^{-2}$ ). The fact that the charges related to the reductive desorption of peak A' (a monolayer) + B' or B'' are similar, indicates that the Au-S bond is reduced before the S-S dimer of equations 3.2a or b. We would not expect the oxidative and reductive charge to be equal for a solution process (3.2c).

The oxidatively deposited layers in Figures 3.1b and 3.2a were characterized with differential capacitance measurements in the potential range of  $-0.30$  to  $-0.50\text{V}$ . After electrodeposition of peak A in  $0.5\text{ M KOH}$ , the capacity was measured in pure  $0.5\text{ M KOH}$

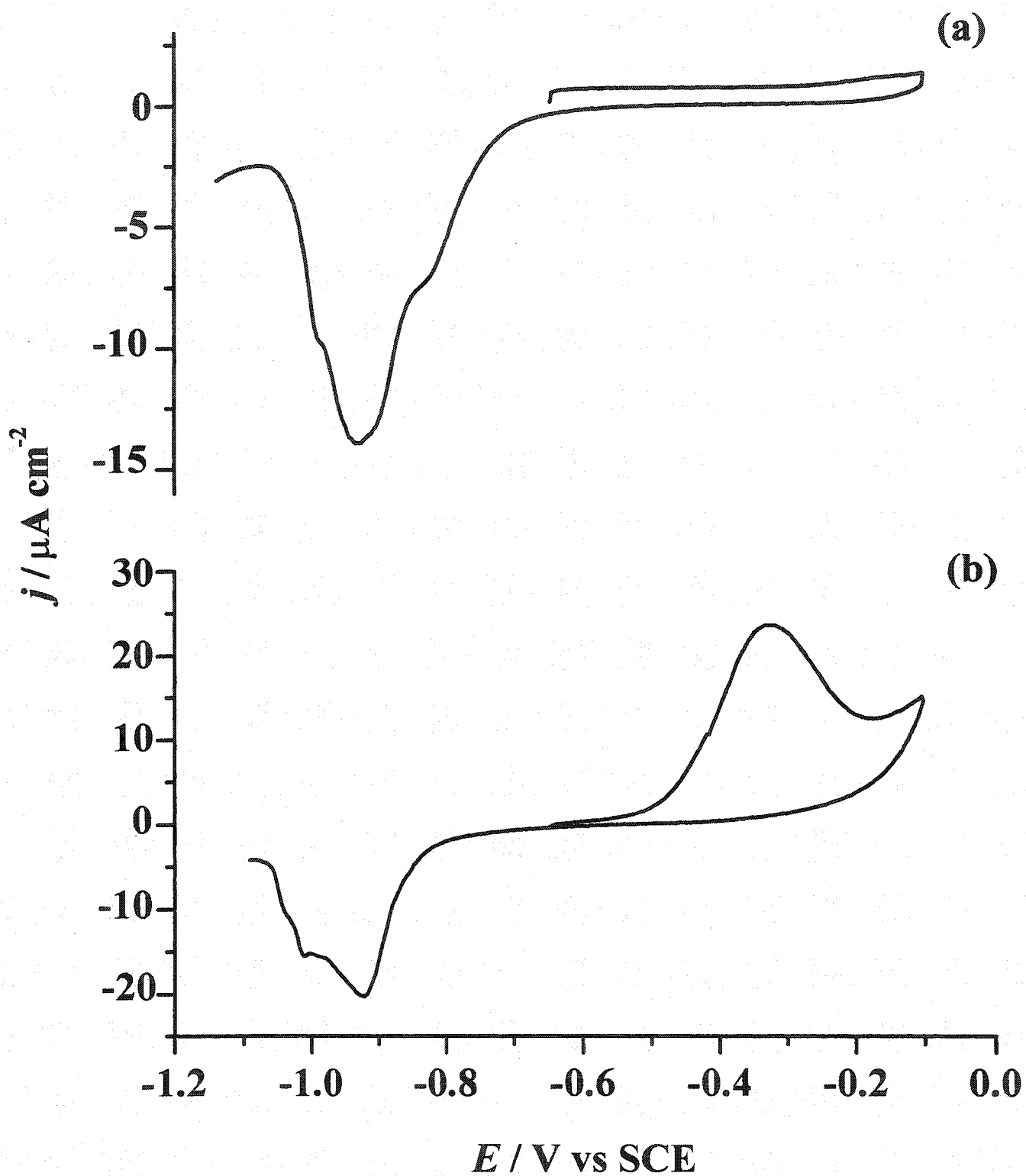


**Figure 3.4:** Chronocoulometric measurements of 1,4-BDMT deposited from a saturated solution in 0.5 M KOH at the Au(111) surface. See text for details.



and found to be  $10.4 \pm 0.8 \mu\text{F cm}^{-2}$ . The capacity measured after oxidative deposition of peaks A and B is  $4.6 \pm 0.5 \mu\text{F cm}^{-2}$  in 0.5 M KOH. The process related to peak B decreases the capacitance of the layer. Clearly, peak B is related to a surface process, so dimerization in solution (3.2c) can be eliminated as a possibility for B. Since the capacitance is inversely proportional to the thickness of the organic film (equation 2.7), the observed decrease in capacity by approximately a factor of two fits well with bilayer formation (3.2a). However, a decrease in the capacity was observed upon protonation of the monolayer, so this decrease could in fact be attributed to (3.2b). Dimerization between adsorbates generates a uncharged surface, similar to protonation of the thiolate end group.

The assignment of peak B to a surface process is further supported by transfer experiments of the monolayer (peak A) into various solutions. A monolayer of 1,4-BDMT was electrodeposited and the meniscus was broken under potential control at  $-0.65 \text{ V}$ . The electrode was rinsed with water and transferred to a solution of pure 0.5 M KOH, under potential control at  $-0.65 \text{ V}$ . The potential was scanned from  $-0.65 \text{ V}$  towards more positive values ( $-0.20 \text{ V}$ ), followed by reduction of the monolayer. No second oxidative peak was observed, as is shown in Figure 3.5a. Obviously, B does not originate from a dimerization between adsorbates, because this oxidation should happen whether or not there is any dithiol in solution. In contrast, when the monolayer was transferred into a 1 mM heptanethiol in 0.5 M KOH solution and a similar experiment was performed, an anodic peak was observed. This second oxidative peak occurs at potentials close to that of peak B and is shown in Figure 3.5b. This suggests that B originates from a reaction of an adsorbed dithiolate with a dithiolate in solution (3.2a).

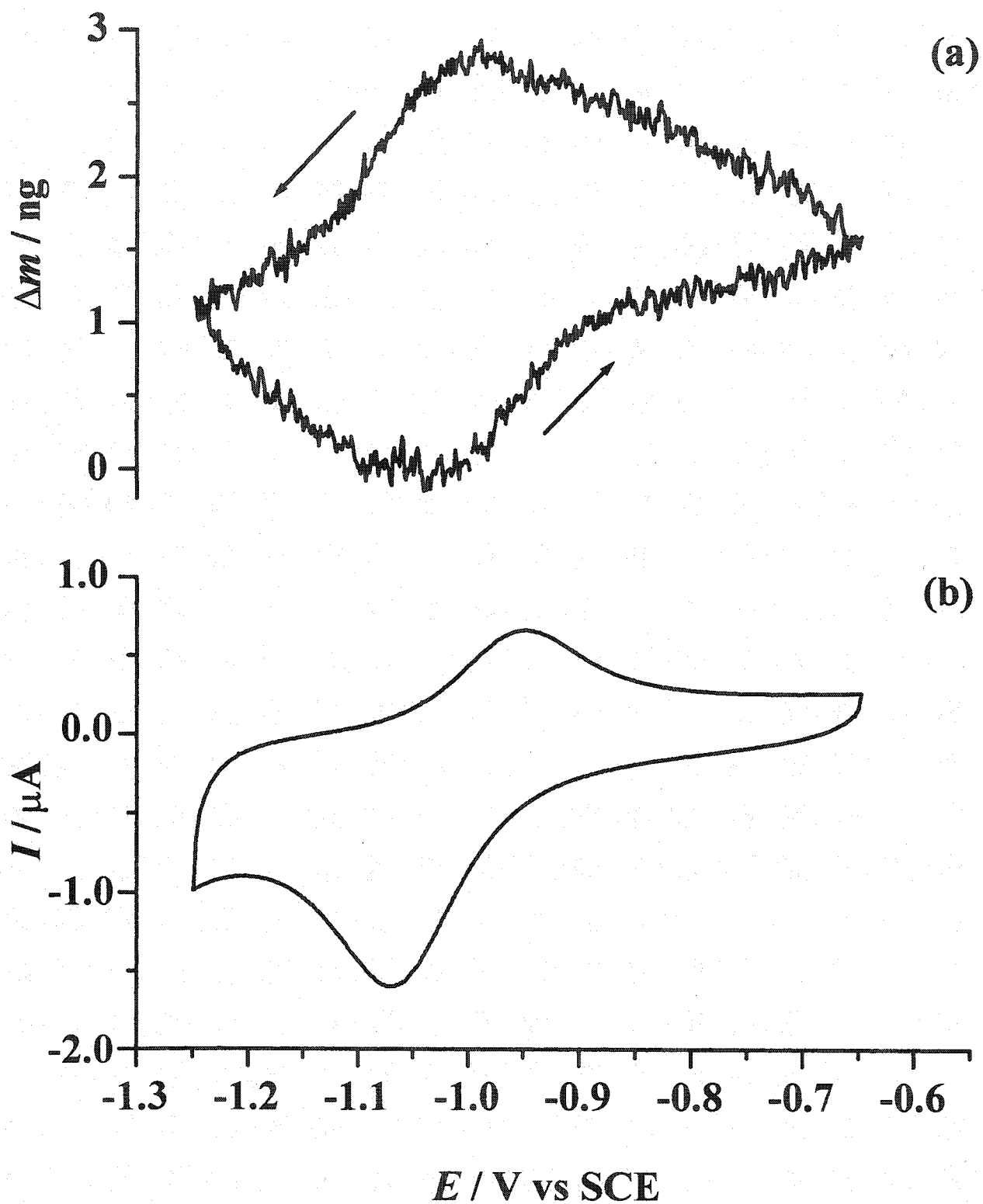


**Figure 3.5:** Cyclic Voltammograms of a monolayer of 1,4- BDMT deposited onto a Au(111) surface and transferred into (a) a pure 0.5 M KOH solution and (b) a 1 mM heptanethiol solution in 0.5 M KOH. Potential scan rate:  $20 \text{ mV s}^{-1}$ . See text for details.

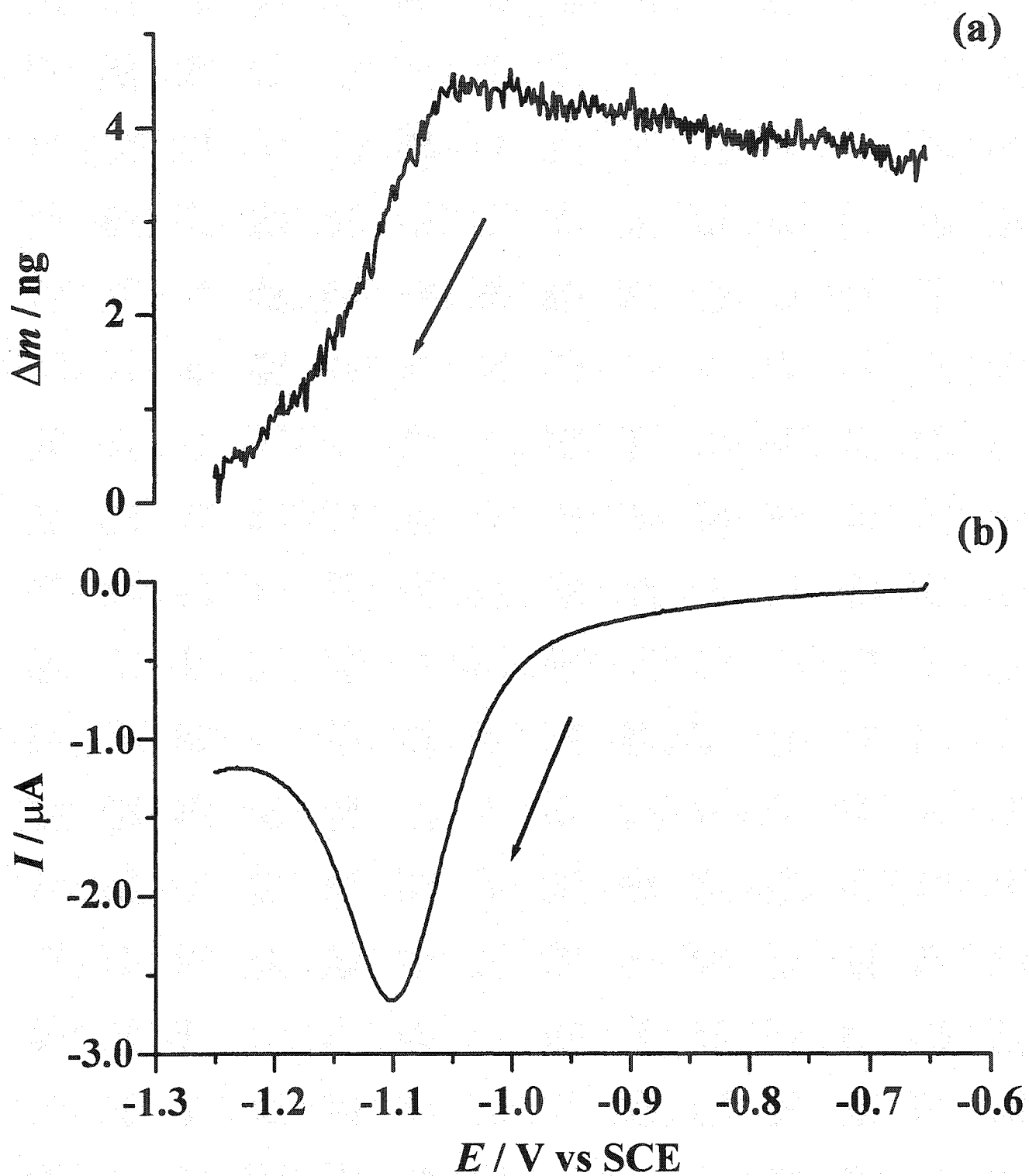
Figure 3.6 shows EQCM measurements of the oxidative deposition and reductive desorption of peak A for 1,4-BDMT in a 0.1 M KOH solution in ethanol. There is an oxidative current peak at  $-0.96$  V and a reductive current peak at  $-1.07$  V. The broadness of the current peaks and their shift to more negative potentials is attributed to the different gold substrate and solvent used for the EQCM measurements. The frequency change was converted to a mass change using the Sauerbrey equation (equation 2.10) [70]. The oxidative deposition gives rise to a mass increase and the reductive desorption to a mass decrease of equal magnitude. There is an average mass increase of  $1.9 \pm 0.1$  ng for the deposition of peak A.

EQCM measurements extending into the oxidative peak B performed as in Figure 3.6 were not very clear. The formation of B was slow and continued into the cathodic (negative-going) potential scan. This made a quantitative discussion of the mass change attributed to B rather difficult. Instead, the potential was held for 10 minutes at  $-0.65$  V in order to ensure full bilayer formation. The kinetics of deposition will be discussed in detail in Chapter 6. The bilayer was reductively removed as shown in Figure 3.7. In this voltammogram, a sharper reductive current peak is seen at  $-1.10$  V. The mass decrease obtained from the reduction of peaks A and B is  $3.8 \pm 0.1$  ng. This is twice the average value observed from the reduction of peak A alone ( $1.9 \pm 0.1$  ng). This indicates that a monolayer of vertically oriented dithiolates (3.1) is first formed, and then as the deposition potential is made more positive, a bilayer (3.2a) is formed. This results in a doubling of the electrodeposited mass.

Further EQCM evidence supporting bilayer formation comes from a study on the desorption peaks related to A and A + B as a function of solvent. Various mixtures of water/ethanol were used and the results are summarized in Table 3.1. The charge of peak A'



**Figure 3.6:** Mass variation (a) and cyclic voltammogram (b) of the oxidative deposition and reductive desorption of a monolayer of 1,4-BDMT on gold from a 0.5 M KOH solution in ethanol. Potential scan rate:  $20 \text{ mV s}^{-1}$ .



**Figure 3.7:** Mass variation (a) and cyclic voltammogram (b) of the reductive desorption of a bilayer of 1,4-BDMT on gold from a 0.5 M KOH solution in ethanol. Potential scan rate:  $20 \text{ mV s}^{-1}$ . See text for details.

is the same in all solvents and, more importantly, the mass change doubles in each solvent when the change for A + B is compared to that for A alone. The fact that in each of these solvents there is a doubling of the mass change is strong evidence for bilayer formation (3.2a). However, closer inspection of the data yields some inconsistencies. First, the charge for peak A yields an expected mass increase of  $10.8 \pm 0.5$  ng. As the dielectric constant decreases (i.e. on going from pure water to pure ethanol), the discrepancy between the masses calculated from the frequency and the charge decreases. This is not the case for pure ethanol, where the expected mass increase (calculated from the charge) is about five times larger than the value obtained from the EQCM ( $1.9 \pm 0.1$  ng).

**Table 3.1:** Absolute values of the mass decrease obtained from experiments identical to those used to obtain the results in Figures 3.6 and 3.7 (see section 3.2.2). The electrolyte was 0.5 M KOH in all solvents. The masses are averages of a minimum of 3 measurements.

| solvent                         | mass A / ng       | mass A + B / ng   |
|---------------------------------|-------------------|-------------------|
| H <sub>2</sub> O                | 1.2 ( $\pm 0.1$ ) | 2.5 ( $\pm 0.3$ ) |
| 70% H <sub>2</sub> O / 30% EtOH | 1.8 ( $\pm 0.2$ ) | 5.6 ( $\pm 0.4$ ) |
| 40% H <sub>2</sub> O / 60% EtOH | 4.4 ( $\pm 0.3$ ) | 8.8 ( $\pm 0.7$ ) |
| EtOH                            | 1.9 ( $\pm 0.1$ ) | 3.8 ( $\pm 0.1$ ) |

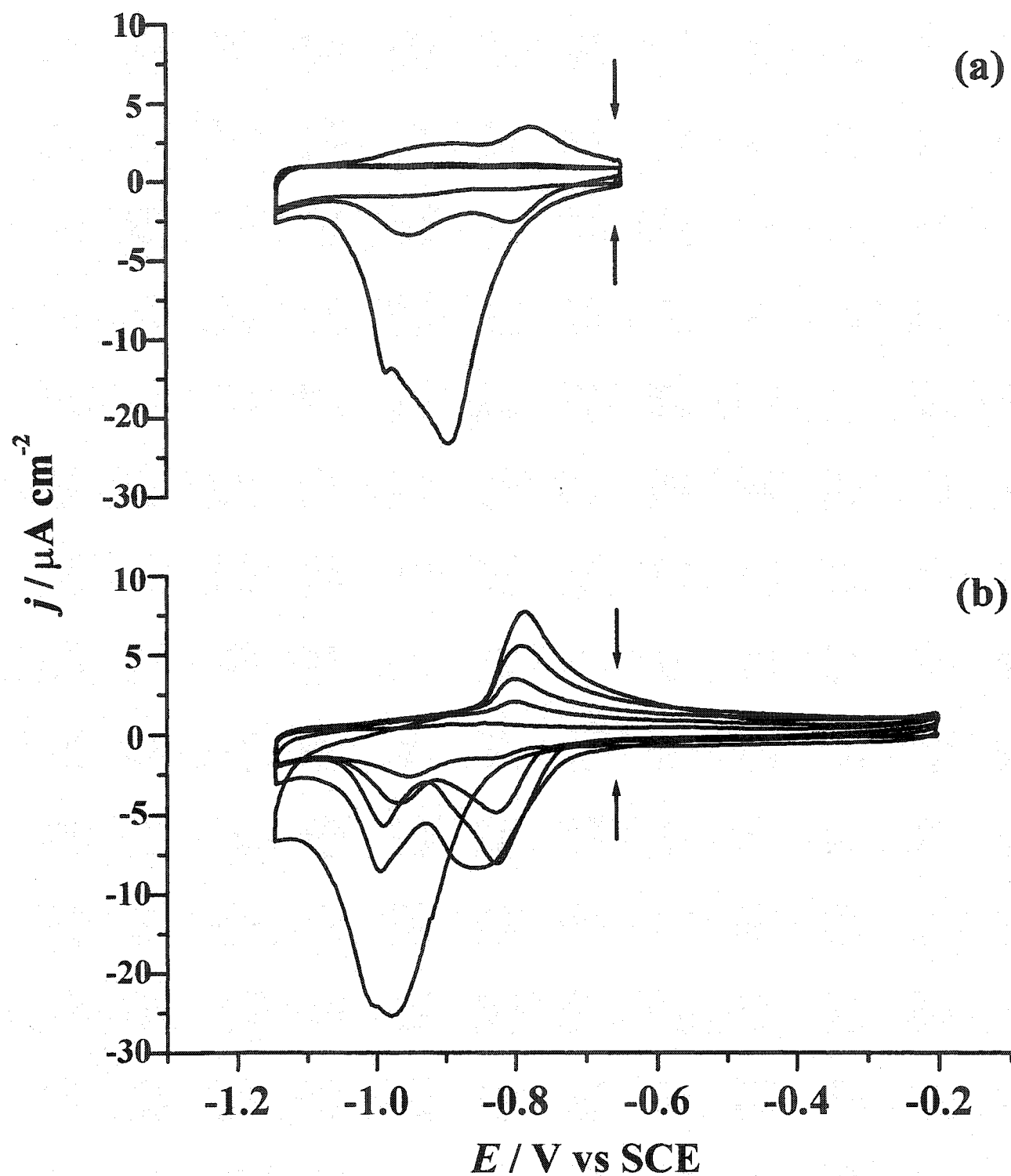
The expected and observed mass changes do not agree and furthermore they are dependent on solvent. A possible explanation for this difference comes from previous work [40], which indicated that desorbed thiol monolayers could remain physisorbed at the

electrode by forming a negatively charged micelle. Such a structure can be maintained close to the electrode surface because of the presence of a layer of cations, which are adsorbed on the electrode surface as a result of the high negative charge that it carries. If the layers were to form an organized structure of some kind after desorption, then there would be minimal changes in the interfacial structure or properties, which will affect the EQCM response.

Physisorbed species are present at the gold surface after the reduction of a monolayer or a bilayer of 1,4-BDMT as is shown in Figure 3.8. In these experiments, the monolayer and bilayer were formed as described above and then transferred to an aqueous solution of pure 0.5 M KOH. When peak A (monolayer) is deposited (Figure 3.8a), there is oxidative redeposition only on the first anodic cycle to  $-0.65$  V. We expect diffusion of the dithiolate monolayer from the electrode surface to be favored, since this has already been reported for some bifunctional molecules [66].

When both peaks A + B are deposited (Figure 3.8b), the oxidative redeposition is more substantial and continues for up to six anodic cycles. These results suggest that the compound corresponding to A + B is less soluble, and therefore remains physisorbed at the surface for a longer time after its reduction. These qualitative results are compatible with the formation of a less soluble 1,4-BDMT dimer when the anodic limit for oxidative deposition is  $-0.20$  V. Similar re-adsorption has been reported for 1,6-hexanedithiol dimers [2]. Consequently, the presence of physisorbed species on the gold substrate should lead to mass changes smaller than the masses expected from the oxidative/reductive charges.

A previous study verified the validity of the Sauerbrey equation for a soluble molecule, namely butanethiol in an alkaline aqueous solution [38]. The number of electrons per deposited butanethiolate was obtained from the slope of a graph of the oxidative charge



**Figure 3.8:** Cyclic voltammograms of a Au(111) surface covered with (a) a monolayer of 1,4-BDMT (first three cycles) and (b) a bilayer of 1,4-BDMT (cycles 1, 2, 4, 6, and 8) in a 0.5 M KOH solution. The arrows indicate the increasing number of cycles. Potential scan rate:  $20 \text{ mV s}^{-1}$ . See text for details.



versus the mass deposited. This method yielded a value of  $1.0 \pm 0.1$  electron per deposited butanethiolate, in agreement with the accepted value. This suggests that the discrepancy between the charge and the mass observed for the dithiolates is related to their poor solubility, since the double layer effect should be similar for thiolates and dithiolates.

The solvent plays a role in causing physisorbed species to dissolve into the bulk. Thus as the content of ethanol increases, the apparent mass loss is greater because of the increased solubility of the organic compounds. The result for pure ethanol is anomalous but represents a significant difference from the nearest result where there is still 40% water present. Substantial changes in ion solvation and interfacial properties will be expected in moving from 40% water to pure ethanol. This result may require a different analysis from the data for solvents containing 100%, 70% and 40% water. It is clear that the EQCM results require further detailed investigation for a complete understanding of the data presented here. However, the doubling of mass in four different solvent systems, together with the other electrochemical evidence discussed above, presents a strong case for the proposed mechanism for bilayer formation (3.2a).

### **3.3 Electrodeposition versus Chemical Deposition: Probing the Structural Characteristics of 1,4-BDMT on Au(111)**

The electrochemical results in the previous section suggest that 1,4-BDMT molecules adsorb vertically on a gold electrode and, at more positive potentials, they form a complete bilayer through dimerization with dithiolates in solution. This method shows improved control over the traditional chemical deposition method used in the formation of dithiol films [1-19,21-25,28-36], but does not provide us with any quantitative information on their assembly. To investigate the quality (i.e. organization and order) of the electrodeposited 1,4-

BDMT layers, both the monolayer and bilayer were characterized with IRAS and the monolayer with SPM. The spectra and topographic images were compared with those obtained through chemical incubation.

### 3.3.1 Spectroscopic Techniques: Orientation and Organization on the Macroscopic Scale

The infrared spectra for the chemically deposited and electrodeposited monolayers of benzylmercaptan (BM), our reference compound, are shown in Figure 3.9. In the low frequency region, a sharp band at  $1494\text{ cm}^{-1}$  is assigned to the ring stretch of the aromatic moiety. A second peak is identified at  $3061\text{ cm}^{-1}$ , corresponding to the aromatic C-H stretch. The relative intensities and wavenumbers of these bands are similar in both cases, and compare well with those reported by Tao et al. [55]. There is no significant difference between the spectra, which suggests that either method of deposition is suitable for a monothiol. These IR results, along with the electrochemistry presented above, imply that BM monolayers of similar orientation and coverage can be achieved through electrodeposition or chemical incubation.

From the IR spectra, the orientation of the molecules of BM on the gold surface can be deduced as described in section 2.4.1. A vibrational analysis, based on a quantum mechanical calculation, (*Gaussian*® 98, HF/6-31G\*) [71] shows that the two aromatic vibrational bands observed have transition dipoles parallel (and in-plane) to the molecular axis. This axis is defined as the line that cuts through C1 and C6 of the benzene ring and is shown in Scheme 3.1a. The selection rule for a vibrational transition of a molecule adsorbed onto a metallic substrate [72] implies that BM must assume a vertical orientation at the Au(111) electrode. In this case, these normal vibrational modes [73] of BM are

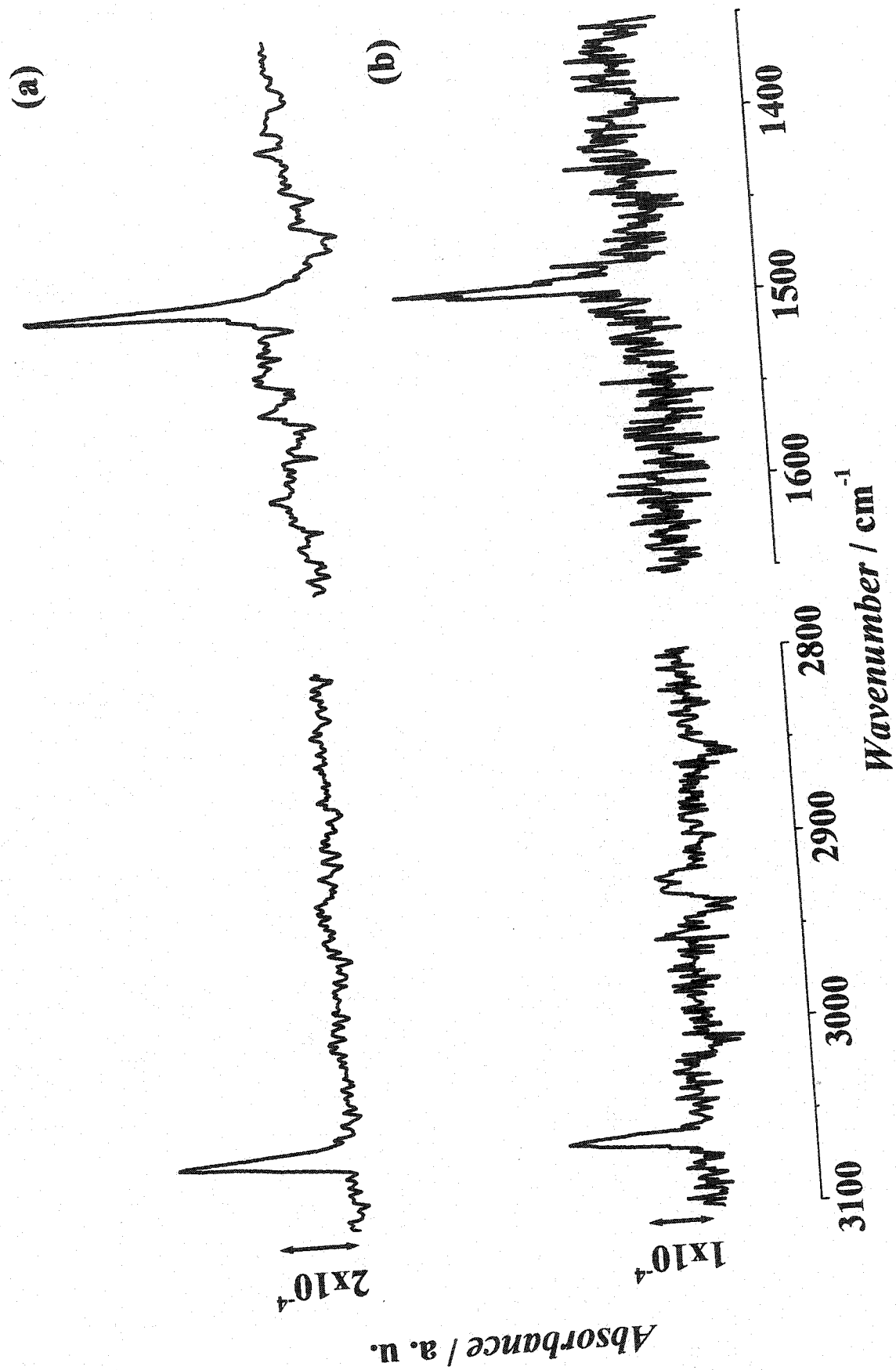
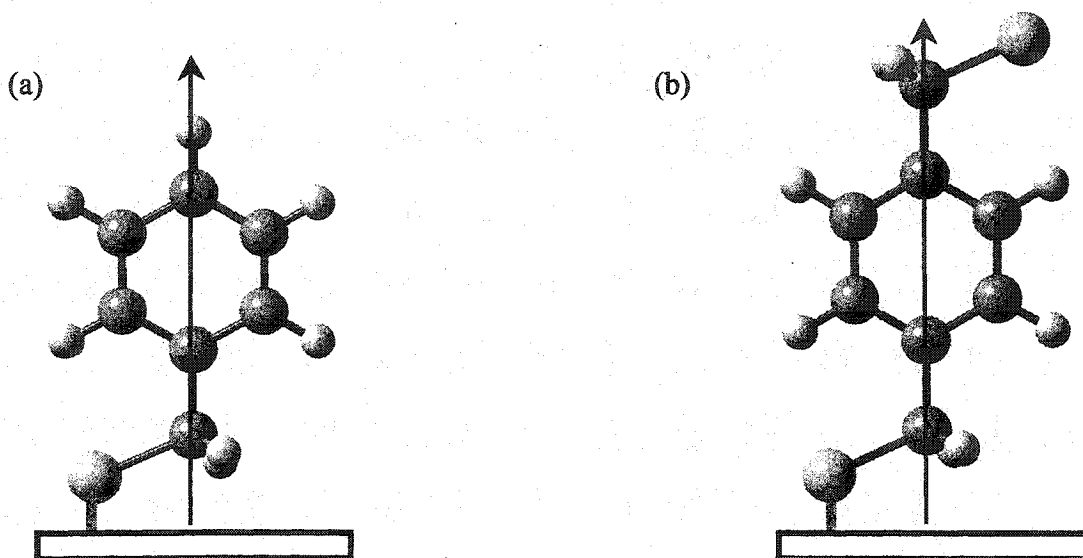


Figure 3.9: IR spectrum of a monolayer of BM (a) chemically deposited and (b) electrodeposited onto an annealed gold film.

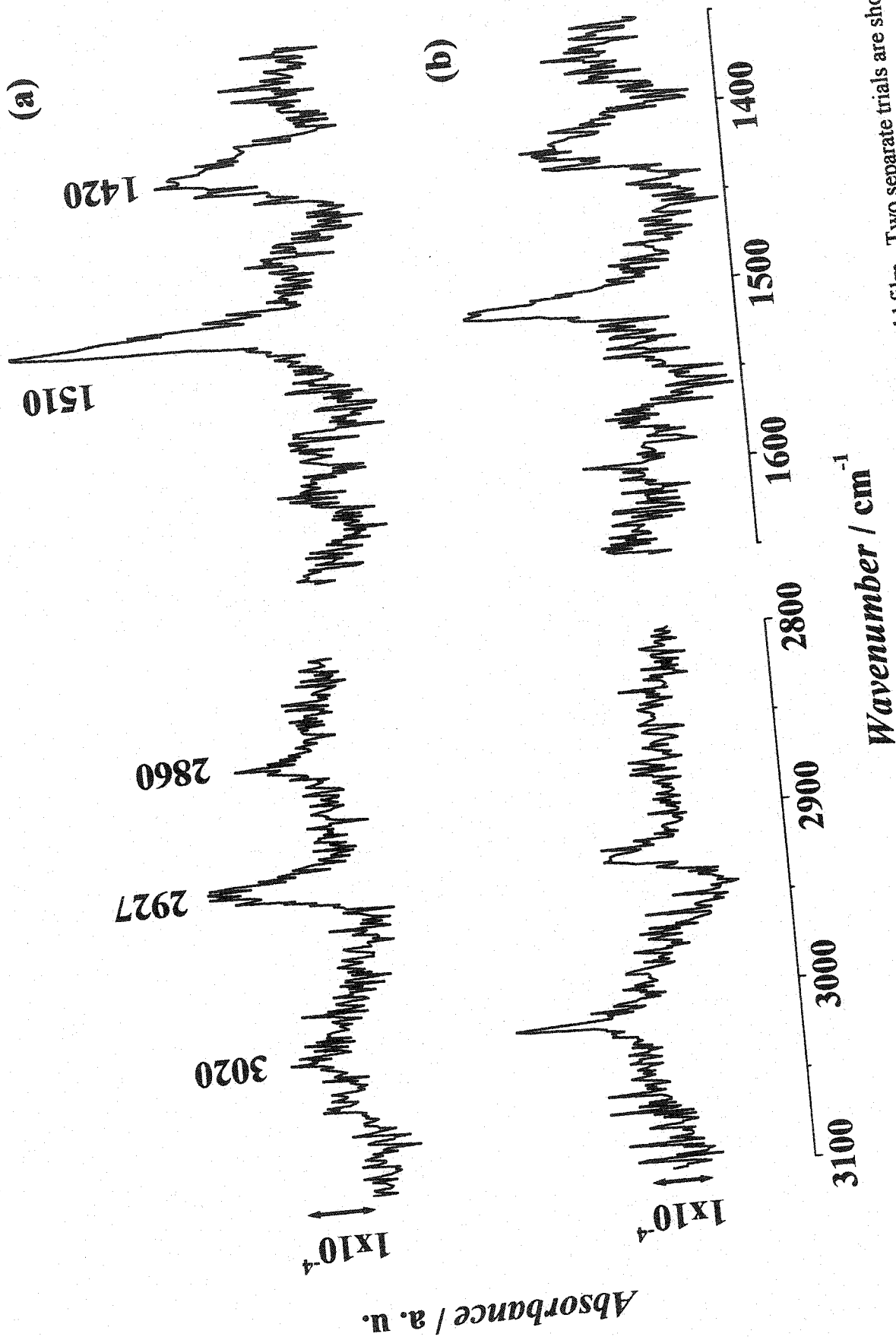


**Scheme 3.1:** Suggested orientations for an oxidatively deposited monolayer of (a) BM and (b) 1,4-BDMT onto gold from a 0.1 M KOH and 0.5 M KOH solution respectively.

perpendicular to the surface and are therefore excited. This arrangement of BM molecules on a gold substrate has been previously reported [55,65]. It was not possible to estimate the average orientation of the molecules through tilt and twist angles because the normal modes of the aromatic ring have transition dipoles that are collinear [73]. Thus, their relative intensities will be the same for all orientations on the surface.

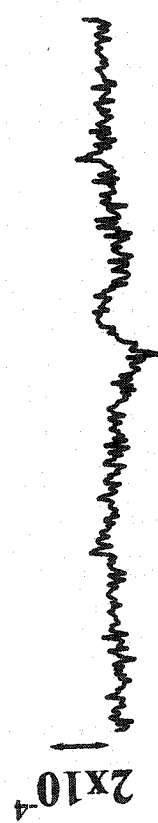
1,4-BDMT was chemically deposited through incubation of the annealed gold-on-glass films in 10 mM ethanol solutions for one hour. The samples were then rinsed with ethanol and dried under a stream of nitrogen prior to measurement. The incubation time was varied from 1 hour up to a week, to allow for sufficient time for molecular reorganization. Reproducibility in the IR spectra was not achieved under any conditions. Figure 3.10 presents two sets of IR spectra for the chemically deposited 1,4-BDMT films. It was not possible to average consecutive trials because the results were variable, even though great precaution was taken in reproducing the exact conditions of the experiment. This suggests that chemical deposition is inconsistent for a bifunctional molecule and would require optimization of several parameters, such as concentration, temperature, solvent, and incubation time, in order to achieve ideal conditions for dithiol adsorption.

In contrast, the IR spectra for the electrodeposited monolayer and bilayer shown in Figure 3.11 were reproducible. The IR spectrum of the monolayer in Figure 3.11a does not show any vibrational bands. On the other hand, when a bilayer is deposited several bands are observed (Figure 3.11b). All of these modes are summarized in Table 3.2 [18,21,22,73], along with the TIR (transmission IR) results of the neat 1,4-BDMT. In the high frequency region it was relatively simple to elucidate the C-H methylene stretches from those of the ring modes. However, the assignment of the aromatic C-H vibrations themselves was less



**Figure 3.10:** IR spectrum of a chemically deposited 1,4-BDMT layer onto an annealed gold film. Two separate trials are shown that were prepared under the same incubation conditions (i.e. incubated in an ethanol solution for ~1 hour).

(a)



(b)

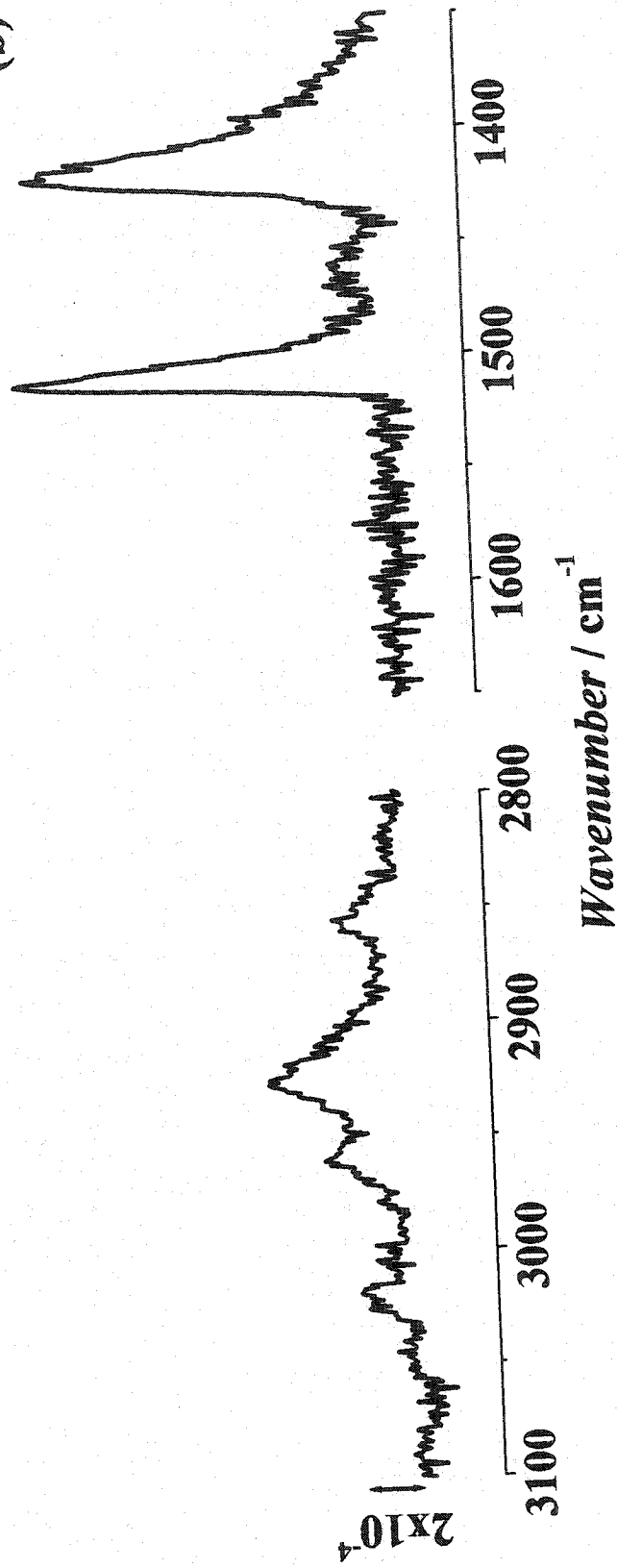


Figure 3.11: IR spectrum of (a) a monolayer and (b) a bilayer of 1,4-BDMT electrodeposited onto an annealed gold film from a 0.5 M KOH electrolyte solution.

straightforward. We therefore turned to previous studies of this compound employing surface-enhanced Raman scattering (SERS) as a spectroscopic surface probe, whose selection rules complement those of IRAS.

**Table 3.2:** Assignment of vibrational bands ( $\text{cm}^{-1}$ ) of 1,4-BDMT electrodeposited onto gold from a saturated dithiol solution in 0.5 M KOH.

| TIR               | monolayer | bilayer | assignment <sup>[18,21,22,73]</sup> |
|-------------------|-----------|---------|-------------------------------------|
| In-Plane Modes    |           |         |                                     |
| 3049              |           |         | 2                                   |
| 3024              |           | 3020    | 20a                                 |
| 3006              |           |         | 20b                                 |
| 2962              |           | 2960    | 7b                                  |
| 1511              |           | 1510    | 19a                                 |
| 1418              |           | 1420    | 19b                                 |
| Substituent Modes |           |         |                                     |
| 2928              |           | 2927    | $\nu(\text{CH}_2 \text{ asym})$     |
| 2840              |           | 2856    | $\nu(\text{CH}_2 \text{ sym})$      |
| 1429              |           |         | $\text{CH}_2(\text{def})$           |

A vibrational transition is IR active if the dipole moment of the molecule changes during the vibration. On the other hand, the transition is considered Raman active if the polarizability of the molecule changes during the vibration. Some transitions are either exclusively IR or Raman active, whereas others may be both [74]. For IR absorption, the



dipole moment operator ( $\hat{\mu}$ ) can be decomposed into three parts which transform as x, y, and z. For Raman transitions, the polarizability operator ( $\hat{\alpha}$ ) has six components, which transform to  $x^2$ ,  $y^2$ ,  $z^2$ ,  $xy$ ,  $xz$ , and  $yz$ . These functions appear in the character tables for each point group and belong to a specific representation [74]. Only modes belonging to a given representation will be active. These selection rules, indicating which transitions are allowed in IR or Raman spectra, will be used in assigning the bands in the IRAS spectra.

The IR results were compared with those reported in a SERS investigation on the monolayer formation of 1,4-BDMT from organic solution (i.e. under open circuit conditions) onto a gold film [18,21] and in an Au sol [22]. The studies assigned the relatively intense  $3052\text{ cm}^{-1}$  band present in their SERS experiment in terms of Wilson notation as a 2. This mode is completely absent in our IR spectra of the bilayer, and quite weak in the solid spectrum. These observations complement one another, and we therefore assign the  $3049\text{ cm}^{-1}$  of the TIR as a 2. The  $3024$  and  $3006\text{ cm}^{-1}$  modes are designated as 20a and 20b respectively.

The low frequency region posed a problem in distinguishing between the  $1418$  and  $1429\text{ cm}^{-1}$  modes. These bands are of similar intensity in both the neat IR and bilayer spectrum. In addition, the *Gaussian*<sup>®</sup> calculations show that these bands have transition dipole moments almost perpendicular to the molecular axis (in the plane of the benzene ring). The axis is again defined as the line that passes through carbons 1 and 6 of the benzene ring and is shown in Scheme 3.1b. Together, these observations imply that these modes are related, and we therefore assign them as  $1418(\nu_{19a})$  and  $1511(\nu_{19b})\text{ cm}^{-1}$ . This leaves an assignment of  $\text{CH}_2(\text{def})$  for the  $1429\text{ cm}^{-1}$  band.

The absence of vibrational bands in the IR spectrum of the monolayer is a strong indication that the 1,4-BDMT molecules are adsorbed vertically, with their molecular axes aligned perpendicular to the metal surface (Scheme 3.1b). If this were not the case, we would expect to observe the C-H aromatic and methylene stretches in the 2800-3100  $\text{cm}^{-1}$  region, in addition to the low frequency ring-stretching modes. The only other configuration that would result in a similar spectrum is the one whereby the 1,4-BDMT binds with both sulfurs, with its ring parallel to the gold surface. This configuration was already eliminated based on the electrochemical results presented in section 3.2.1. We recall that the surface concentration alone could not distinguish between a vertical monolayer versus a monolayer of 1,4-BDMT bound by both sulfurs with its benzene ring perpendicular to the surface. The IRAS results, along with the observed pH effect and transfer experiments, support the former orientation. If it were the latter of the two, we would expect to see bands in the IR of the monolayer.

The presence of bands upon electrodeposition of a second layer of 1,4-BDMT indicates that there is a re-orientation of the adsorbates, whereby their molecular axes are no longer normal to the surface. The actual tilt ( $\theta$ ) and twist ( $\psi$ ) angles could not be quantified, because the three aromatic vibrational modes observed all have collinear dipole moments. To calculate a molecular orientation, two modes are required whose unit dipole vectors are orthogonal (or not collinear) to one another, since their intensities will vary differently with the orientation of the molecule (section 2.4.1). The methylene C-H stretching bands were not used for IR fits, because these bands were weak in the IR spectrum of the bilayer. It is also observed that the bands of the bilayer are at almost the same wavenumbers as those in the bulk. This suggests that the environment of the bilayer is similar to the bulk, and that 1,4-

BDMT is not interacting strongly with the gold surface. These vibrational results only indicate that 1,4-BDMT is not in a vertical orientation in the layer.

Raman spectra of the 1,4-BDMT spontaneously adsorbed onto gold colloids and a rough gold surface also suggest that the molecules are in a relatively vertical orientation [18,21,22]. However, the presence of the ring stretch at  $1609\text{ cm}^{-1}$  and aromatic C-H vibrations in the low frequency requires that the aromatic ring of the chemically deposited 1,4-BDMT be more tilted than the electrodeposited monolayer. This could be due to the fact that both monolayer and bilayer growth are occurring simultaneously from spontaneous deposition, since the S-S stretching is observed in the Raman spectra. Unfortunately, the S-S stretching band that is located around  $500\text{ cm}^{-1}$  [75,76] cannot be measured with the FTIR spectrometer. Furthermore, this band is extremely weak in IR. SERS measurements could be used to identify the S-S bond [18,21,22], however this method requires a roughened gold substrate. Such a substrate differs from the smoother Au(111) substrate that we used, and could change the electrochemistry reported here.

HREELS is another spectroscopic technique, which could be used to identify the S-S stretching band and to provide non-electrochemical evidence of the formation of a bilayer of 1,4-BDMT. Figure 3.12 shows the HREEL spectrum of an electrodeposited bilayer of 1,4-BDMT on gold. The peaks are assigned in Table 3.3 [18,21,22,73] and include the vibrational signature for the S-S stretch at  $480\text{ cm}^{-1}$ . However, this weak band disappeared on consecutive scans. This is attributed to electron beam damage, since it is well known that thiols are sensitive to oxidation [11,12]. Nevertheless, no evidence for a S-S stretch was observed in the monolayer spectrum. This supports bilayer formation through equation 3.2a.

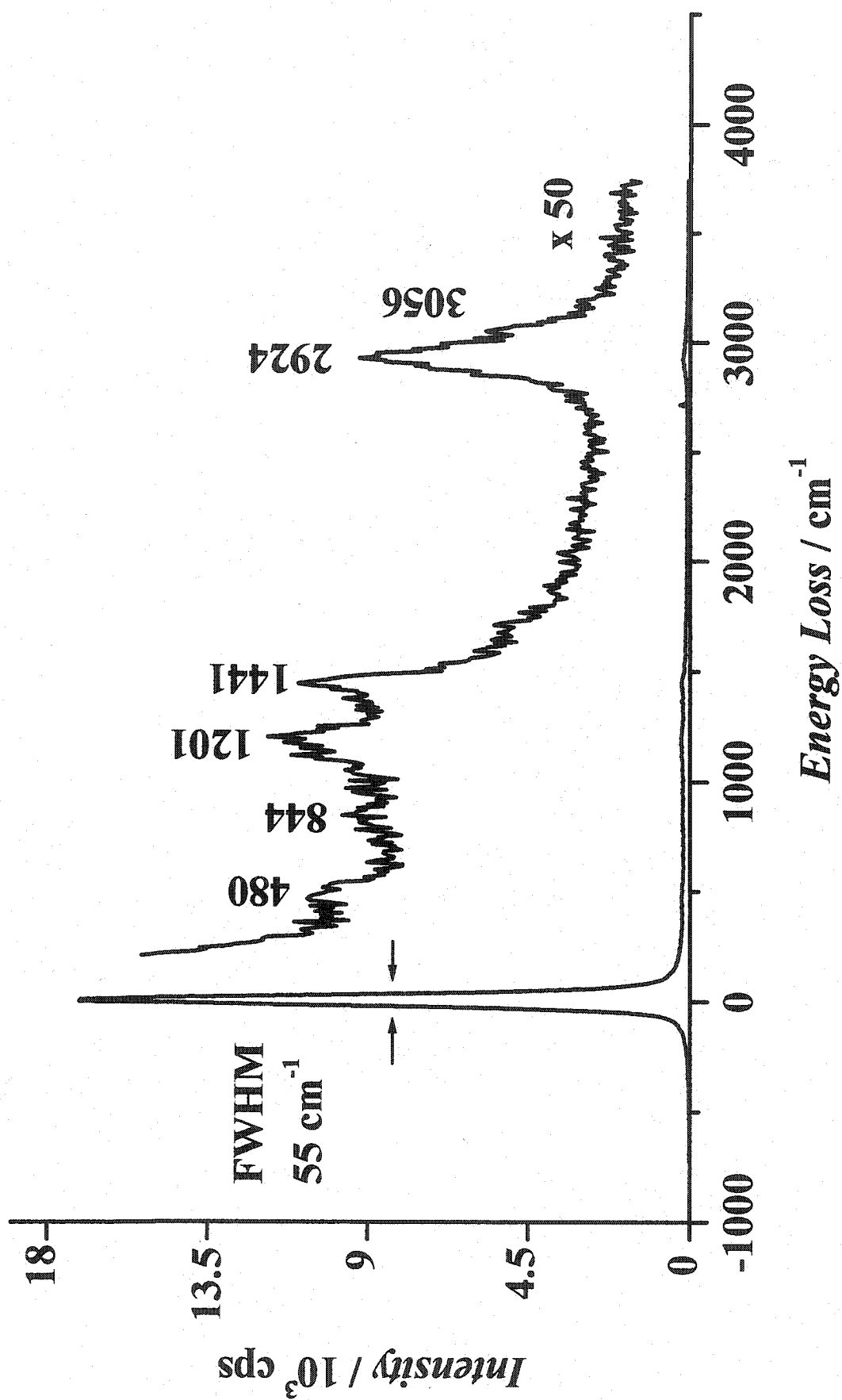


Figure 3.12: HREEL spectrum of a bilayer of 1,4-BDMT electrodeposited onto an annealed gold film from a saturated dithiol solution in 0.5 M KOH.

**Table 3.3:** HREELS peak assignments for an electrodeposited 1,4-BDMT bilayer on gold from 0.5 M KOH.

| peak position / $\text{cm}^{-1}$ | assignment <sup>[18,21,22,73]</sup> |
|----------------------------------|-------------------------------------|
| 3056                             | $\nu(\text{CH arom})$               |
| 2924                             | $\nu(\text{CH}_2 \text{ asym})$     |
| 1441                             | $\text{CH}_2(\text{def})$           |
| 1201                             | sub.-sen. band                      |
| 844                              | $\gamma(\text{CH})$                 |
| 480                              | S-S stretch                         |

IR spectra were taken on the electrodeposited monolayer of 1,4-BDMT from a 0.1 M NaF solution, and the results are shown in Figure 3.13. The purpose of this measurement was to examine the role of the solvent in the electro-adsorption process, i.e. dithiol versus dithiolate. In addition, the IR spectrum of the electrodeposited neutral 1,4-BDMT was compared with that of the chemically deposited ones. This gives us a direct comparison of these two deposition methods. Many bands are present in the protonated monolayer, which are summarized in Table 3.4. This contrasts with the absence of bands in the electrodeposited monolayer of the dithiolate (Figure 3.11a). Again, an exact orientation could not be quantified from these bands, because of their collinear transition dipole moments. However, qualitatively, a more tilted orientation of the dithiol monolayer from 0.1 M NaF solution is suggested. The IR results of the electrodeposited monolayer from neutral solution are more reproducible than those made through chemical incubation.

Absorbance / a. u.

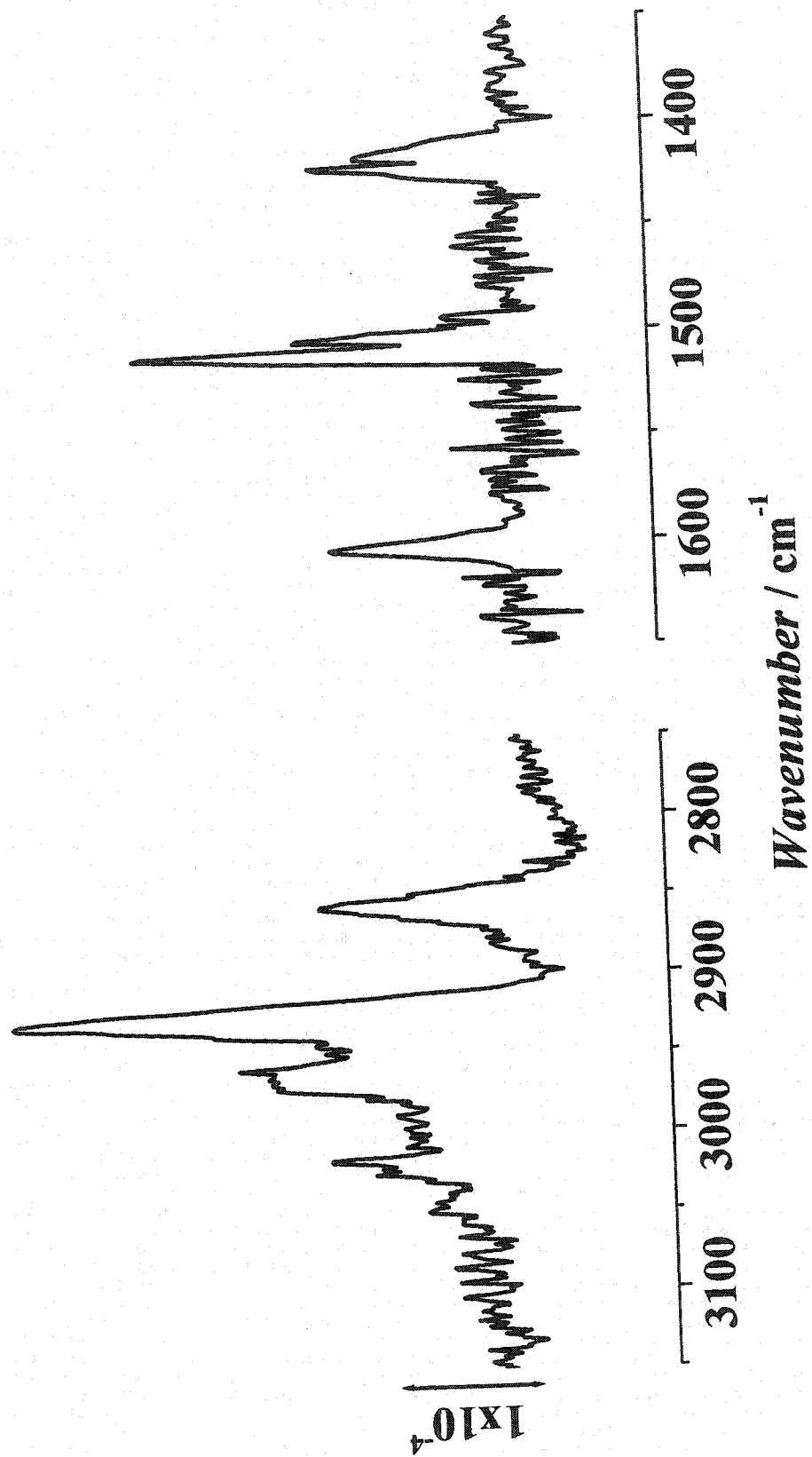


Figure 3.13: IR spectrum of a monolayer of 1,4-BDMT electrodeposited onto an annealed gold film from a saturated dithiol solution in 0.1 M NaF.

**Table 3.4:** Assignment of vibrational bands ( $\text{cm}^{-1}$ ) of 1,4-BDMT electrodeposited onto gold from a saturated dithiol solution in 0.1 M NaF.

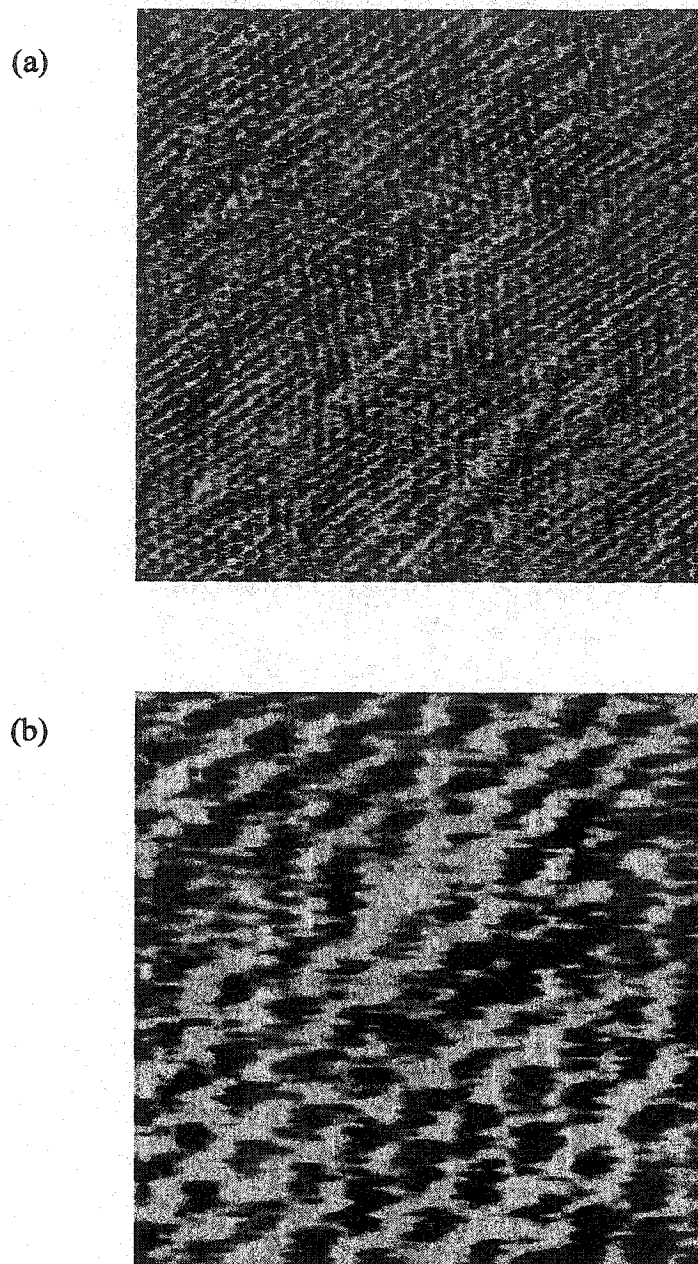
| TIR               | monolayer | assignment <sup>[18,21,22,73]</sup> |
|-------------------|-----------|-------------------------------------|
| In-Plane Modes    |           |                                     |
| 3049              |           | 2                                   |
| 3024              | 3017      | 20a                                 |
| 3006              |           | 20b                                 |
| 2962              | 2965      | 7b                                  |
|                   | 1603      | 8a                                  |
| 1511              | 1511      | 19a                                 |
| 1418              | 1422      | 19b                                 |
| Substituent Modes |           |                                     |
| 2928              | 2927      | $\nu(\text{CH}_2 \text{ asym})$     |
| 2840              | 2857      | $\nu(\text{CH}_2 \text{ sym})$      |
| 1429              |           | $\text{CH}_2(\text{def})$           |

### 3.3.2 Scanning Probe Microscopy: Order on the Microscopic Scale

Scanning probe microscopes are unique in their ability to characterize structure, non-destructively, from the atomic to micron scale. Alkanethiol monolayers on gold surfaces have been extensively studied using this family of imaging techniques [77-85]. A well known system, hexadecanethiol, was first examined. An hexadecanethiol monolayer was prepared by chemisorption on gold from an ethanolic solution using previously described protocols [86]. AFM images containing molecularly resolved features were observed for hexadecanethiol. Figure 3.14 shows a typical image of a hexadecanethiol monolayer on Au(111). A hexagonal pattern of bright spots with similar separations is observed. All images given are in a top-view presentation in which the brighter portions of the grey vertical scale correspond to higher regions of the surface and the darker portions correspond to the lower regions of the monolayer. These distances are markedly larger than those of uncoated Au(111). The average respective nearest- and next-nearest-neighbor distances in Figure 3.14b equal  $0.51 \pm 0.01$  and  $0.92 \pm 0.05$  nm.

These values are in good agreement with the well-known commensurate ( $\sqrt{3} \times \sqrt{3}$ )R30° adlayer adopted by alkanethiols on Au(111), having spacings of 0.50 and 0.87 nm respectively. This two-dimensional arrangement was previously determined for these types of monolayers using helium diffraction [87] and scanning tunneling microscopy [88] techniques. These results are also comparable with those obtained by Porter et al., who have examined monolayer films formed by the chemisorption of alkanethiols ( $\text{CH}_3(\text{CH}_2)_n\text{SH}$ ,  $n = 1-17$ ) on Au(111) using atomic force microscopy under ambient conditions [77]. This image, which is representative of findings from several different samples scanned, functions as a



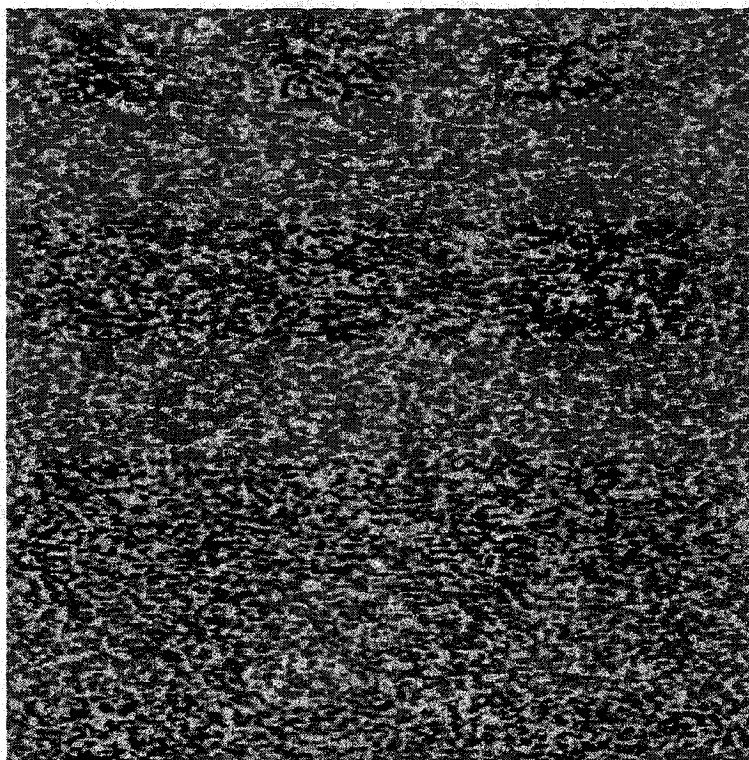


**Figure 3.14:** (a) A  $20 \times 20$  nm AFM image of hexadecanethiol chemically deposited onto an annealed gold film and (b) a  $5 \times 5$  nm AFM image extracted from (a).

reference for comparison to the images of 1,4-benzenedimethanethiol (1,4-BDMT) coated gold surfaces to be presented.

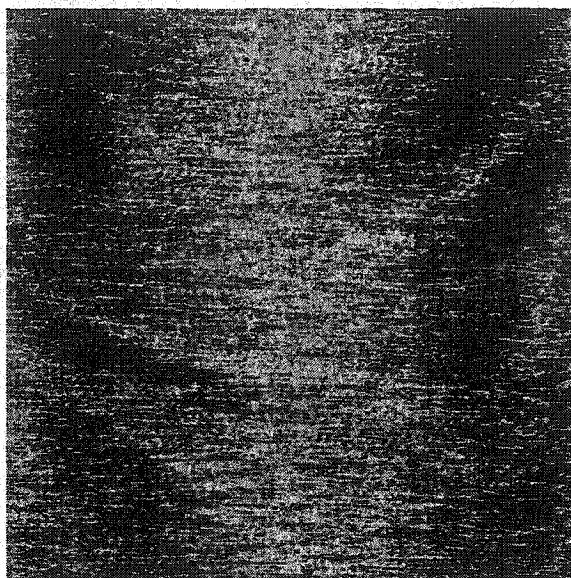
Samples of 1,4-BDMT monolayers were prepared for imaging with AFM through chemical deposition and electrodeposition. Figure 3.15 presents a typical image of an incubated sample of 1,4-BDMT. A sample of an electrodeposited monolayer of 1,4-BDMT is shown in Figure 3.16. The incubated sample shows no ordered structure and is in agreement with the results of Scoles [1] and Kolb [2]. Scoles et al. recently reported that no ordered structure of 1,6-hexanedithiol (essentially the alkyl-counterpart of 1,4-BDMT) was observed with UHV-STM when monolayers were prepared through chemical deposition. Only after annealing were small domains of striped phases observed, and these were attributed to the molecules lying prone to the surface [1]. Kolb et al. obtained very similar results using the same system and the same standard protocol for assembly. Their electrochemical STM results showed no ordered structures for the freshly made samples. Only upon partial reductive desorption did they observe a striped structure [2].

In contrast, the electrodeposited sample shows an ordered adlayer of 1,4-BDMT molecules. Figure 3.16a is an electrodeposited image of 1,4-BDMT, which shows an organized structure that is not present in the incubated sample. The “folds” appearing in Figure 3.16a are attributed to the gold surface topography. This indicates that the observed order is representative of the monolayer of dithiols and not simply noise (i.e. we are in fact imaging the surface and not some artifact). Also, the features scale with scans of different sample size (e.g. Figure 3.16b), which provides further support that the image is real. In addition, when the scan angle (i.e. direction) was changed, the topography changed as well. This would not be the case if noise was an issue.

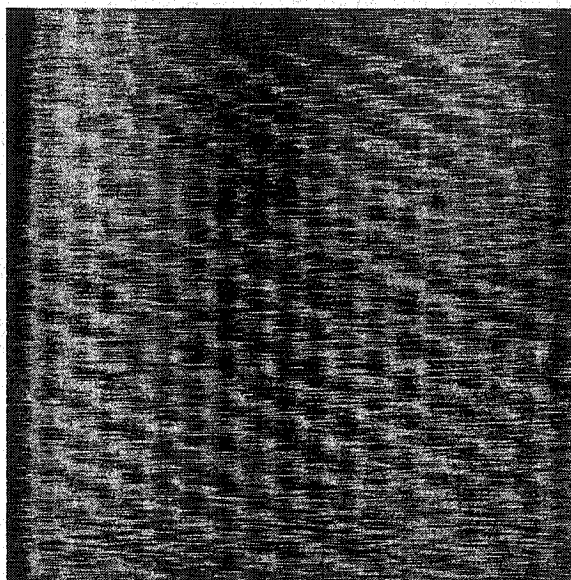


**Figure 3.15:** Contact-mode AFM image measuring  $20 \times 20$  nm of an incubated 1,4-BDMT sample on an annealed gold film.

(a)

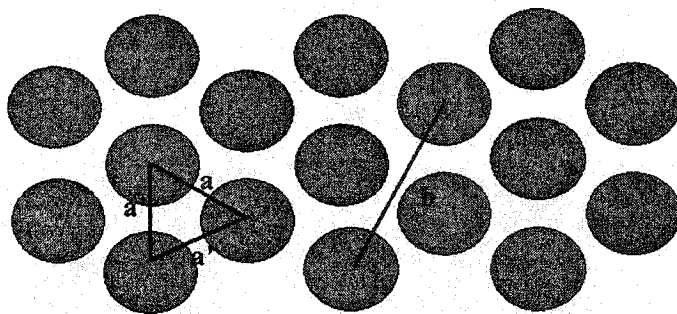


(b)



**Figure 3.16:** Contact-mode AFM image measuring  $20 \times 20$  nm of (a) an electrodeposited monolayer of 1,4-BDMT onto an annealed gold film. (b) A  $5 \times 5$  nm high-resolution AFM image of the same sample as in (a).

A detailed analysis of Figure 3.16b was performed in an attempt to extract information on the packing of 1,4-BDMT. The spacings between the bright spots in the electrodeposited zoomed image are presented in Figure 3.17. Only the monolayer is shown as a representation of the adlayer of 1,4-BDMT, which is somehow organized on the gold lattice. The values obtained for  $a$ ,  $a'$ , and  $b$  are  $0.30 \pm 0.01$ ,  $0.35 \pm 0.01$ ,  $0.56 \pm 0.03$  nm respectively. These results are neither those observed with the typical hexagonal ( $\sqrt{3} \times \sqrt{3}$ )R30° adlayer (i.e. adsorption in the three-fold hollow sites of Au(111)), nor are they directly on top of every gold atom (there is no possible way for the dithiolates to occupy that amount of a space). Although these spacings are very close to those expected for gold, imaging of the substrate lattice has been ruled out. A corrugation of  $3.1 \pm 0.3$  Å between bright spots in all directions was obtained, which is significantly larger than the reported 2.36 Å thickness of an atomic layer of gold [79,81].



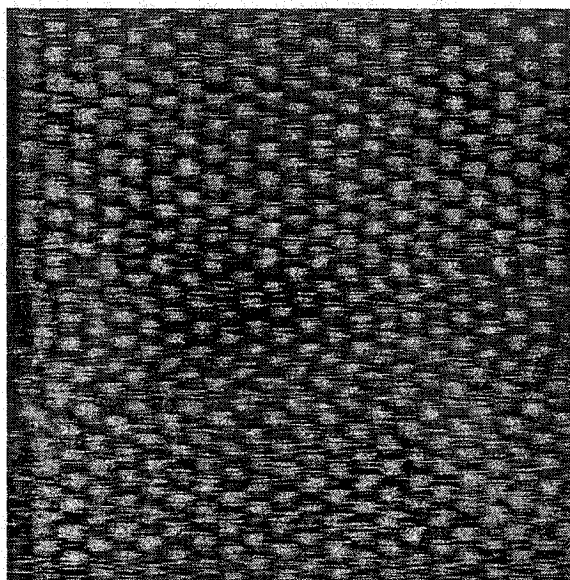
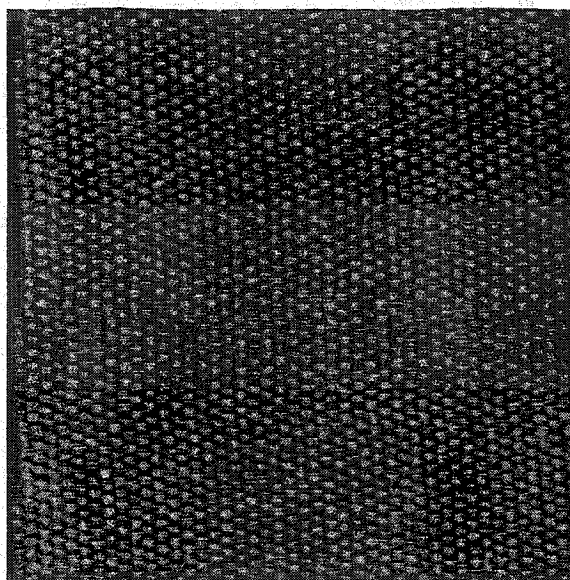
**Figure 3.17:** Schematic diagram of the adlayer of 1,4-BDMT on gold; it is simply a representation of the bright spots in Figure 3.16b and has not been drawn to scale.

As a further check, an estimate of  $9.4 \pm 0.8$  Å<sup>2</sup>/ bright spot was obtained. If each bright spot corresponded to a gold atom, then the value would have to be closer to 6.6 Å<sup>2</sup>/

atom. However, this also indicates that each bright spot does not in fact represent a single molecule, since we would expect a value closer to the one we obtained electrochemically ( $23.2 \pm 2.0 \text{ \AA}^2/\text{molecule}$ ). This illustrates one of the major drawbacks of AFM, namely that the technique does not necessarily provide *true atomic resolution*, but rather an averaging of electron densities. The *tip effect* (section 2.5.2) in AFM could indeed explain the extra bright spots observed in the electrodeposited image.

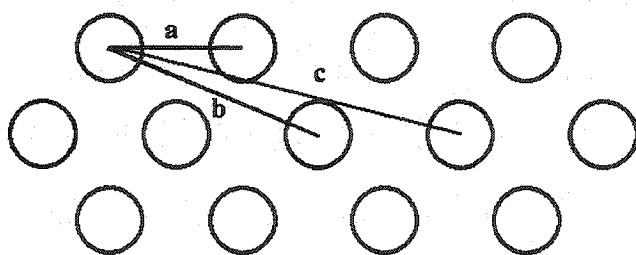
In an attempt to improve upon the AFM image of the monolayer of electrodeposited 1,4-BDMT, scanning tunneling microscopy was employed as a surface analysis tool. Graphite was used as a reference to ensure that the system was well calibrated. A typical image of graphite is presented in Figure 3.18. A detailed analysis of the spacings between the carbon atoms was performed, where a, b, and c (Figure 3.19) are  $0.255 \pm 0.004$ ,  $0.433 \pm 0.005$ , and  $0.663 \pm 0.019 \text{ nm}$  respectively. These values are comparable to the actual ones of 0.255, 0.433, and 0.666 nm [89]. Both an incubated sample of 1,4-BDMT and an electrodeposited monolayer of 1,4-BDMT with STM were imaged, but no order (on the large and small scale) was observed with either sample. STM is a much more sensitive technique than AFM to noise, cleanliness, and other such external factors. More work would have to be done in order to reach any conclusive observations with STM. In situ electrochemical STM or UHV STM would be obvious next approaches to achieving *true atomic resolution*, as most of the results published thus far on such conjugated systems are not under ambient conditions [46-53].

Porter et al. reported that atomically resolved images could be obtained with AFM, corresponding to a  $(\sqrt{3} \times \sqrt{3})R30^\circ$  adlayer, for alkyl chains  $(\text{CH}_3(\text{CH}_2)_n\text{SH})$  of length  $n \geq 4$  [77]. AFM images with a well-defined periodicity were not achieved for monolayers with  $n$



**Figure 3.18:** (a) A  $10 \times 10$  nm constant current STM topograph. (b) A high-resolution STM image ( $5 \times 5$  nm) of the same sample of graphite. Imaging conditions: 20.0 mV and 1.97 nA.

$\leq 3$ . In contrast, with STM, atomically resolved images of ethanethiol ( $n = 1$ ) monolayers were routinely obtained [88]. This discrepancy was attributed to the fact that the AFM tip might have induced disorder in the shorter chain monolayers; they were able to reasonably rule out imaging of the Au-S bond, and believed that the tip actually imaged the underlying polymethylene chain structure (i.e. the tip pushed through the first few carbons) [77].



**Figure 3.19:** Illustration of the graphite lattice.

This could explain why well-resolved images of hexadecanethiol were obtained, and none for the electrodeposited 1,4-BDMT. The length of this dithiol is close to an alkanethiol of  $n = 7$ , which is relatively short. Also, the sulfur end group is more electron rich than the methyl chain terminus of the corresponding alkanethiol. As a result, less of a contrast in electronic density would be expected between the gold substrate and the dithiol, than that of the equivalent alkanethiol monolayer. Since AFM is limited in its ability to image *true atomic resolution*, a poor atomically resolved image of the electrodeposited 1,4-BDMT is obtained.

Although no unit cell could be deduced for the adlayer of electrodeposited 1,4-BDMT on Au(111), the image in Figure 3.16b is real. All of the appropriate tests, e.g. change of scan size, scan rate, scan angle etc., confirm that the image is not simply noise or some other



artifact. We have ruled out the possibility that the image is of the gold substrate through corrugation measurements, as well as the general structure of the lattice. The hexadecanethiol results obtained with AFM, and those of graphite in STM indicate that the Nanoscope II system is well calibrated and that the conditions were appropriate for imaging a soft organic layer.

### 3.4 Mechanism for the Oxidative Adsorption of 1,4-BDMT onto Au(111)

#### 3.4.1 Monolayer Formation

The electrochemical measurements suggest that 1,4-BDMT is oxidatively adsorbed via a single S-Au bond from a 0.5 M KOH solution. The potential and charge of peak A are compatible with the one-electron process reported for the chemical deposition of a monolayer of benzylmercaptan on Au(111) [55]. The pH effect, observed in the capacitance measurements and the transfer experiments, clearly indicates the presence of unreacted thiolates. The absence of bands in the IR spectra of the electrodeposited monolayer from alkaline solution also supports a vertical orientation of the 1,4-BDMT molecules (i.e. one S-Au bond). The following chemical equation is used to describe monolayer formation:



Our oxidative deposition of a monolayer differs from the spontaneous adsorption of dithiols via both sulfurs that has recently been reported [1-6,14]. These differences are not caused by the gold surface, since we and others [1,2] used Au(111) single crystal substrates. It is the phase from which the dithiols are deposited, their adsorption rate, and molecular structures that determine their adsorption geometries. Under the experimental conditions of

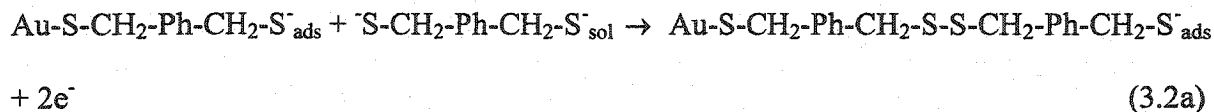
electrodeposition that we used, the thiols are deprotonated and solvated. Also, the high dielectric constant of the aqueous solution and high ionic strength decreases the repulsion between the thiolates (section 2.2.3). These conditions favor a rapid electroformation of a compact, vertically aligned monolayer.

This is in contrast to the measurements performed at lower pH. In this case, the S-H bond dissociation slowed down the adsorption process, which is obvious in the shape of the voltammetry in Figure 3.2b [39,40]. This is also reflected in the IR spectra of the monolayer deposited from neutral solution, which suggests a tilted orientation. The deposition of (protonated) thiols is even slower in the absence of an applied potential [45,90]. In this case, this gives more time for the second thiol group to orient itself to form a bond with the gold surface. However, the increase of the rate of adsorption with an applied potential reduces the likelihood of dithiols binding to the surface via both sulfurs.

### 3.4.2 Bilayer Formation

The unreacted thiolates of the monolayer were oxidized by scanning towards more positive potentials, and a second oxidative peak B was observed. The charge ratio  $Q_B/Q_A$  obtained from chronocoulometry was  $1.9 \pm 0.2$ . Both a decrease in the capacity and an increase in the EQCM frequency change by a factor of two were observed upon scanning from A (monolayer) to A + B. These simple relationships between the properties of the two anodic peaks (A and B) are found to be compatible with a step-wise oxidative deposition of a bilayer of dithiols. This deposition of a second layer is also supported by the electrochemical transfer experiments. The preliminary HREELS results provide evidence for a weak S-S stretch at  $480 \text{ cm}^{-1}$ , which was only observed in the bilayer spectrum. Our results show that

peak B originates from the dimerization between adsorbed dithiolates and dithiolates in solution to form bilayer:

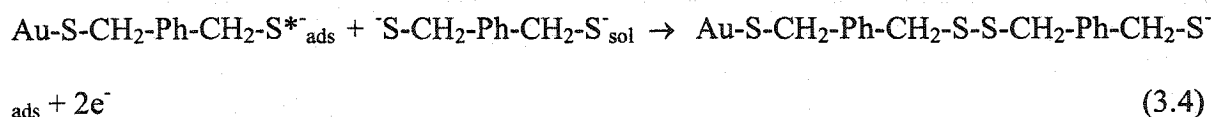
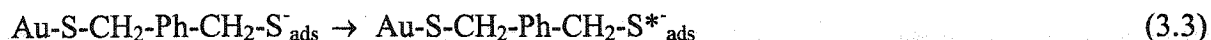


We believe that the differences between the electrodeposition method that we used and the methods reported previously [11,12,16,21-23,33] regarding the growth of a bilayer are related to the way the sulfurs are oxidized. A recent study reported that disordered multilayers of dithiols could be obtained after many hours [23] of incubation. These authors suggested that the slow and uncontrolled formation of multilayers of dithiols is caused by varying amounts of oxidants (such as oxygen and water), which are present in the incubation medium. These oxidants cannot be completely eliminated from the incubation solution and therefore some oxidative dimerization of dithiols always occurs.

Our results demonstrate the advantages of electrochemical oxidation over chemical oxidation of the sulfur in the formation of bilayers of dithiols. The oxidation of the sulfur is controlled by the applied potential and occurs only at sufficiently positive potentials. We also note that the dimerization (peak B) is well separated from the oxidative adsorption of the dithiolate (peak A). This is probably related to the fact that the unreacted thiolate groups are further away from the gold surface and require a more positive potential to be oxidized (section 2.2.3b). Furthermore, the electrodeposition of a complete bilayer of dithiolates takes only a few minutes in contrast to the many hours required to form a partial bilayer in absence of an applied potential [23].

Surprisingly, the formation of dimers is not observed between neighboring adsorbed dithiolates. In addition, the formation of the S-S bond in the bilayer is found to be irreversible; a charge equality (i.e.  $Q_A = |Q_{A'+B'}| = |Q_{B''}|$ ) was observed and fits well with the direct desorption of a bilayer. These observations can be rationalized by looking at the well-characterized electrochemistry of the biological thiols glutathione [91] and cysteine [92-95]. These compounds are known to dimerize by forming a disulfide via a two-electron process. The electrochemical dimerization of cysteine [93,95] occurs just before the formation of the surface oxide on gold. This is also the case for the 1,4-BDMT system. The bulk dimerization of cysteine was found to be irreversible [95]. This explains the absence of a reductive current peak that could be assigned to the de-dimerization of the S-S bond. This contrasts with the reversibility of the oxidation/reduction of the Au-S bond [38,39].

Based on the known behavior of sulfur compounds, the following mechanism for the preferential formation of a bilayer of dithiolates is suggested:



The proposed mechanism consists of two consecutive steps. The first one (3.3) represents the activation of the unreacted sulfur of the adsorbed dithiolate, as the potential is scanned towards more positive values. It is assumed that the activated sulfur displays similar chemistry to that of a thyl radical. With this in mind, the activated sulfur (thyl) is probably

not very reactive [91]. Since all of the adsorbed thiolate end groups are activated at the same time, the reaction between them is expected to be slow. The second step (3.4) involves the nucleophilic attack of an adsorbed activated sulfur by a dithiolate in solution. This concerted two-electron reaction is probably fast since the reaction between a thyl radical and a thiolate is known to be fast [91]. The different rates for these two possible reactions would suggest that the formation of a bilayer dimer is faster than the dimerization of two adsorbed dithiolates.

A recent study on the photooxidation of 1,8-octanedithiol on gold reported a similar mechanism [12]. Upon exposure to light ( $\lambda > 400$  nm), an electron was transferred from the Au substrate to the terminal thiol. The resulting radical anion reacted with ground-state dioxygen from the atmosphere. Rieley et al. proposed that the reaction was concerted, given the short lifetimes of negative ion resonances at surfaces, and terminated with the tail group in sulfonic acid form [12]. The mechanism suggested above also yields activated sulfurs (equation 3.3) that could react with oxidants such as oxygen. However, we conducted our experiments in deoxygenated solution. Instead, there is a reaction with a weaker nucleophile, namely a thiolate. This reduces the likelihood of reactions between oxygen and the activated sulfur. The products of these reactions were checked (i.e. sulfinic and sulfonic acids) with IRAS and no S-O stretching modes were observed.

The formation of more than two layers is not possible, because the oxidation of the thiolate end group in the bilayer would require even more positive potentials. At such potentials, dithiolates are known to oxidize to sulfoxo species by reacting with the surface oxide [94].

Our results illustrate the advantages of the electrochemical oxidation of the dithiolates over the chemical oxidation of dithiols previously reported [11,12,16,21-23,33]. The electrochemical method allows for gentler oxidative conditions. By this method, the sulfur is oxidized from a  $-2$  to a  $-1$  state upon forming a bilayer through S-S dimerization. This property is extremely important in the development of organic molecular conductors, where defects must be minimized. In the presence of oxygen or UV light, the oxidation of the sulfur is much more substantial. No disulfides were observed and various sulfoxo species were formed [11,12]. Under these harsher oxidative conditions, sulfur oxidation states ranging from  $+5$  to  $+1$  were generated. The reactivity of the sulfurs in these oxidation states will vary greatly. It is difficult to imagine homogeneous surface reactions for controlled multilayer growth under these conditions.

### 3.5 Summary

An electrodeposition method was used to form a (complete) bilayer of 1,4-BDMT at the Au(111) surface in a step-wise fashion. A complete monolayer of vertically oriented dithiolates was first formed at potentials between  $-0.82$  V to  $-0.85$  V. The unreacted sulfur end groups were then oxidized by scanning the potential to values more positive than  $-0.65$  V. This resulted in dimerization between an adsorbed dithiolate and a dithiolate in solution. A mechanism for bilayer formation was proposed, which consisted in the nucleophilic attack of an activated thiolate end group (adsorbed) by a dithiolate from solution. The electrochemical method resulted in reproducible monolayers and bilayers of 1,4-BDMT. This reproducibility was reflected in the IRAS and SPM results; the electrodeposited monolayers showed an improvement in film order [1,2] over those prepared through chemical incubation.

### 3.6 References

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## Chapter 4: Isomeric Effect on the Oxidative Formation of Bilayers of Benzenedimethanethiol (BDMT) on Au (111)

### 4.1 Introduction

In Chapter 3, we reported that more homogeneous monolayers and bilayers of 1,4-BDMT could be electrodeposited onto the gold surface [1] than those layers formed in the absence of an electric field (i.e. under open circuit conditions) [2-4]. The primary purpose of the present work is to investigate if we can apply our electrodeposition scheme to the other two isomers of BDMT. This series of compounds permits us to investigate the effect of the substituent position on the oxidative deposition of aromatic dithiols.

Our assertion is that bilayer growth will be dependent on the availability of the second sulfur end group. A direct approach of the dithiolate in solution with the unreacted adsorbed sulfur is more likely to result in complete bilayer formation, which was the case with 1,4-BDMT. However, if the second sulfur is less accessible for nucleophilic attack, dimer formation will probably be hindered. For instance, when a S-S bond is formed between an adsorbed 1,2-BDMT and one in solution, the approach of another solution dithiolate may be difficult. With this in mind, our expectation is that 1,3-BDMT will be less reactive than 1,4-BDMT, but more than 1,2-BDMT.

In addition, *Gaussian*<sup>®</sup> calculations show that the distance between the two sulfur atoms of 1,2-BDMT can readily achieve a span of 5.0 Å (Figure 2.12) [5]. This value is equivalent to the spacing between three-fold hollow sites on Au(111) [6, p279]; this implies that 1,2-BDMT is capable of binding to gold via both sulfur end groups. In fact, this orientation has been previously assigned for 1,2-BDMT through absence of the S-H

stretching band in the IRAS spectra [7], as well as other chelating dithiols [8-10]. Therefore, 1,2-BDMT is a good model compound with which to test our electrodeposition scheme.

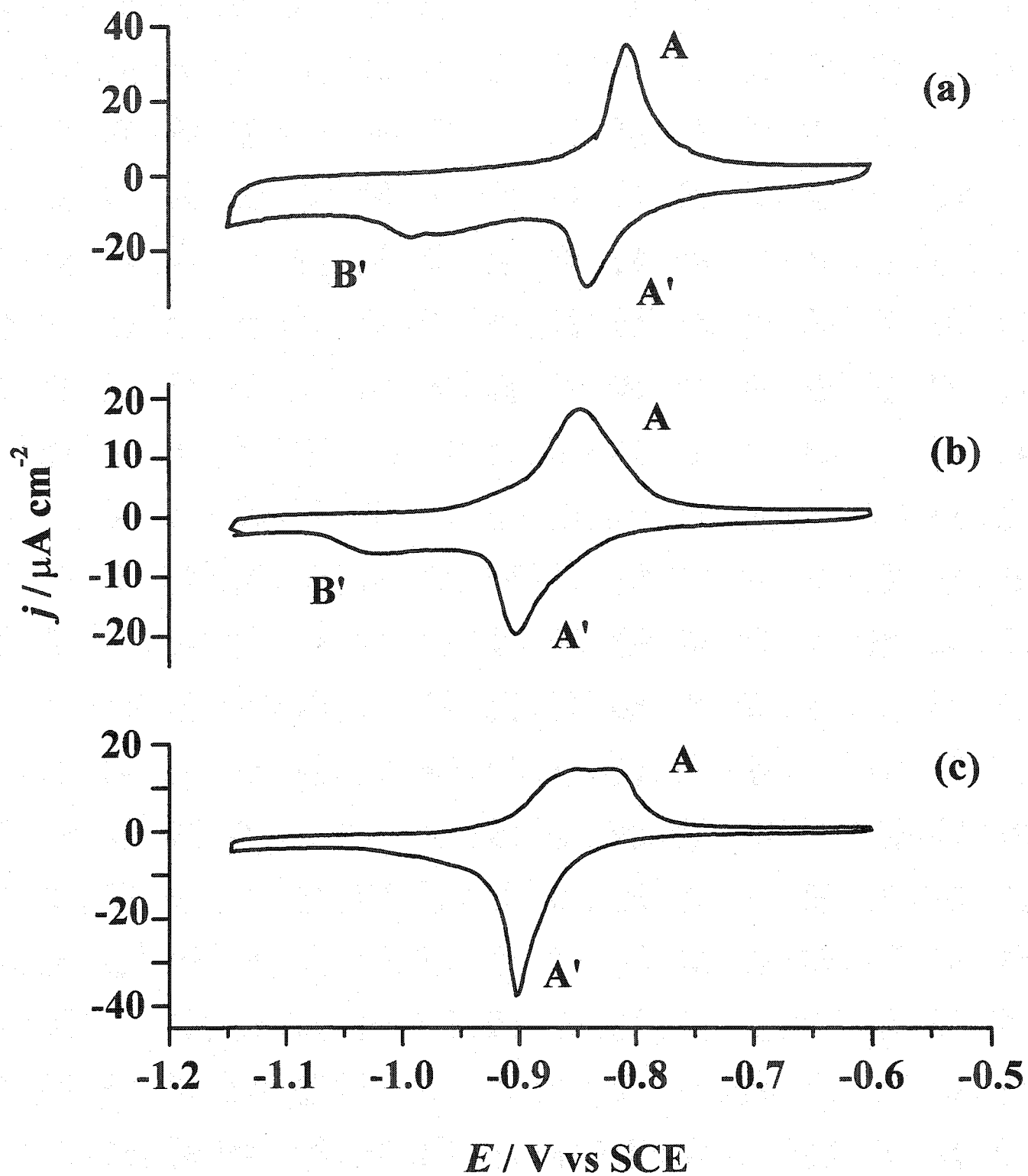
## Results and Discussion

### 4.2 Electrochemical Techniques

#### 4.2.1 Oxidative Deposition of Monolayers of the Isomers of BDMT

The oxidative deposition of the three isomers of BDMT on a Au(111) single crystal electrode with cyclic voltammetry has been examined. In the first set of voltammetric measurements, the potential was cycled between  $-0.60$  V and  $-1.15$  V at  $20$  mV s<sup>-1</sup>, in a saturated BDMT aqueous electrolyte solution ( $0.5$  M KOH) of each isomer. The results are presented in Figure 4.1. All of the compounds display an oxidative current peak, A. The peaks A are located at a potential of  $-0.81$  V for the *para*,  $-0.85$  V for the *meta*, and  $-0.84$  V for the *ortho* isomer. Upon proceeding from the *para* to the *ortho* isomer, there is a change in peak shape from sharp to broad. The sharpness of the *para* peak A suggests that its electrodeposition onto the gold electrode is a relatively homogeneous process [11, p521]. The broader peak A of the *meta* and *ortho* isomers suggests that the electrodeposition of a monolayer of these isomers is a less homogeneous process.

Even though the shape of peak A changes with the substituents' position, the baseline corrected oxidative charge of peak A,  $Q_A$ , does not. A value for  $Q_A$  of  $73 \pm 4$   $\mu\text{C cm}^{-2}$  is obtained for the *para* isomer and a  $Q_A$  of  $75 \pm 5$   $\mu\text{C cm}^{-2}$  and  $73 \pm 5$   $\mu\text{C cm}^{-2}$  is obtained for the *meta* and *ortho* isomers respectively. The fact that the oxidative charges and current peak potentials are almost identical for all of the isomers, and that these values are similar to what is observed for the oxidative deposition of alkanethiolates [12], strongly suggests that they adsorb on Au(111) via one sulfur. The oxidative charges ( $Q_A$ ) were converted to surface



**Figure 4.1:** Cyclic voltammograms of the oxidative deposition and reductive desorption of a monolayer of ( a ) 1,4-BDMT, ( b ) 1,3-BDMT, and ( c ) 1,2- BDMT on Au(111) from saturated dithiol solutions in 0.5 M KOH. Potential scan rate: 20 mV s<sup>-1</sup>.



concentrations (assuming a one-electron process), and values of  $7.5(\pm 0.4) \times 10^{-10} \text{ mol cm}^{-2}$ ,  $7.8(\pm 0.6) \times 10^{-10} \text{ mol cm}^{-2}$ , and  $7.5(\pm 0.6) \times 10^{-10} \text{ mol cm}^{-2}$  were obtained for the *para*-, *meta*-, and *ortho*-BDMT isomers respectively. These values are identical to, within error, the one corresponding to an alkanethiol monolayer [12].

To eliminate the possibility that the charge of peak A (for all three cases) corresponds to a two-electron process per adsorbate, we calculated values for the charge of A based on potential orientations that the isomers could assume at the gold surface. The neutral structures were optimized at the HF/6-31G\* level of theory to obtain bond lengths and bond angles. The standard Van der Waals atomic radii were also incorporated in the calculations. We report here the results for 1,2-BDMT, which is the isomer most likely to bind via two sulfur atoms [7,10]. A detailed discussion of the *para* isomer was presented in section 3.2.1.

If 1,2-BDMT were to bind via both sulfurs ( $sp$  hybridization of the sulfur atoms, i.e. a linear Au-S-C bond angle), with its benzene ring parallel to the gold surface, the area per adsorbate should be larger than  $50 \text{ \AA}^2$ , corresponding to a theoretical charge for A less than  $64 \mu\text{C cm}^{-2}$ . On the other hand, if the benzene ring were perpendicular to the gold surface the molecular area would be about  $27 \text{ \AA}^2$ , i.e.  $120 \mu\text{C cm}^{-2}$  assuming a cross-sectional dimension of  $7.3 \text{ \AA}$  and a Van der Waals thickness of  $3.7 \text{ \AA}$ . In contrast, if the ring is oriented perpendicular to the gold surface via formation of a single S-Au bond ( $sp^3$  hybridization in the sulfur atom, i.e. a  $109.5^\circ$  Au-S-C bond angle), an area of  $24 \text{ \AA}^2$  ( $6.6 \text{ \AA} \times 3.7 \text{ \AA}$ ) is calculated, which corresponds to  $68 \mu\text{C cm}^{-2}$ . This value is equal (within error) to the one obtained experimentally. This particular orientation is also supported by further electrochemical experiments, as well as the IRAS results to follow.

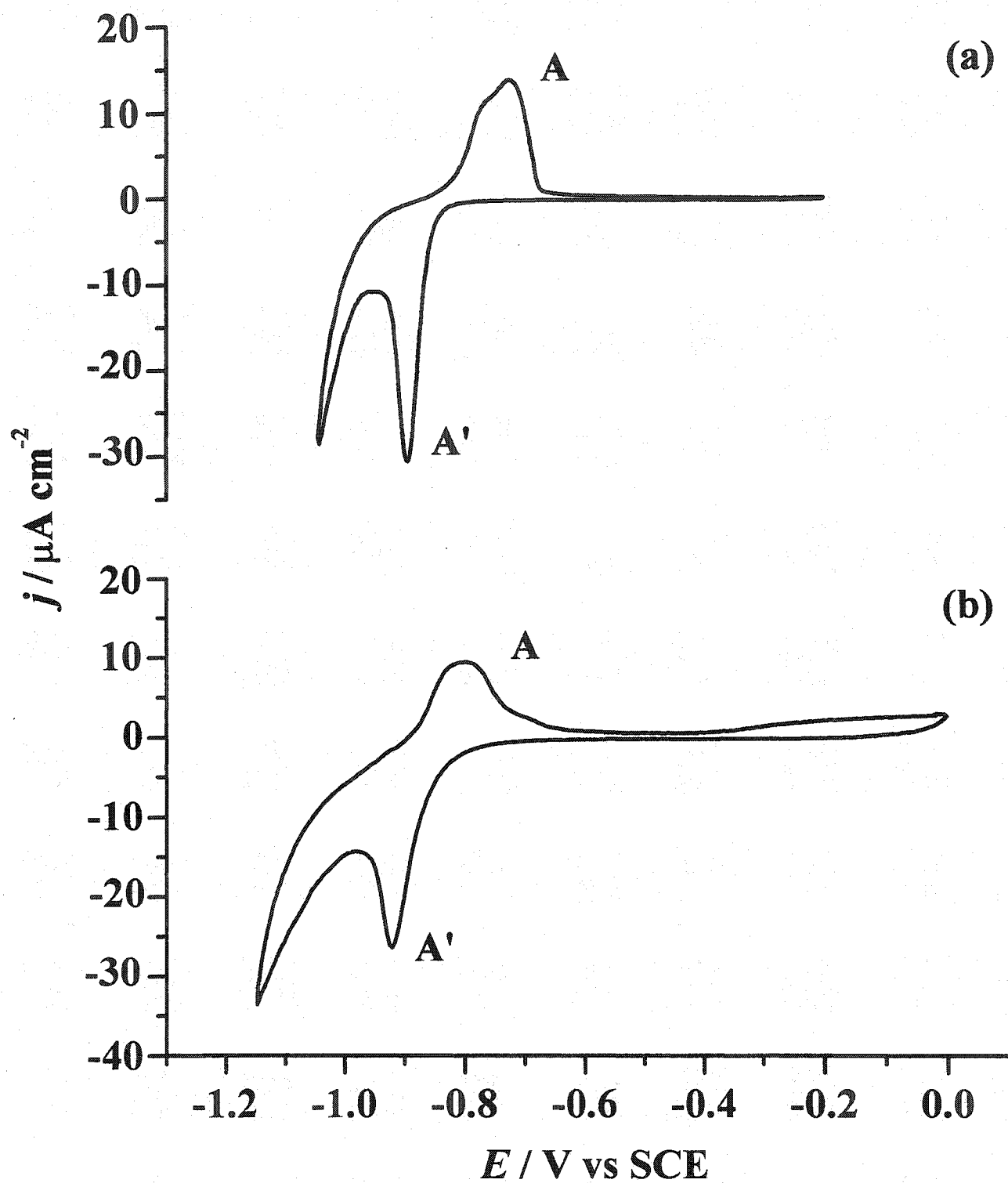
The ion blocking properties of the oxidatively deposited monolayers were characterized through differential capacitance. Such measurements provide information on the thickness of the deposited layer, as well as its permeability to water and anions (section 2.3.3) [13]. After electrodeposition of peak A in 0.5 M KOH, the capacity was measured in pure 0.5 M KOH from  $-0.30$  to  $-0.50$  V. Values of  $10.4 \pm 0.8$ ,  $15.4 \pm 3.0$ , and  $15.4 \pm 1.4$   $\mu\text{F cm}^{-2}$  were obtained for the *para*, *meta*, and *ortho* isomers respectively. These capacities are relatively high due to the presence of unreacted thiolate groups [1]. The larger capacitances of the *meta* and *ortho* isomers are indicative of more defects, which is also suggested by their broader peak A.

On the negative going potential scan from  $-0.60$  to  $-1.15$  V, a symmetric cathodic peak (A') at  $-0.84$  V is followed by a smaller peak (B') at  $-0.99$  V for the *para* isomer. In Chapter 3, peak A' was assigned to the reduction of the monolayer of the *para* isomer. A small separation of 30 mV between peaks A and A' ( $\Delta E_p$ ) suggests that this oxidative deposition/reductive desorption of a monolayer is a relatively reversible process. It was also concluded that peak B' is related to inhomogeneous (i.e. partial) bilayer formation [1]. The reduction potential of a peak depends on the chain length of the adsorbate. As the chain length increases, there is an increase in the difficulty of ion penetration through the film during reduction, which results in a shift of the potential to more negative values [13-16]. This explains why B' (bilayer) is approximately 150 mV more negative than A' (monolayer).

In comparing the reductive scan of the *meta* isomer with that of the *para*, it is noted that they are very similar in nature. In Figure 4.1b, peak A' is slightly asymmetric and located at  $-0.90$  V and is followed by B' at  $-1.00$  V. Again, A and A' are separated by about only 50 mV, which is indicative of a reversible process. This implies that the

electrochemistry of the *meta* isomer is similar to that of the *para*, and that there is some bilayer formation for the *meta* isomer. In contrast, the reductive scan for the *ortho* isomer is different from those of the other two BDMT isomers (Figure 4.1c). There is a single symmetric reductive current peak A' located at -0.90 V. Once again the oxidative deposition/reductive desorption is a relatively reversible process since peaks A and A' are separated by only 60 mV. There is no evidence for peak B', which indicates that there is no bilayer formed.

The oxidative deposition of the protonated *para* and *meta* isomers from a 0.1 M NaF solution shows that the voltammetry changes with pH (Figure 4.2). In both cases, the oxidative peak A shifts to more positive potentials and broadens. It is located at -0.79 V for the *para* isomer and -0.82 V for the *meta* isomer. However, the charge of peak A remains the same (within error) as that measured in 0.5 M KOH. The value of  $Q_A$  from 0.1 M NaF is  $73 \pm 5$  and  $68 \pm 6 \mu\text{C cm}^{-2}$  for the *para* and *meta* isomers respectively. More energy is therefore required to deposit the dithiols at lower pH because of the additional difficulty of having to break the S-H bond. There is a single reductive peak A', which is at slightly more negative potentials by 60 and 20 mV than in 0.5 M KOH for the *para* and *meta* isomers respectively. This is attributed to the negatively charged thiolate end groups in alkaline solution; the repulsive interaction between them makes it easier to remove the monolayer from the gold surface in basic solution. The absence of B' indicates that bilayer formation occurs only in alkaline solution. The separation between the protonated peaks A and A' increases for the *para* and *meta* isomers, having respective values of 170 and 150 mV. Similar observations were reported for the electrochemical study of nonanethiol on Au(111) [14].



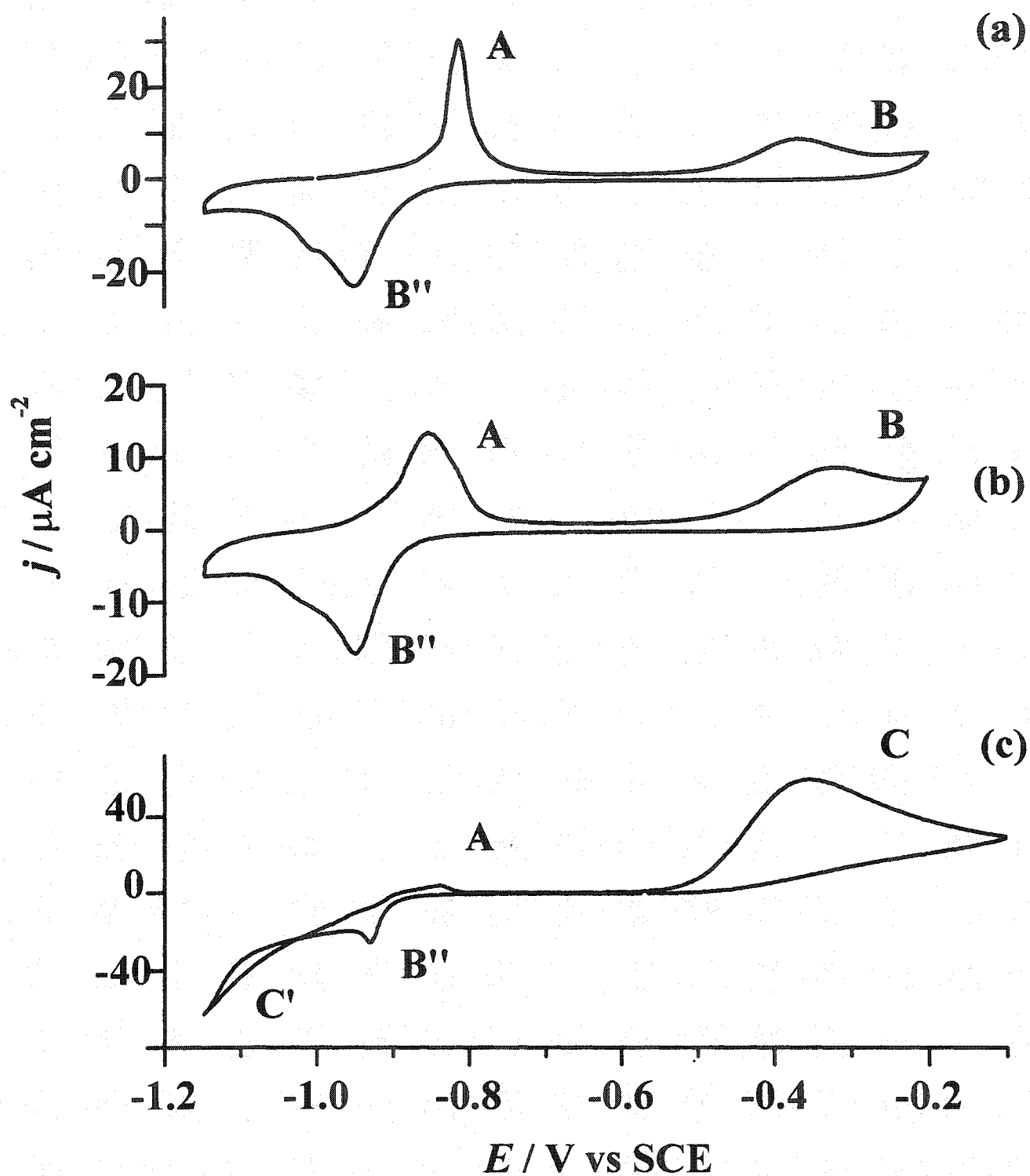
**Figure 4.2:** Cyclic Voltammograms of the oxidative adsorption and reductive desorption of (a) 1,4-BDMT and (b) 1,3-BDMT on Au(111) from saturated dithiol solutions in 0.1 M NaF. Potential scan rate: 20  $\text{mV s}^{-1}$ .

The pH also influences the capacitance measurements performed after monolayer deposition (peak A). A capacity of  $3.8 \pm 0.3$  and  $4.0 \pm 0.3 \mu\text{F cm}^{-2}$  was obtained for the *para* and *meta* isomers respectively, when peak A was deposited in 0.1 M NaF and measured in pure 0.1 M NaF. This decrease is attributed to the protonation of the sulfur end groups as was previously reported for a carboxylate-terminated thiol monolayer [16]. This pH dependence supports our suggestion that these isomers are bound to the Au(111) surface via a single S-Au bond, and hints at a possible electroactive surface. It was not possible to do these measurements for the *ortho* isomer, because it was not soluble in 0.1 M NaF.

#### 4.2.2 Oxidative Deposition of Bilayers of the Isomers of BDMT

To oxidize the sulfur at the organic/solution interface, the potential was scanned towards more positive values and the resulting cyclic voltammograms are shown in Figure 4.3. In all three cases, a new oxidative peak appears at roughly the same peak potential (*para* -0.36 V, *meta* -0.32 V, and *ortho* -0.33 V). The magnitude of this new oxidative current peak is similar for the *para* and *meta* isomers, but it is much larger for the *ortho* isomer. The separation between the two anodic peaks is significant and equals 450, 530, and 570 mV for the *para*, *meta*, and *ortho* isomers respectively. This implies that peak A and the new peak (B for the *para* and *meta* isomers, and C for the *ortho* isomer) correspond to two separate oxidative processes.

The reductive current peak B'' is similar for both the *para* and *meta* isomers. It is located at -0.96 V for the *para* isomer, and -0.98 V for the *meta* isomer. However, there is in addition to the peak B'' (-0.93 V) for the *ortho* isomer, a very large reductive current labelled C'. The origin of the second oxidative peak for the *ortho* and *meta* isomers was investigated to see if it corresponds to bilayer growth previously reported [1].



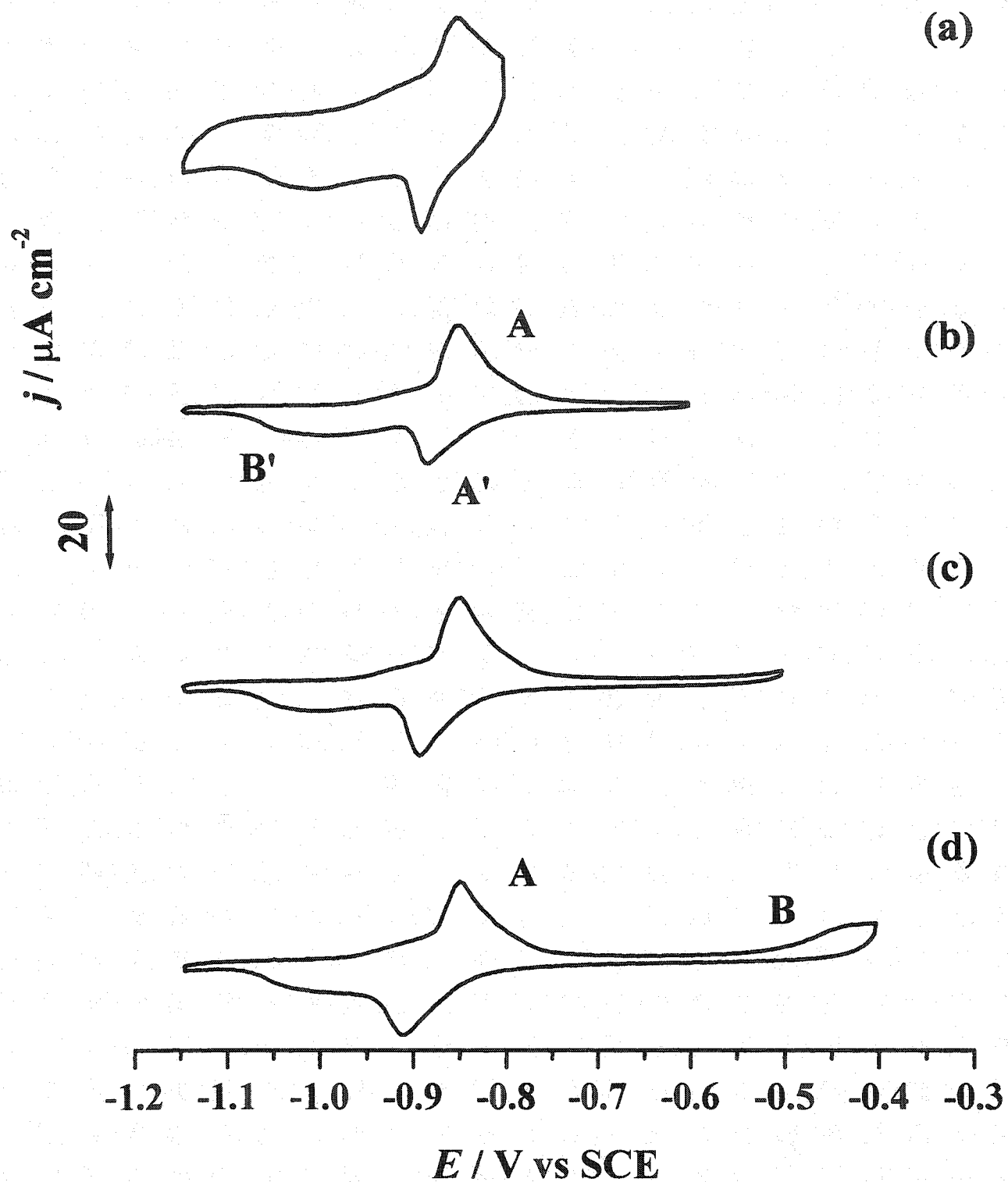
**Figure 4.3:** Cyclic voltammograms of the oxidative deposition and reductive desorption of (a) 1,4-BDMT, (b) 1,3-BDMT, and (c) 1,2-BDMT on Au(111) from saturated dithiol solutions in 0.5 M KOH. Potential scan rate: 20 mV s<sup>-1</sup>.

#### 4.2.2a *Para* and *Meta* Isomers

Window-opening experiments for the *para* (Figure 3.3) and *meta* (Figure 4.4) isomers show that the oxidative peak B is related to the reductive peak B''. An accurate measure of the reductive charge of B'' was not possible, because it overlaps with the hydrogen evolution current. Within these limitations, the absolute charge of the reductive peak B'' is  $82 \pm 5 \mu\text{C cm}^{-2}$  and  $93 \pm 7 \mu\text{C cm}^{-2}$  for the *para* and *meta* isomers respectively. These values are similar to those of their respective oxidative peak A.

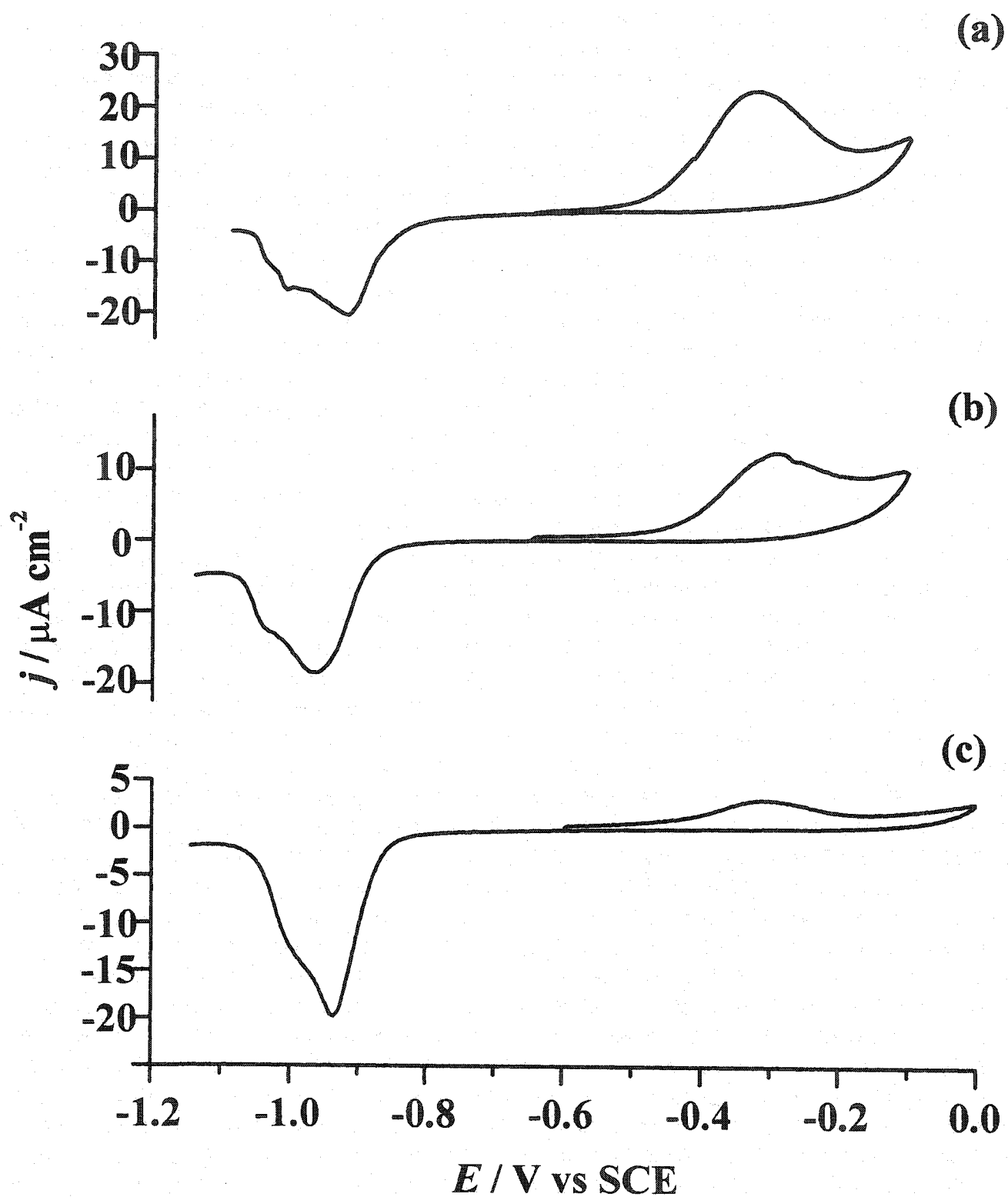
A significant decrease in the capacity was observed on scanning from A to B for the *meta* isomer, from  $15.4 \pm 3.0$  to  $5.6 \pm 0.6 \mu\text{F cm}^{-2}$  in 0.5 M KOH. A similar decrease from  $10.4 \pm 0.8$  to  $4.6 \pm 0.5 \mu\text{F cm}^{-2}$  was observed for the *para* isomer [1]. This decrease in capacity can be attributed to the formation of a thicker film with fewer defects, and implies that peak B is a surface process and not a solution one.

The assignment of peak B to a surface process is further supported by transfer experiments of the monolayer (peak A) into various solutions. These experiments were performed in the same way as those described in section 3.2.2. After electrodepositing peak A, the electrode was transferred to a 1 mM heptanethiol solution (in 0.5 M KOH) and the potential was scanned towards positive values. The results of these experiments are presented in Figure 4.5. An anodic peak at a similar potential to B was observed for the *para* (Figure 4.5a) and the *meta* (Figure 4.5b) isomers. This clearly suggests that B originates from a reaction of an adsorbed dithiolate with a dithiolate in solution. The magnitude of peak B is smaller for the *meta* isomer. In contrast, when the monolayer coated electrode was transferred into a solution of pure 0.5 M KOH and the potential was scanned towards more positive values, no oxidative peak B was observed for either isomer (Figure 4.6). Obviously,

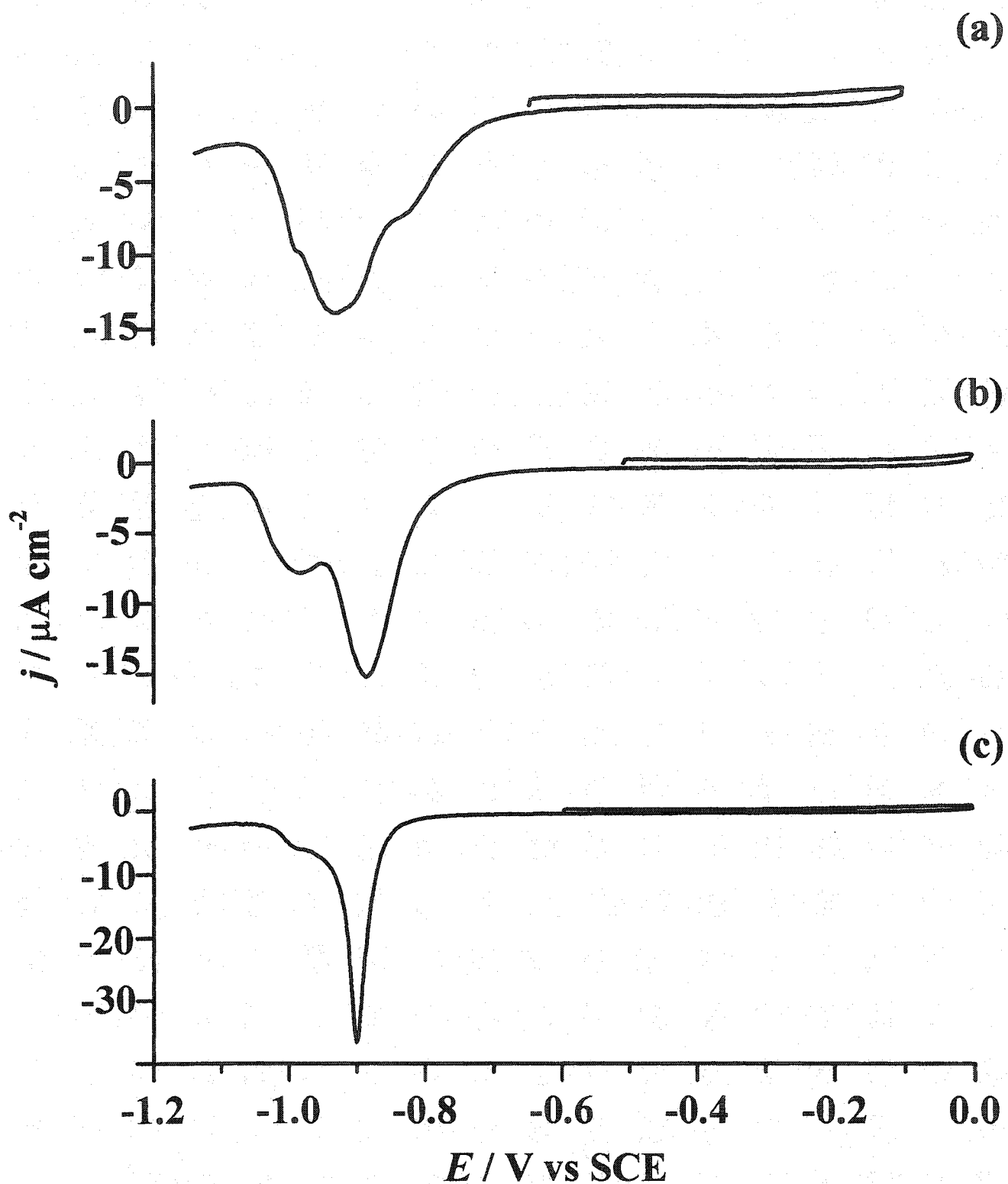


**Figure 4.4:** Cyclic Voltammograms of the oxidative adsorption and reductive desorption of 1,3- BDMT on Au(111) in 0.5 M KOH at anodic limits of (a) -0.80 V, (b) -0.60 V, (c) -0.50 V, and (d) -0.40 V. Potential scan rate: 20 mV s<sup>-1</sup>.





**Figure 4.5:** Cyclic voltammograms of a Au(111) surface coated with a monolayer of (a) 1,4-BDMT, (b) 1,3-BDMT, and (c) 1,2-BDMT transferred into a 1 mM heptanethiol solution in 0.5 M KOH. Potential scan rate:  $20 \text{ mV s}^{-1}$ . See text for details.

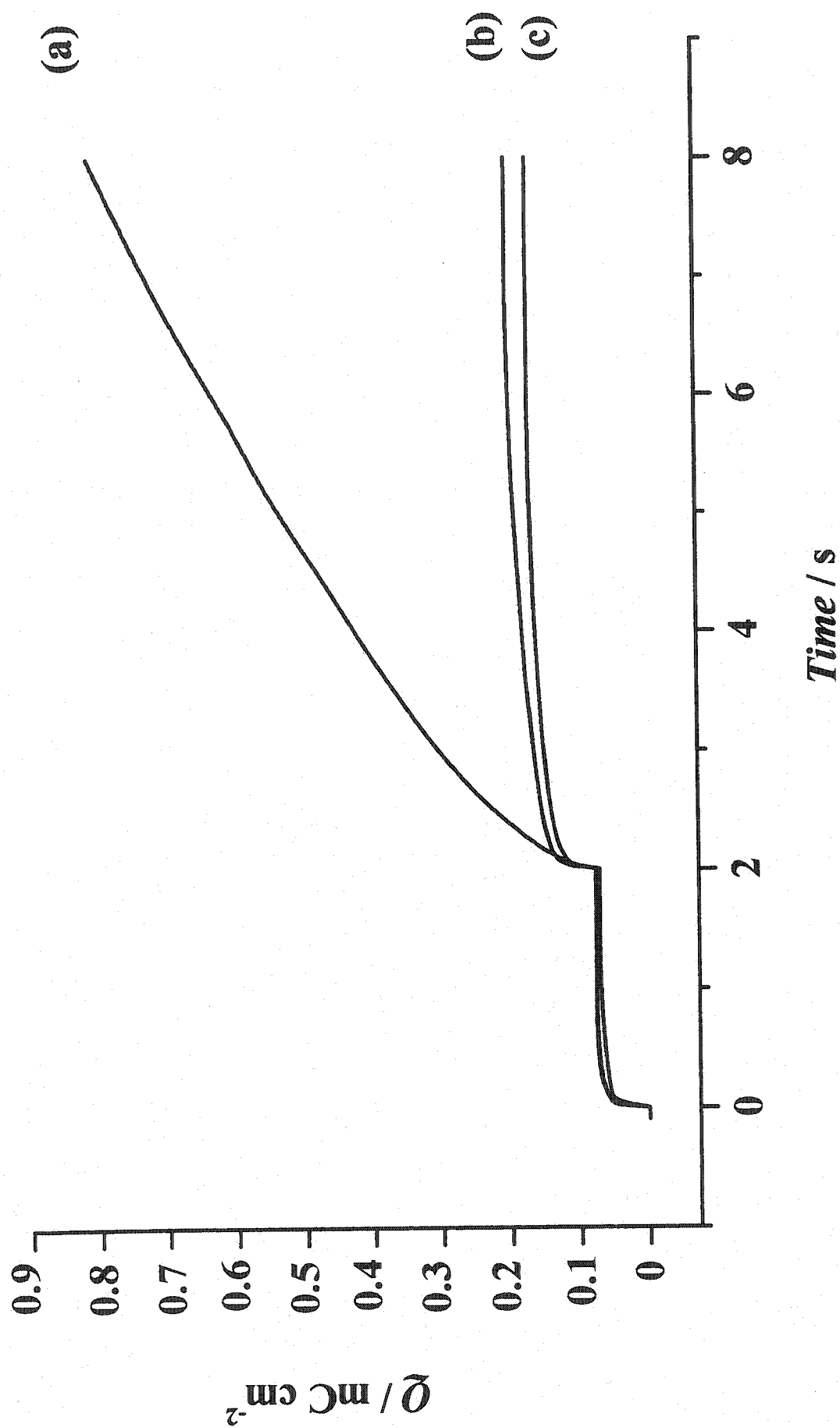


**Figure 4.6:** Cyclic voltammograms of a Au(111) surface coated with a monolayer of (a) 1,4-BDMT, (b) 1,3-BDMT, and (c) 1,2-BDMT transferred into a pure 0.5 M KOH solution. Potential scan rate:  $20 \text{ mV s}^{-1}$ . See text for details.

B does not result from dimerization between adsorbates, because this oxidation should happen whether or not there is any dithiol in solution.

The oxidative peak B of the *meta* isomer displays similar characteristics as peak B of the *para* isomer, and is thus assigned to the formation of a bilayer. The extent of formation of a bilayer was quantified for these isomers with chronocoulometry. The potential was first set at  $-1.00$  V for five minutes to obtain an uncoated gold surface. The potential was next stepped to  $-0.75$  V (electrochemical reaction for peak A) and a charge-time response was recorded for 2 seconds. Finally, the potential was stepped to  $-0.20$  V (for 1,3- and 1,2-BDMT) and  $-0.10$  V (for 1,4-BDMT) to ensure bilayer formation, and a charge-time trace was measured for the next 6 seconds. The results shown in Figure 4.7 give charge ratios of B/A for the *para* (Figure 4.7a) and *meta* (Figure 4.7b) isomers of  $1.9 \pm 0.2$  and  $1.2 \pm 0.2$  respectively. The percent of the monolayer that reacted to form a bilayer was calculated from these ratios by assuming a two-electron process per adsorbate via the formation of a S-S bond. The monolayer of the *para* isomer reacts completely ( $95 \pm 10\%$ ), whereas the monolayer of the *meta* isomer reacts at only  $60 \pm 9\%$ .

The charges related to the reductive desorption of a monolayer (peak A' + B') or a bilayer (peak B'') are similar, although there is an increase of the total oxidative charge by 200% for the formation of a bilayer of the *para* isomer and 120% for the formation of a bilayer of the *meta* isomer. This suggests that the Au-S bond is being reduced, and that the S-S bond is not. Thus, reduction leads to the direct desorption of a bilayer. It is concluded that Au-S bond formation is a reversible process, while dimerization is not. The shift of the reduction potential for the bilayer (peak B'') to more negative values is also consistent with an increase in the layer's thickness [13-16].



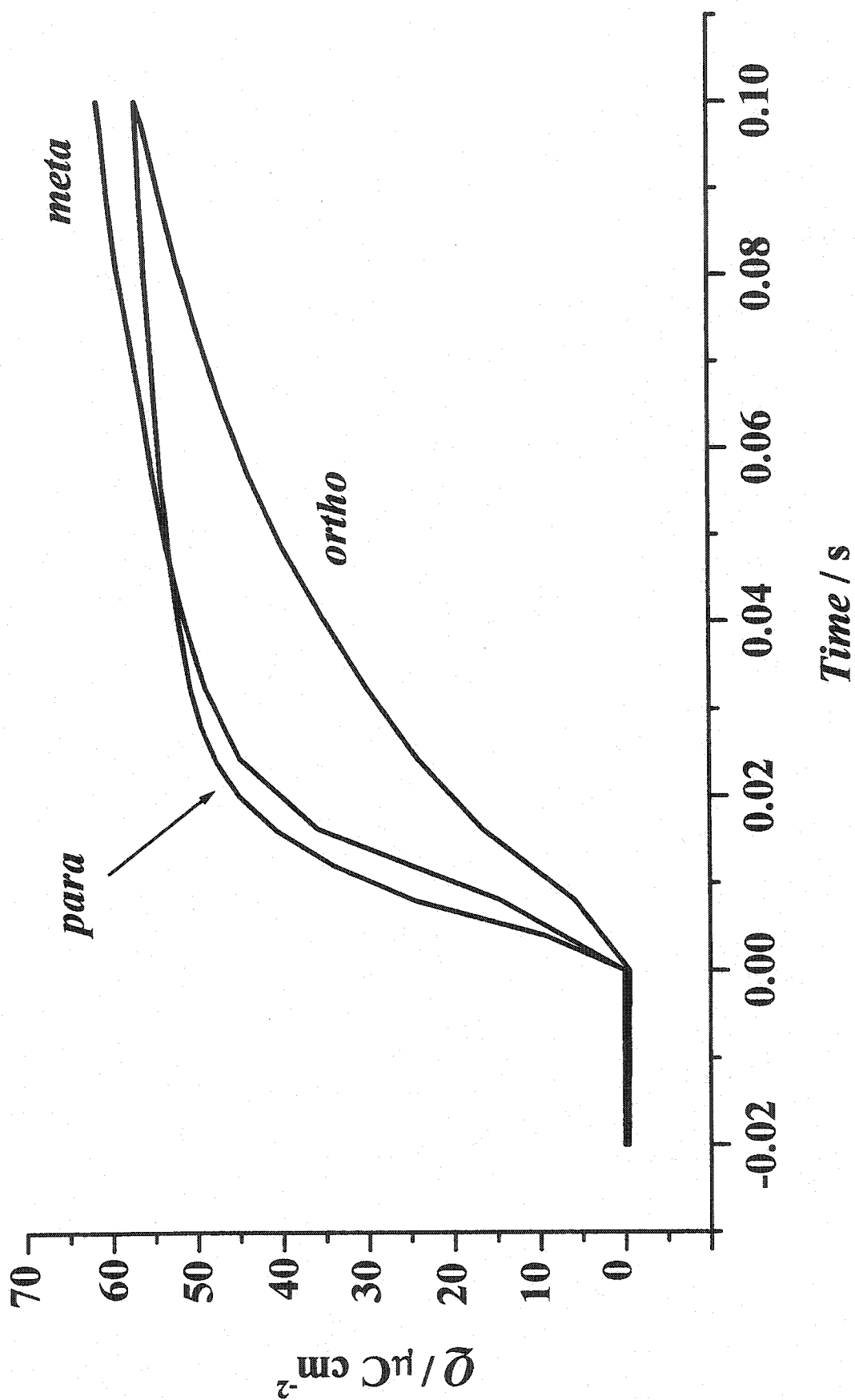
**Figure 4.7:** Chronocoulometric measurements of (a) 1,4-BDMT, (b) 1,3-BDMT, and (c) 1,2-BDMT deposited from saturated dithiol solutions in 0.5 M KOH at the Au(111) surface. See text for details.

If we examine the first 100 ms of deposition in Figure 4.7, we can see from the curve shape (Figure 4.8) that the deposition of the *ortho* isomer is in fact a slower process than that of the *meta* and *para* isomers. This trend complements the results obtained in the voltammetry presented in Figure 4.1. We recall that peak A became broader on proceeding from the *para* to the *ortho* isomers.

#### 4.2.2b *Ortho* Isomer

At first glance, the *ortho* isomer appears to react differently than the other two isomers. There is a large oxidative peak C in Figure 4.3c, which is directly related to the second reductive current labeled C'. The overlap of the currents B'' and C' prevented the quantification of the charge of the first reductive peak B''. Similar experiments were performed on the *ortho* isomer, as those discussed above for the *para* and *meta* isomers. Again, a decrease in the capacity was observed on scanning from A ( $15.4 \pm 1.4 \mu\text{F cm}^{-2}$ ) to C ( $5.1 \pm 1.2 \mu\text{F cm}^{-2}$ ), which is indicative of a better ion blocking layer. It is clear that the oxidative charge related to C is not due to the formation of multilayers of the *ortho* isomer, since a more important decrease of the capacitance would be expected. The decrease is similar to the one observed for the *meta* isomer, where a partial bilayer is formed.

The transfer experiments generated the same results as those for the other two isomers. In Figure 4.5c, there is a small peak at  $-0.30 \text{ V}$  upon transfer into a solution of 1 mM heptanethiol in 0.5 M KOH. This smaller charge implies that both a solution process and surface process are occurring simultaneously in the *ortho* solution. Upon transferring an *ortho* monolayer to a pure 0.5 M KOH, and scanning towards more positive potentials, no second anodic peak is observed (Figure 4.6c). This confirms that the adsorbed *ortho*

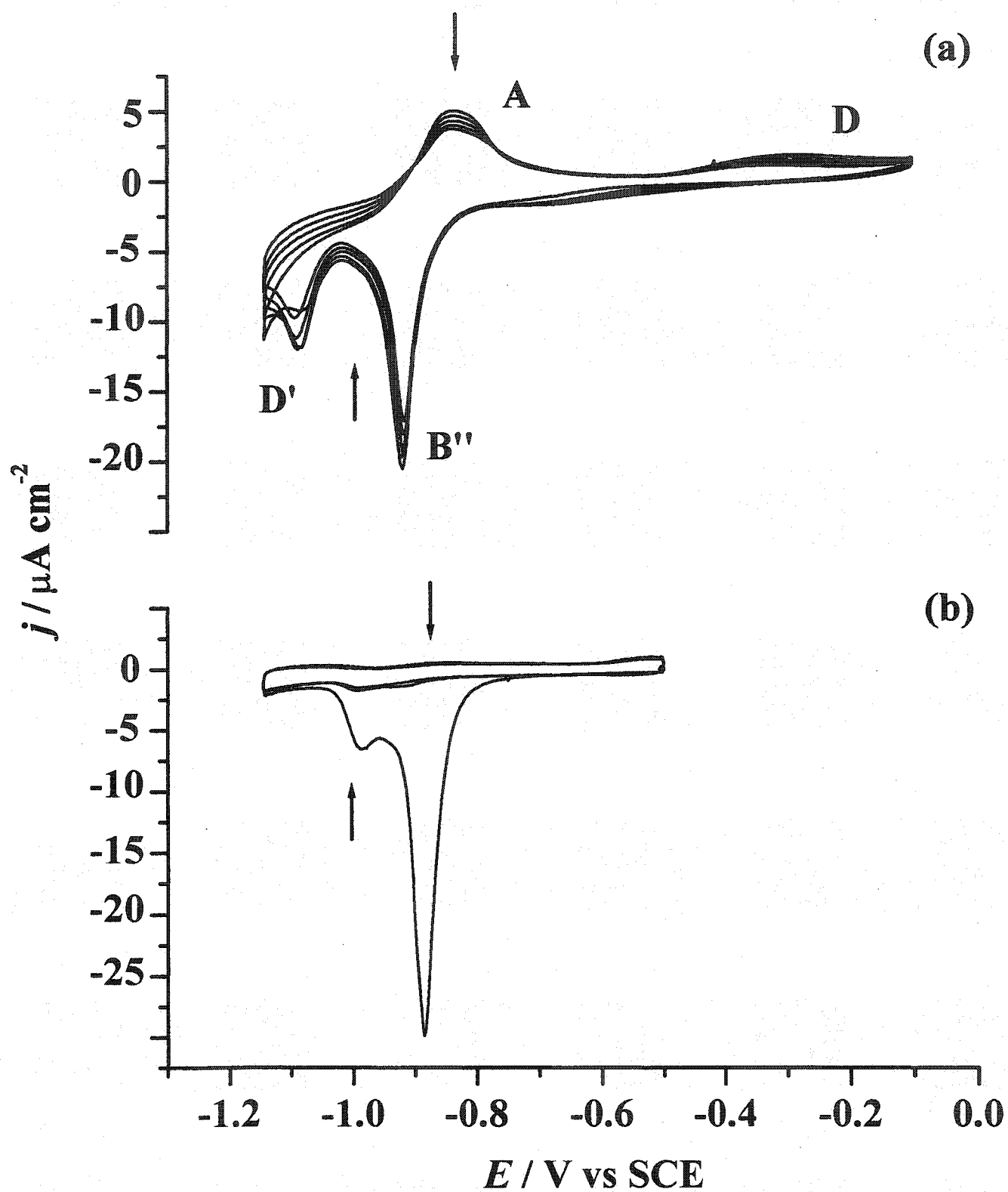


**Figure 4.8:** Chronocoulometric measurements of the first 100 ms of monolayer deposition of the BDMT isomers from a saturated dithiol solution in 0.5 M KOH at the Au(111) surface. See text for details.

dithiolates do not react together. The transfer experiments show that some bilayer formation occurs with the *ortho* isomer, as was the case for the other two isomers.

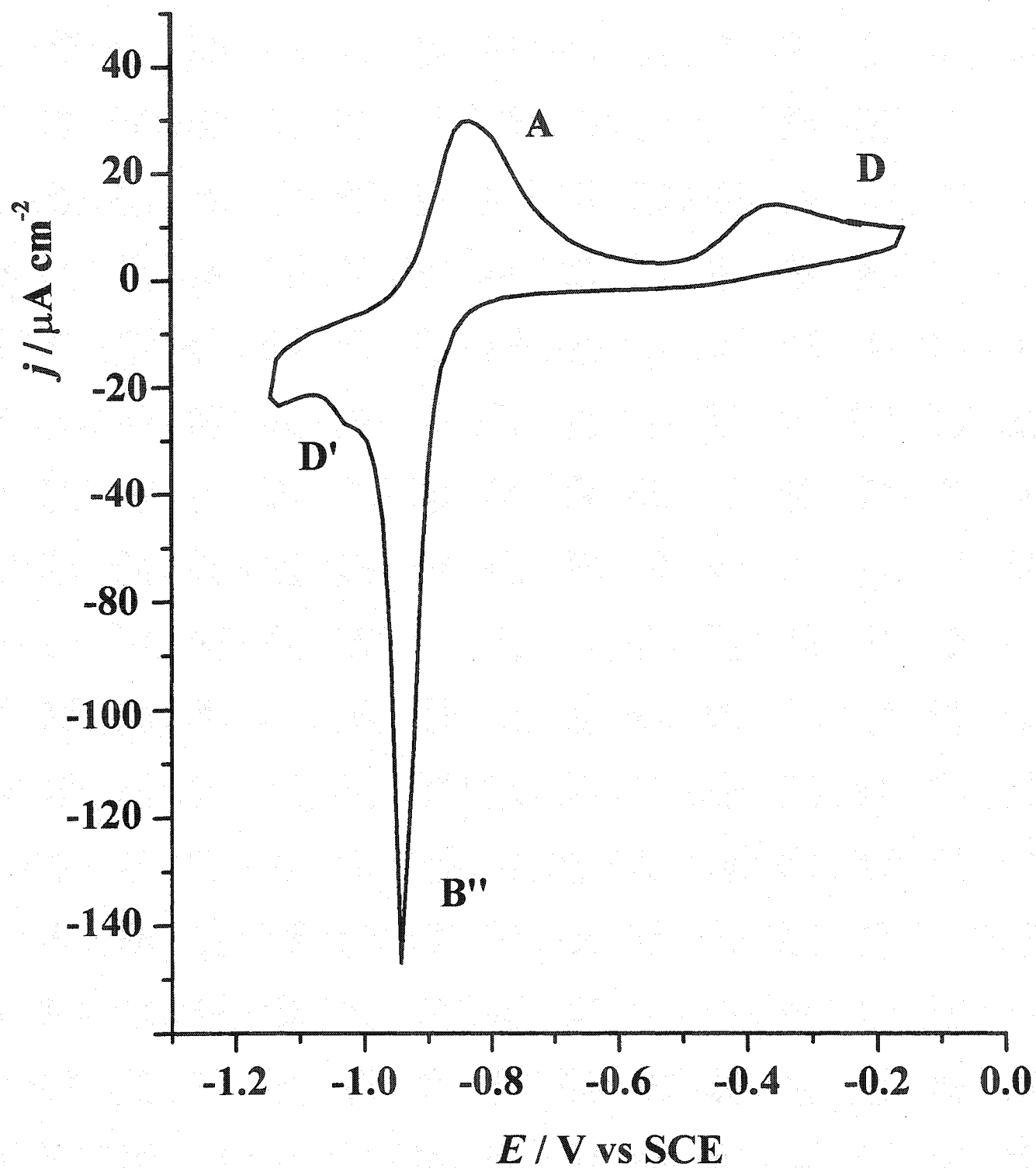
The presence of a solution process was confirmed by the chronocoulometric data in Figure 4.7c. The second potential step indicates that peak C is related to a diffusion-limited process, because the charge increases almost linearly with  $(\text{time})^{1/2}$  [11, p438] and never actually reaches a limiting value. This important solution process is obviously masking a surface process. The two processes were deconvoluted through a slight modification to the transfer experiments. Instead of transferring the electrode directly after monolayer formation, the potential was scanned through peaks A and C, and then transferred to a solution of 0.5 M KOH. The potential was cycled continuously between  $-0.20$  and  $-1.15$  V, starting with the negative going cycle. The voltammetry in Figure 4.9 is representative of the electrochemistry of adsorbed 1,2-BDMT. There is a significant amount of re-adsorption (Figure 4.9a), which contrasts cycling in KOH after deposition of a monolayer shown in Figure 4.9b. Thus, the product formed by scanning into C is less soluble than the monolayer formed in A. This fits well with partial bilayer growth, since one would expect the dimers to be less soluble than the monomers in aqueous solution [17].

Window-opening measurements (performed on the experiment described in Figure 4.9) indicate that peaks A and B'' are related, while D and D' are related. Therefore, peak B'' is attributed to the reductive removal of monolayer and partial bilayer by desorption at the S-Au bond, and D' to de-dimerization in solution of the partial bilayer. On the subsequent anodic scan, peak A is attributed to redeposition of a monolayer and D to partial bilayer reformation. Further support for the surface dimer is provided in Figure 4.10. The cyclic voltammogram represents the same transfer experiment as in Figure 4.9a, but is taken at a



**Figure 4.9:** Cyclic Voltammograms of Au(111) after depositing (a) A + C of 1,2-BDMT and (b) A (monolayer) of 1,2-BDMT in a 0.5 M KOH solution. The arrows indicate the increasing number of cycles. Potential scan rate:  $20 \text{ mV s}^{-1}$ . See text for details.





**Figure 4.10:** Cyclic Voltammograms of Au(111) after depositing A + C of 1,2-BDMT in a 0.5 M KOH solution. Only one cycle is shown since consecutive cycles were the same. Potential scan rate:  $100 \text{ mV s}^{-1}$ . See text for details.

a scan rate of  $100 \text{ mV s}^{-1}$  instead of  $20 \text{ mV s}^{-1}$ .  $D'$  is not as prominent at faster sweep rates. This corresponds well with the fact that de-dimerization is likely a slow process, and requires for the molecules to orient in such a way as to approach the surface more closely in order to “feel” the effect of the applied potential.

The solution process (peak C) is only observed for the *ortho* isomer (Figure 4.3c). This is ascribed to the proximity of the two sulfurs, which makes it likely that an intramolecular S-S bond is formed at sufficiently positive potentials. The solution process in C is therefore assigned to the formation of an intramolecular disulfide. The ill-defined reductive current  $C'$  corresponds to the destruction of the *ortho* disulfide in the solution.

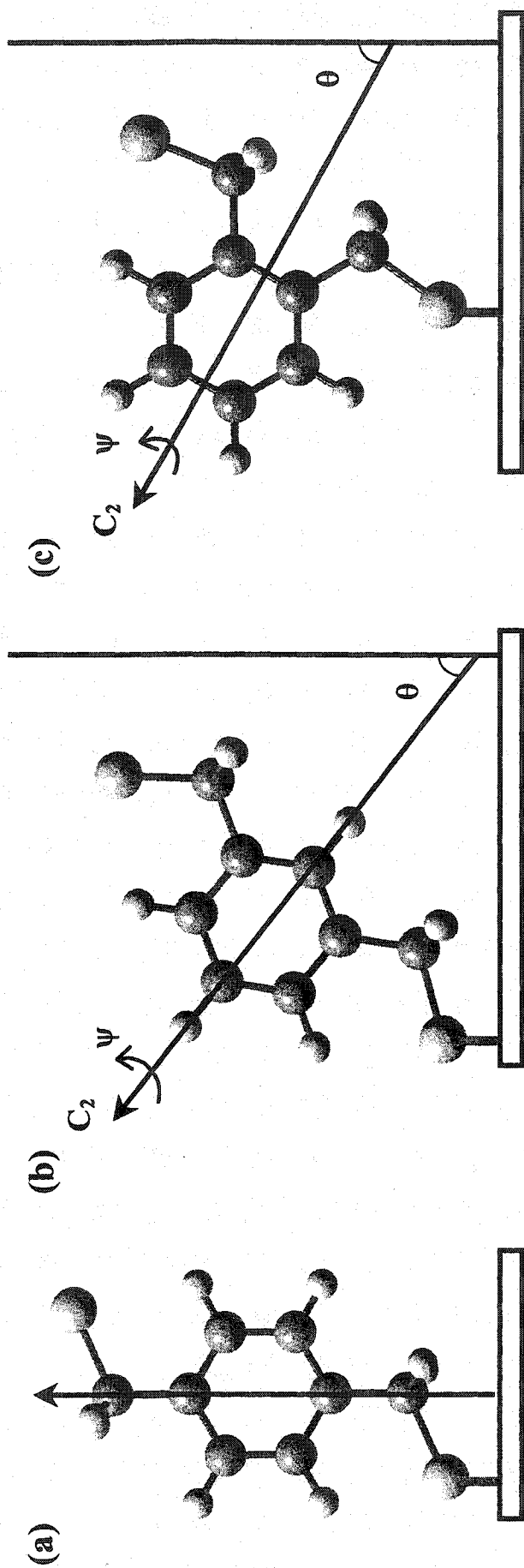
### 4.3 IRAS

The electrochemical results of the previous section reveal differences in the oxidative adsorption of the BDMT isomers. All of the isomers can be oxidatively adsorbed as a monolayer from alkaline solution. Also, a monolayer of the *para* and *meta* isomers can be formed from neutral solutions. These experiments could not be done for the *ortho* isomer because it was not soluble in neutral solution. However, it is only in alkaline solution and at sufficiently positive potentials that they form bilayer. Furthermore, the extent of formation of a bilayer varies greatly (Figures 4.3, 4.5, and 4.7). It is clear that the position of the methylenethiol substituents influences the oxidative deposition of the isomers of BDMT. To gain more insight into the process of electrodeposition of these compounds, the electrodeposited monolayers and bilayers of all the isomers were characterized using IRAS. These measurements provide information on the average orientation of the adsorbed BDMT isomers and are described below.

The IR spectra of the *para* isomer were described in detail in section 3.3.1 [1]. Briefly, no bands were observed in the monolayer. A vertical orientation of the benzene ring, with its molecular axis perpendicular to the gold surface, was suggested (Scheme 4.1a). Bilayer formation resulted in a reorientation of the 1,4-BDMT molecules that could not be quantified, because the transition dipole moments of the observed aromatic bands were collinear.

In Figure 4.11, the spectra of the monolayer and partial bilayer of the *meta* isomer are shown. In the case of the monolayer, bands are observed in the C-H stretching region, as well as in the lower wavenumber C-C stretching bands (Figure 4.11a). When a partial bilayer (60%) is deposited, there are few differences between the two spectra (Figure 4.11b). This contrasts with the large changes observed when a second layer of the *para* isomer is deposited (Figure 3.11). A summary of the modes and their assignments is given in Table 4.1 [2-4,7,18]. All of the bands that are present in the bulk, are also observed in the monolayer and bilayer spectra. Once again, there is not much difference in the wavenumbers of the bands of the monolayer and bilayer versus those in the bulk. This suggests that the environment at the surface is similar to that in the bulk, and that the interactions with the gold surface are not important.

Assuming a  $C_{2v}$  symmetry of the molecule, the ring modes were classified in Table 4.1 into two kinds. The molecular axis, i.e.  $C_2$  axis, of the *meta* isomer is defined as the line passing through carbons 2 and 5 of the aromatic ring (Scheme 4.1b). The transition dipole of a mode of the first kind is parallel to the  $C_2$  axis, while that of a mode of the second kind is perpendicular to the  $C_2$  axis and in the plane of the aromatic ring. The ratio of intensities of



**Scheme 4.1:** Suggested orientations from fits of IR spectra for (a) 1,4-BDMT, (b) 1,3-BDMT, and (c) 1,2-BDMT oxidatively deposited onto an annealed gold film from a saturated dithiol solution in 0.5 M KOH.

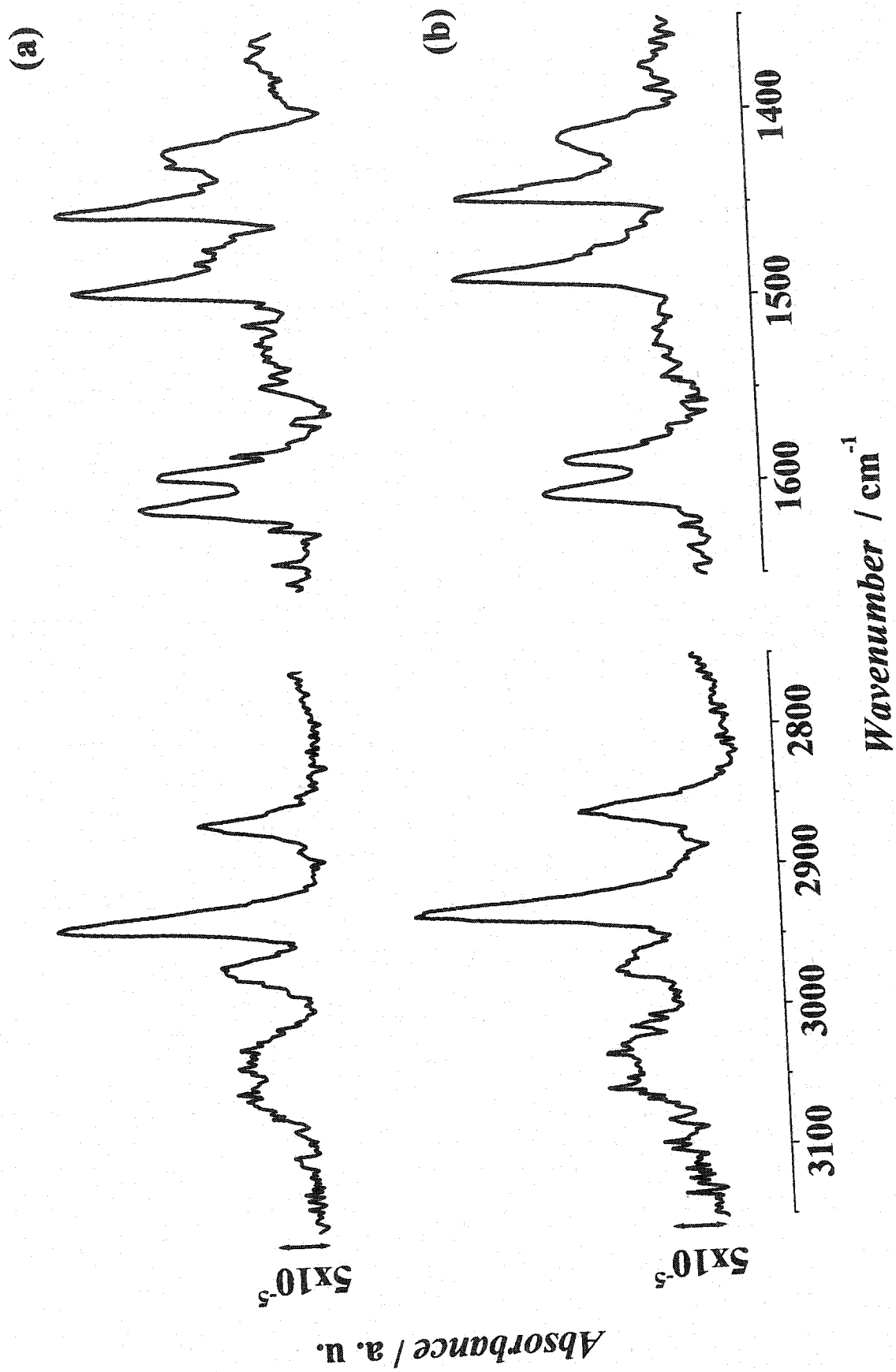


Figure 4.11: IR spectrum of (a) a monolayer and (b) a bilayer of 1,3-BDMT electrodeposited on annealed gold films.

**Table 4.1:** Assignment of vibrational bands ( $\text{cm}^{-1}$ ) of 1,3-BDMT electrodeposited on gold from a saturated dithiol solution in 0.5 M KOH.

| TIR                                       | monolayer | bilayer | assignment <sup>[2-4,7,18]</sup> |
|-------------------------------------------|-----------|---------|----------------------------------|
| Modes of First Kind (In-Plane Modes)      |           |         |                                  |
| 3055                                      | 3050      | 3055    | 2                                |
| 3024                                      | 3020      | 3030    | 20a                              |
| 2961                                      | 2962      | 2972    | 7a                               |
| 1588                                      | 1586      | 1586    | 8a                               |
| 1412                                      | 1412      | 1412    | 19a                              |
| Modes of the Second Kind (In-Plane Modes) |           |         |                                  |
| 3100                                      |           |         | 20b                              |
| 1605                                      | 1603      | 1604    | 8b                               |
| 1487                                      | 1486      | 1487    | 19b                              |
| Substituent Modes                         |           |         |                                  |
| 2929                                      | 2927      | 2928    | $\nu(\text{CH}_2 \text{ asym})$  |
| 2842                                      | 2858      | 2859    | $\nu(\text{CH}_2 \text{ sym})$   |
| 1444                                      | 1443      | 1443    | $\text{CH}_2(\text{def})$        |

modes of the second and first kind were used to estimate the orientation of the aromatic ring (section 2.4.1) [19]:

$$\left[ I\{\nu_{\text{second kind}}\} / I\{\nu_{\text{first kind}}\} \right]_{\text{SURF}} = \left[ I\{\nu_{\text{second kind}}\} / I\{\nu_{\text{first kind}}\} \right]_{\text{SOLID}} \times \cos^2 \psi \tan^2 \theta, \quad (4.1)$$

where the tilt angle ( $\theta$ ) is the angle between the molecular axis and the surface normal. The twist angle ( $\psi$ ) corresponds to the angle between the plane of the benzene ring relative to the plane formed by the molecular axis and the surface normal.  $I$  represents the intensity of the modes,  $\nu$ , either in the bulk (SOLID) or at the surface (SURF).

We used the ratio of the low wavenumber bands of the aromatic ring (8a, 8b, 19a and 19b) to calculate the tilt and twist angles of the ring. For the monolayer of the *meta* isomer, the values of the tilt and twist angles for the aromatic ring are  $53 \pm 6^\circ$  and  $53 \pm 10^\circ$  respectively. For the (partial) bilayer the tilt angle is  $50 \pm 5^\circ$  and the twist angle is  $53 \pm 6^\circ$  for the aromatic ring. The angles are similar for the monolayer and partial bilayer, as would be expected from the small changes in the spectra in Figure 4.11. Thus, the formation of a partial bilayer does not cause significant changes in the average orientation of the aromatic ring.

The orientation of the aromatic ring for the *meta* isomer is clearly different (i.e. less vertical) than that of the *para* isomer and is presented in Scheme 4.1b. This orientation is compatible with the electrochemical data, which show that there are some reactive thiolates. It is also compatible with an ion/surface reactive collisions study that proposed that the *meta* isomer is adsorbed via one sulfur on gold [20]. We can rule out that all the *meta* isomers are

bound by two sulfurs based on the fact that we would see only modes of the first kind in the IRAS spectra for such an orientation.

The spectra of the monolayer and the layer corresponding to peak C for the *ortho* isomer are shown in Figure 4.12. The same bands are present in both spectra. There is an increase of the intensities of the bands as well as small changes in the relative intensities of the bands for the spectrum corresponding to C. Table 4.2 summarizes the assignment of bands in the solid spectrum and at the surface [2-4,7,18]. The aromatic modes were separated into those of the first and second kind, again with respect to the molecule's  $C_2$  axis. The molecular axis is a line intersecting the C-C bonds of carbons 1 and 2 and 4 and 5 of the aromatic ring (Scheme 4.1c).

Our mode assignments vary from those reported by Kim et al., who present a study on the adsorption of 1,2-BDMT onto a gold film from organic solution, i.e. under open circuit conditions [7]. For example, they report a band at 1640( $\nu_{8b}$ ) in the TIR (transmission IR) spectra that we do not detect at all. In fact, there is a discrepancy with their own SERS results performed on the adsorption of 1,2-BDMT onto silver [21]. In their ordinary (bulk) Raman spectrum (ORS), the 1640  $\text{cm}^{-1}$  mode is absent. Instead, they assign the mode at 1603  $\text{cm}^{-1}$  as  $\nu_{8b}$ . Similarly to the *meta* isomer, all of the bands present in the bulk spectrum are present in the spectra of the deposited layers of the *ortho* isomer except for the 3042  $\text{cm}^{-1}$  mode. Once again, the *ortho* isomer does not seem to interact strongly with the gold surface.

IR fits, similar to the ones described for the 1,3-BDMT isomer, were performed. The low frequency modes were used in the monolayer fit. All of the aromatic modes were used in the bilayer fit, because they were all relatively intense. The average orientation of the aromatic ring was obtained from equation 4.1. Respective tilt and twist angles of  $63 \pm 5^\circ$  and



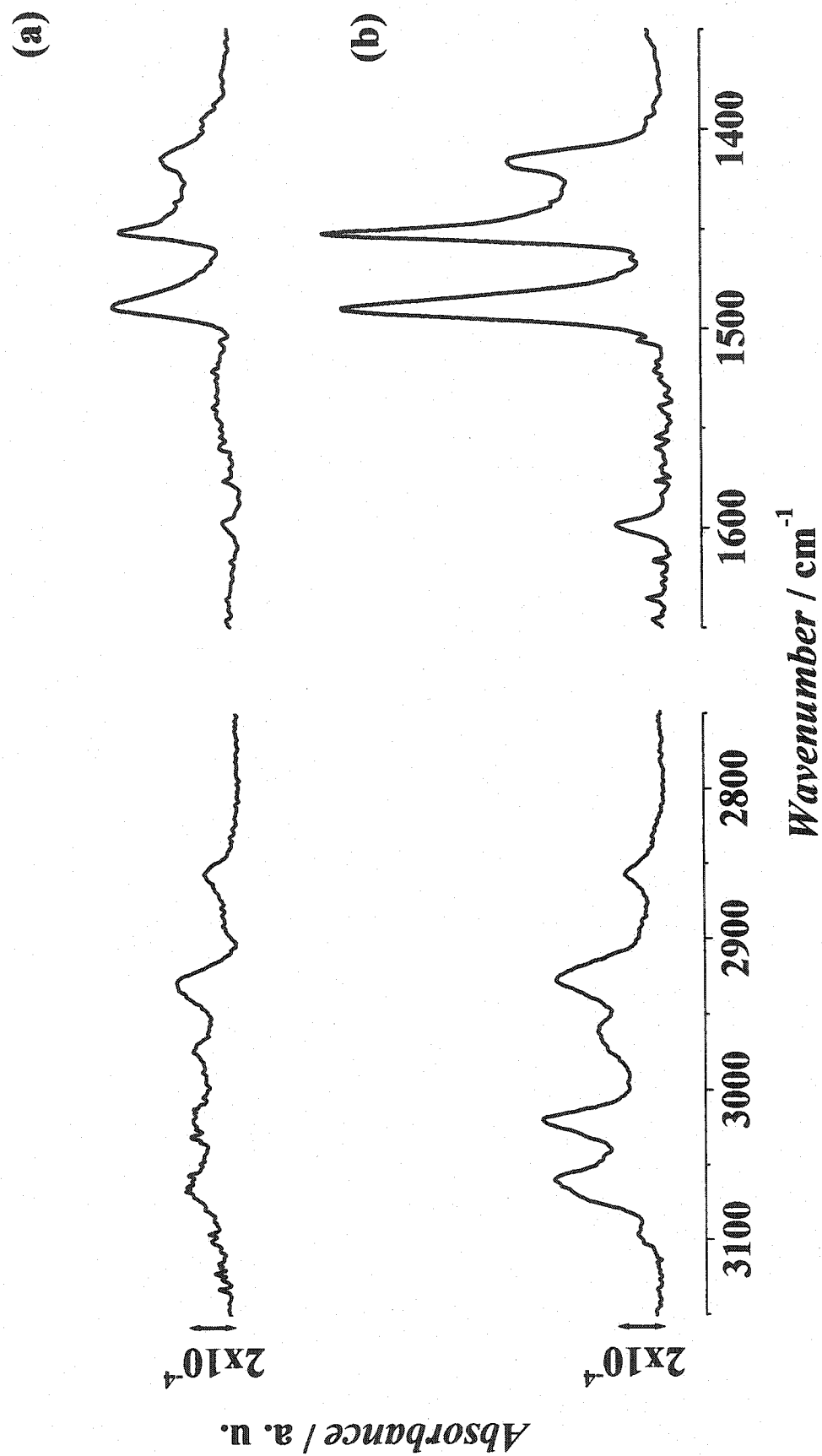


Figure 4.12: IR spectrum of (a) a monolayer and (b) a bilayer of 1,2-BDMT electrodeposited on annealed gold films.

**Table 4.2:** Assignment of vibrational bands ( $\text{cm}^{-1}$ ) of 1,2-BDMT electrodeposited on gold from a saturated dithiol solution in 0.5 M KOH.

| TIR                                   | monolayer | bilayer | assignment <sup>[2-4,7,18]</sup> |
|---------------------------------------|-----------|---------|----------------------------------|
| Modes of First Kind (In-Plane Modes)  |           |         |                                  |
| 3042                                  |           |         | 2                                |
| 3018                                  | 3020      | 3020    | 20a                              |
| 1424                                  | 1415      | 1416    | 19a                              |
| Modes of Second Kind (In-Plane Modes) |           |         |                                  |
| 3060                                  | 3061      | 3060    | 20b                              |
| 2974                                  | 2975      | 2961    | 7b                               |
| 1598                                  | 1598      | 1599    | 8b                               |
| 1486                                  | 1490      | 1490    | 19b                              |
| Substituent Modes                     |           |         |                                  |
| 2937                                  | 2928      | 2928    | $\nu(\text{CH}_2 \text{ asym})$  |
| 2849                                  | 2856      | 2857    | $\nu(\text{CH}_2 \text{ sym})$   |
| 1454                                  | 1451      | 1452    | $\text{CH}_2(\text{def})$        |

$45 \pm 5^\circ$  were calculated for the monolayer. Values of  $60 \pm 5^\circ$  ( $\theta$ ) and  $50 \pm 6^\circ$  ( $\psi$ ) were obtained for the bilayer. These results correspond well with monolayer adsorption via formation of a S-Au bond. The same argument is proposed for 1,2-BDMT, as that presented above for the 1,3-BDMT. Our results differ from other studies [7,10] of the *ortho* isomer, which found that it adsorbed via its two sulfurs. We can rule out this possibility, since only modes of the first kind should be observed in the IRAS spectra. This is clearly not the case for the electrodeposited layers of the *ortho* isomer, since both kinds of modes are observed.

#### 4.4 Mechanism for the Oxidative Adsorption of the BDMT Isomers onto Au(111)

##### 4.4.1 Monolayer Formation

The electrochemical measurements suggest that the three isomers of BDMT are oxidatively adsorbed via single S-Au bond formation. The potential and charge of peak A are compatible with the one-electron process reported for the oxidative deposition of a monolayer of alkanethiols on gold [12]. The pH effect observed in the capacitance measurements for the *para* and *meta* isomers, and the transfer experiments performed on all three isomers, clearly support the presence of unreacted thiolates. The IRAS results also support monolayer deposition. The average orientation of the aromatic ring of the BDMT isomers in a monolayer varies greatly, as is shown in Scheme 4.1. The *para* isomer is oriented perpendicular to the surface, whereas the *meta* isomer is significantly tilted from the surface normal, and the *ortho* even more so. In these orientations, it is clear that it is not possible to form two gold sulfur bonds with the surface. The following expression describes the monolayer formation of the isomers of BDMT [1]:



Our oxidative deposition of a monolayer contrasts with the spontaneous adsorption of the *ortho* isomer via two sulfurs that was recently reported [7,10]. We briefly discussed the origin of the differences between electrodeposition and chemical deposition in section 3.4.1 [1]. We believe that it lies in the rate of oxidative adsorption of the dithiolate. The adsorption of a monolayer in about one second (Figure 4.7) leads to the formation of a monolayer of the isomers bound to the surface via one sulfur. Binding via two sulfurs is expected to require longer times since the molecule needs to be in a proper orientation. Solvation of the negatively charged thiolate also plays a role and is discussed here in more detail.

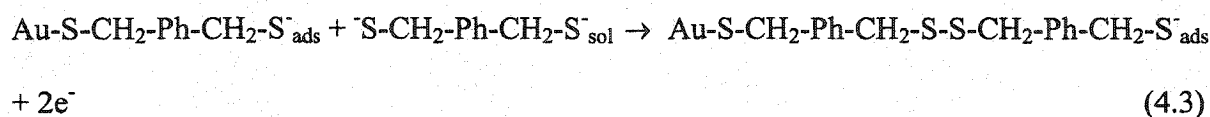
The amount of tilt and twist associated with the respective monolayers (IRAS results) is directly related to the availability of the second sulfur for reactivity. The various orientations seem to favour the exposure of the thiolate group to the solution where it is more stable since it is solvated. The solvation of the thiolate is likely to play a role in the orientation of the BDMT isomers. Since the thiolate is well solvated [22], significant energy is required to desolvate this group. Furthermore, for small adsorbates such as the BDMT isomers, the interadsorbate interactions are weak. Thus the interaction between the unreacted thiolate and the electrolyte solution (i.e. solvation) might be the driving force in orienting the molecule at the surface.

In the absence of strong solvation, such as the deposition of dithiols from the gas phase [23] or for small (protonated) dithiols [7,10] adsorbing from an organic solution, only adsorption via both sulfurs has been observed. In this case, the adsorbed dithiols do not have a strong preferential orientation of the SH group away from the gold surface. Therefore, the

second thiol end group could reorient towards the gold surface and form a second S-Au bond. We thus think that solvation of the thiolate groups is the main factor in orienting the BDMT isomers as shown in Scheme 4.1.

#### 4.4.2 Bilayer Formation

The unreacted thiolates are found to react with dithiolates in solution to form bilayer. This oxidative dimerization was presented in section 3.4.2 for the *para* isomer and is summarized in the following expression [1]:



The dimerization was found to occur to a larger extent in the following order: *para* > *meta* > *ortho*. We were able to quantify the amount of reactivity for both the *para* and *meta* isomers with chronocoulometry, but were limited in the case of the *ortho* isomer. However, the transfer experiments in the heptanethiolate solution (Figure 4.5) and into pure 0.5 M KOH (Figure 4.6) provided a qualitative idea of the reactivity of the *ortho* isomer. From the voltammetry, we remark that the anodic peak corresponding to reactivity with heptanethiolate is larger for the *para* isomer, than the *meta* isomer, which is in turn larger than that of the *ortho* isomer.

In addition, the position of the reductive peak B'' in Figure 4.3 adds some insight to the isomers' reactivity. The more negative its position, the thicker and more compact the film (i.e. the more difficult it is for ion penetration) [13-16]. The separation between the monolayer reduction peak A' (Figure 4.1) and bilayer peak B'' (Figure 4.3) is a good measure

of the extent of bilayer formation. Values of 120, 80, and 30 mV were obtained for *para*, *meta* and *ortho*-BDMT isomers respectively. Obviously, the film formed on scanning through A and C for the *ortho* isomer has less bilayer character than that of the other two.

Surprisingly, the formation of dimers is not observed between neighboring adsorbed dithiolates. Only in the case of the *ortho* isomer is there formation of disulfide in the solution. It is known that solution dimerization occurs at more positive potentials than dimerization between an adsorbed dithiolate and a solution dithiolate [24,25]. This is due to the fact that the adsorbed dithiolates are closer to the surface. Also, the formation of a S-S bond (i.e. bilayer) was found to be irreversible for both the *para* and *meta* isomers. These observations have already been rationalized for the *para* isomer through comparison with the well-characterized electrochemistry of glutathione [26] and cysteine [24,25,27,28].

The *ortho* isomer displays slightly different electrochemistry than the other two isomers. The close proximity of the sulfurs in the *ortho* isomer facilitates the formation of an intramolecular S-S bond (i.e. bulk dimerization). In addition, both solution dimerization and bilayer formation were found to be reversible in this case (Figures 4.4c and 4.9a). The reduction is attributed to the fact that 1,2-BDMT is less soluble than the other two isomers, and therefore remains more closely to the surface.

All of the adsorbed isomers react with thiolates in solution and they do not react with each other. This is most likely related to the mechanism of electro-oxidation of the adsorbed thiolate that we presented in equations 3.3 and 3.4 for the *para* isomer. The extent of bilayer formation depends on the accessibility (i.e. orientation) of the adsorbed activated thiolate. The average orientations of the isomers in the monolayer shown in Scheme 4.1 indicate that it would be easiest to form a bilayer of the *para* isomer, since the thiolate groups are readily

accessible. Obviously, it would be more difficult to form bilayers of the *meta* and *ortho* isomers. These predictions fit well with the electrochemical results that show that a complete bilayer is formed in the case of the *para* isomer, whereas only partial bilayer (60%) of the *meta* isomer is formed. The extent of bilayer formation for the *ortho* isomer is even smaller than that of the *meta*.

For the *meta* and *ortho* isomers, it is also noted that the aromatic ring in the bilayer has an orientation similar to that observed in the monolayer. This suggests that the driving force for the orientation of the isomer is still keeping the thiolate group well solvated at the organic/solution interface. We expect that this is also the case for the *para* monolayer and bilayer, since the formation of a complete bilayer requires a relatively vertical orientation of the *para* molecules.

#### 4.5 Summary

The three isomers of BDMT were found to oxidatively adsorb via one of their two sulfurs to form complete monolayers. Vibrational measurements indicate that the isomers are oriented such that the unreacted thiolate is at the electrolyte interface. All of the isomers formed bilayers when the potential was scanned to more positive values. The extent of bilayer formation depends on the accessibility of the adsorbed activated thiolate, as suggested by IR. This causes the bilayer to be formed to a greater extent on the *para* monolayer, than on that of the *meta* monolayer. The formation of bilayer at the *ortho* monolayer is the smallest. Our results suggest that the interaction between the negatively charged thiolate and the aqueous electrolyte plays a major role in the assembly of these compounds. Finally, our results show that new self-assembled layers can be formed by electrodeposition.

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## Chapter 5: Effect of Alkanedithiol Chain Length on the Oxidative Formation of a Bilayer

### 5.1 Introduction

We have shown that monolayers and bilayers of the BDMT isomers can be electrodeposited onto Au(111) from alkaline electrolyte [1,2]. Similar reactivity (i.e. dimerization) was not observed in neutral medium. The assembly of the aromatic dithiols was found to be dependent on the solvation of the unreacted thiolates. Bilayer formation was facilitated by a greater accessibility of the negatively charged thiolate end groups. The BDMT molecules have a relatively rigid structure, despite the fact that the unbound thiolate can rotate due to its bond with a methylene group. Here, we explore the effect of a more flexible molecular framework on the bilayer mechanism, by studying the electrodeposition of a series of alkanedithiols ( $\text{HSC}_n\text{H}_{(2n+1)}\text{SH}$ ) having varying chain lengths ( $n$ ). In doing so, we also gain insight into the effect of chain length (i.e. surface-interface distance) on  $\text{S}^-$  activation for bilayer formation.

Conflicting results have been presented in the literature as to how alkanedithiols bind to the gold surface. They were found to adsorb by both sulfur atoms to gold from the vapor phase [3-6]. In contrast, they adsorbed via a single S-Au bond when deposited from organic solution [3,7-15]. It has been reported that 1,2-EDT can form up to four layers on gold from *n*-hexane [12]. As many as eight covalently attached layers onto a gold substrate have been observed for 1,6-HDT, 1,8-ODT, and 1,9-NDT through spontaneous adsorption, but only after exposure of each layer to air [13]. This contrasts the partial bilayer formation that has been shown for aromatic dithiols deposited in the absence of oxidants [16-19]. This illustrates that the limiting step in S-S dimer formation is not governed by electronic

properties alone. If this were the case, one would expect that multilayer growth would occur more readily with the conjugated systems [18,19]. Obviously, the presence of oxidants is necessary (excluding 1,2-EDT) to promote dimerization between adsorbed dithiols and those in solution. In addition, having films with the thiol groups arranged in such a way as to maximize their exposure for reactivity, facilitates multilayer growth.

The self-assembly of dithiol molecules results from several interactions, which were discussed in the previous chapters. They will be explored here in more detail through studying the electrodeposition of alkanedithiols. Numerous questions will be addressed including how does the proximity of the sulfurs to the gold surface affect the reactivity? Is multilayer formation observed for the short chain alkanedithiols? Do longer chain alkanedithiols react to form bilayer, or is the unbound thiolate group too far away from the surface to respond to the applied field? Does increased flexibility result in “looping” (i.e. binding via two sulfurs), or a more organized platform for bilayer formation? At what point do Van der Waals interactions prevail over the repulsive interactions of the thiolate end groups?

To address these issues, we examined the oxidative deposition of 1,2-ethanedithiol (1,2-EDT), 1,3-propanedithiol (1,3-PDT), 1,4-butanedithiol (1,4-BDT), 1,6-hexanedithiol (1,6-HDT), 1,8-octanedithiol (1,8-ODT), and 1,9-nonanedithiol (1,9-NDT). It is anticipated that through application of the electrodeposition scheme, the reactivity of the alkanedithiols at the Au(111) surface could be controlled in the same way as the BDMT isomers (section 3.4.2).

## **Results and Discussion**

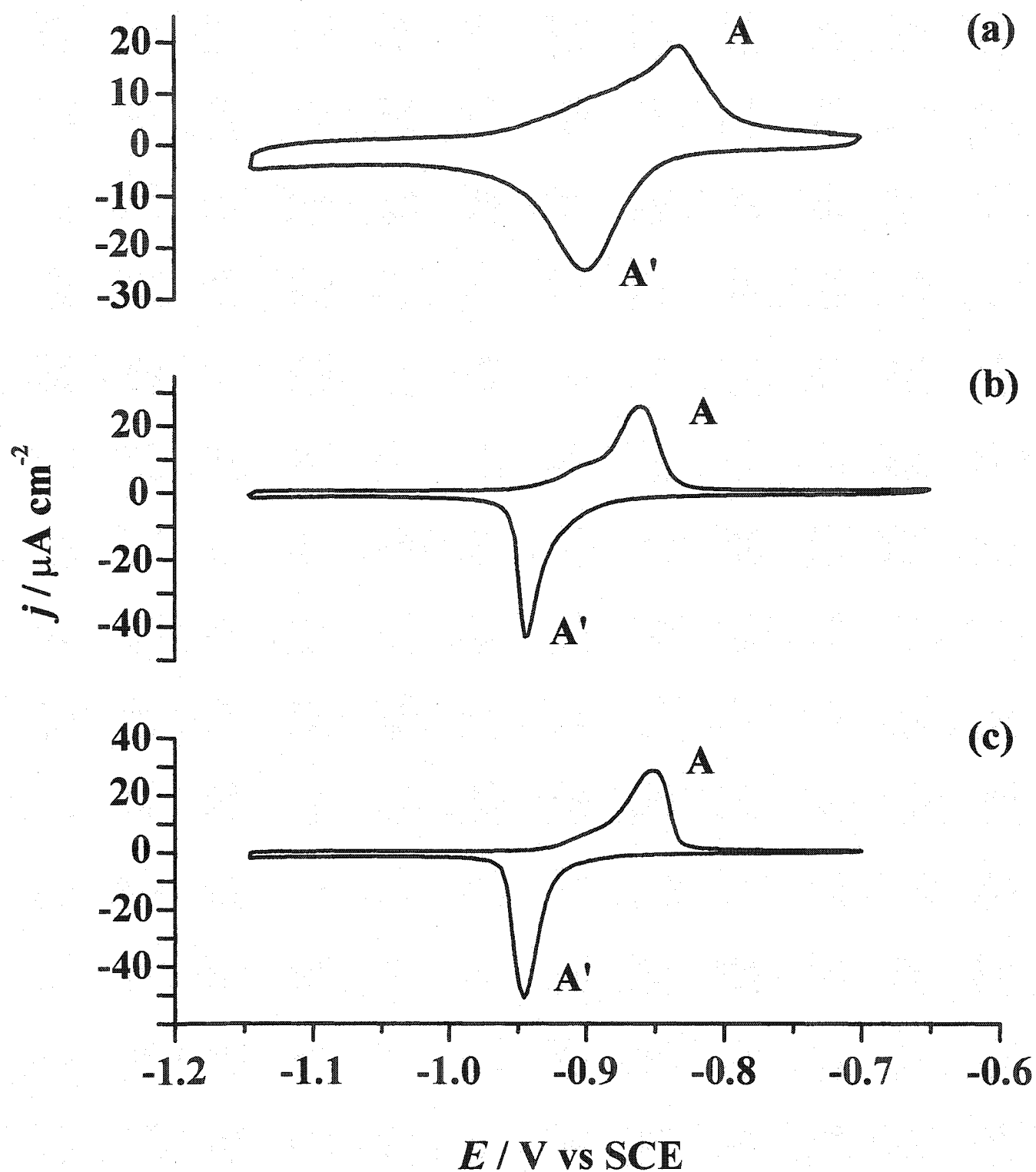
### **5.2 Cyclic Voltammetry**

### 5.2.1 Oxidative Deposition of Monolayers of Alkanedithiols

The alkanedithiols were classified into three main categories based on their oxidative electrochemistry: short chain length dithiols ( $n = 2, 3$ , and  $4$ ), medium chain length dithiols ( $n = 6$ , and  $8$ ), and finally long chain length dithiols ( $n = 9$ ). A representative dithiol from each of the three categories is used in the figures to describe general electrochemical trends. However, a summary of the electrochemical data of every dithiol is given in the attached tables.

Figure 5.1 presents the cyclic voltammograms for the electrodeposition of (a) 1,2-EDT, (b) 1,6-HDT, and (c) 1,9-NDT from 1 mM solutions in 0.5 M KOH. The potential was cycled between  $-0.70$  or  $-0.65$  V and  $-1.15$  V, at a scan rate of  $20 \text{ mV s}^{-1}$ . A single oxidative peak A is located at a potential of  $-0.83$  V for 1,2-EDT and  $-0.86$  V for 1,6-HDT and 1,9-NDT. Table 5.1 summarizes the electrochemical results for all of the dithiols within this potential region. The shape of peak A is relatively broad for 1,2-EDT and the oxidative current is important in this range of potentials. Peak A sharpens and there is a smaller current after the peak for the medium chain length dithiols (Figure 5.1b). This is also evident in the voltammetry of 1,9-NDT (Figure 5.1c). The sharpness of peak A for the medium and long chain length dithiols implies that their electrodeposition is relatively homogeneous process [20, p521]. The broader peak A for the shorter chain length compounds suggests that their electrodeposition is a less homogeneous process.

Even though the broadness of peak A changes upon going from the shorter to the longer alkanedithiols, they retain their asymmetric shapes of peaks A and A'. The slow growth of the oxidative peak A, followed by a sharp decrease, is characteristic of a nucleation and growth deposition. This was also observed in the electrodeposition of



**Figure 5.1:** Cyclic voltammograms of the oxidative deposition and reductive desorption of a monolayer of (a) 1,2-EDT, (b) 1,6-HDT, and (c) 1,9-NDT from 1 mM dithiol solutions in 0.5 M KOH at the Au(111) surface. Potential scan rate:  $20 \text{ mV s}^{-1}$ .

monolayers of alkanethiols [21]. In addition, the baseline corrected oxidative charge of peak A ( $Q_A$ ) is similar for all of the dithiols. The fact that the oxidative charges and current peak potentials for peak A are alike, and that they are close to those expected for a typical alkanethiolate [21,22], suggests that all of the alkanedithiols adsorb via single S-Au bond formation. The oxidative charges were converted to surface concentrations ( $\Gamma_A$ ) (assuming a one-electron process), and values ranging from  $5.8 - 8.7 (\times 10^{-10} \text{ mol cm}^{-2})$  were obtained (Table 5.1). The surface concentration of a typical alkanethiol monolayer on gold,  $7.6 \times 10^{-10} \text{ mol cm}^{-2}$ , fits well within this range [21,22].

**Table 5.1:** Data obtained from cyclic voltammograms of monolayers deposited onto Au(111) from 1 mM alkanedithiol solutions in 0.5 M KOH, where  $Q_A$  represents the charge of the oxidatively deposited monolayer,  $E_A$  represents its peak potential,  $Q_{A'}$  represents its reductive charge, and  $E_{A'}$  represents the reductive peak position. Each value is an average of at least three measurements.

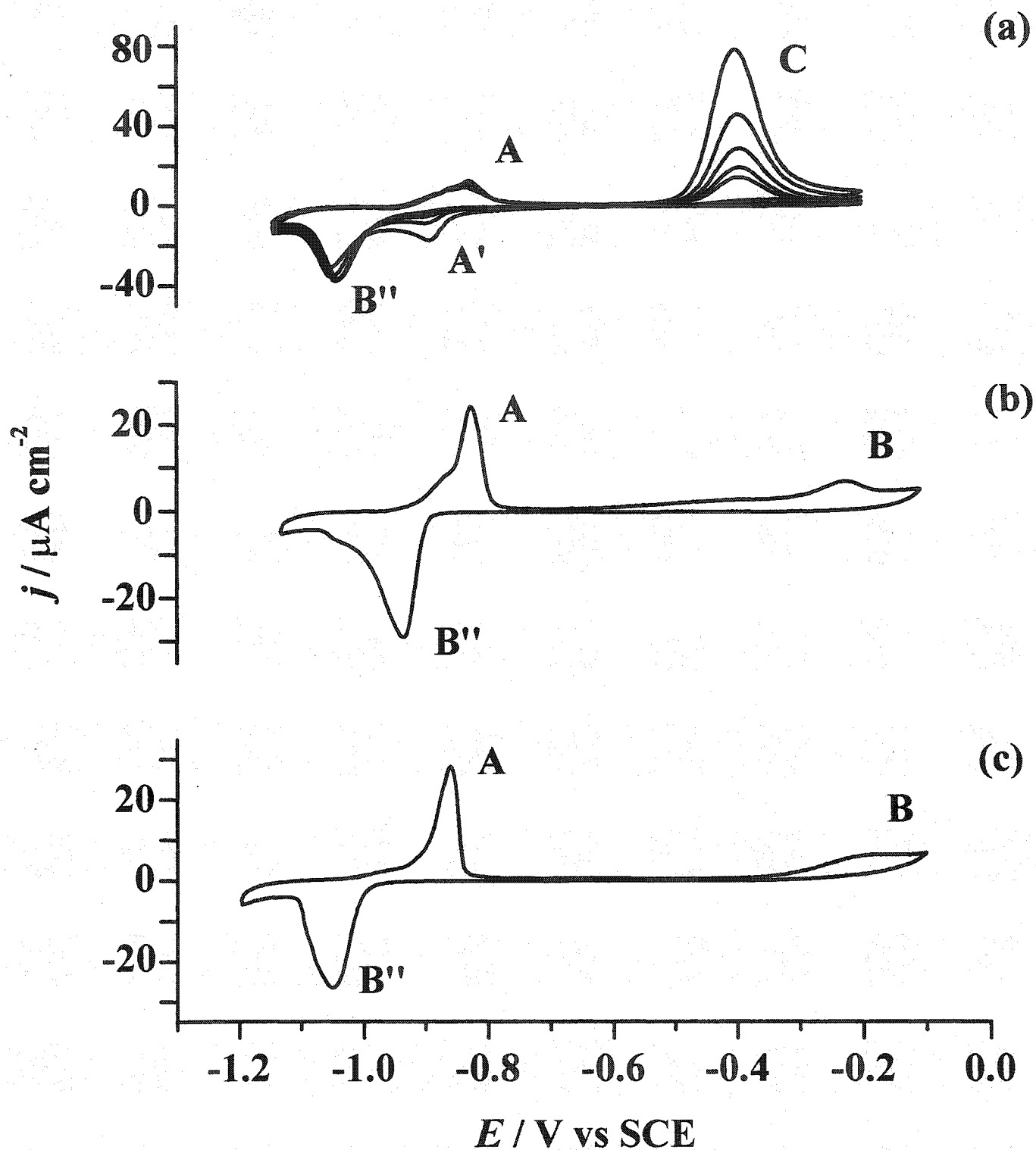
| dithiol | $Q_A / \mu\text{C cm}^{-2}$ | $\Gamma / \times 10^{-10} \text{ mol cm}^{-2}$ | $E_A / \text{V vs SCE}$ | $Q_{A'} / \mu\text{C cm}^{-2}$ | $E_{A'} / \text{V vs SCE}$ |
|---------|-----------------------------|------------------------------------------------|-------------------------|--------------------------------|----------------------------|
| 1,2-EDT | $71 \pm 7$                  | $7.4 \pm 0.7$                                  | -0.83                   | $103 \pm 8$                    | -0.89                      |
| 1,3-PDT | $65 \pm 6$                  | $6.7 \pm 0.6$                                  | -0.85                   | $72 \pm 6$                     | -0.88                      |
| 1,4-BDT | $84 \pm 8$                  | $8.7 \pm 0.8$                                  | -0.86                   | $74 \pm 7$                     | -0.91                      |
| 1,6-HDT | $61 \pm 4$                  | $6.3 \pm 0.4$                                  | -0.86                   | $62 \pm 4$                     | -0.95                      |
| 1,8-ODT | $56 \pm 3$                  | $5.8 \pm 0.3$                                  | -0.86                   | $60 \pm 4$                     | -0.94                      |
| 1,9-NDT | $65 \pm 4$                  | $6.7 \pm 0.4$                                  | -0.86                   | $67 \pm 5$                     | -0.95                      |

On the cathodic scan from  $-0.70$  V or  $-0.65$  V to  $-1.15$  V, a single reductive peak A' is located at  $-0.89$  V for 1,2-EDT and  $-0.95$  V for both 1,6-HDT and 1,9-NDT. The small separation of 60 mV between peaks A and A' ( $\Delta E_p$ ) for 1,2-EDT, and 90 mV for 1,6-HDT and 1,9-NDT, suggests that the oxidative deposition and subsequent reductive removal of the respective monolayers is a relatively reversible process. This is also supported by the reductive charge ( $Q_{A'}$ ), which (within error) balances with  $Q_A$  for all of the alkanedithiols except for 1,2-EDT. The difference for 1,2-EDT is due to the difficulty in integrating the peaks, since there is an important current at all potentials. There is no second reductive peak B', which was attributed to inhomogeneous bilayer formation for the *para*- and *meta*-BDMT isomers (section 4.2.1).

### 5.2.2 Oxidative Deposition of Bilayers of Alkanedithiols

To oxidize the unreacted sulfur end group, the potential was scanned towards more positive values and the resulting cyclic voltammograms are given in Figure 5.2. A second oxidative peak appears for all of the alkanedithiols. The new peak is labeled B for the medium and long chain alkanedithiols, since it displays similar voltammetry as the *para*- and *meta*-BDMT isomers (Figures 4.3a and b). The new peak is designated as C for the shorter chains, because of its resemblance to the voltammetry of *ortho*-BDMT (Figure 4.3c). The magnitude and position of this new current peak changes as a function of the chain length. The short chain length dithiols exhibit a much larger second anodic peak C than the medium chain lengths. This is indicative of a solution process and/or multilayer growth. Of all of the dithiols, the 1,9-NDT exhibits the smallest peak B. The potential of peak B or C shifts towards more positive values on going from the short chain lengths to the longer ones. The peak current potential (B and C) is plotted as a function of chain length in Figure 5.3. The





**Figure 5.2:** Cyclic voltammograms of the oxidative deposition and reductive desorption of (a) 1,2-EDT, (b) 1,6-HDT, and (c) 1,9-NDT from 1 mM dithiol solutions in 0.5 M KOH at the Au(111) surface. Potential scan rate:  $20 \text{ mV s}^{-1}$ .

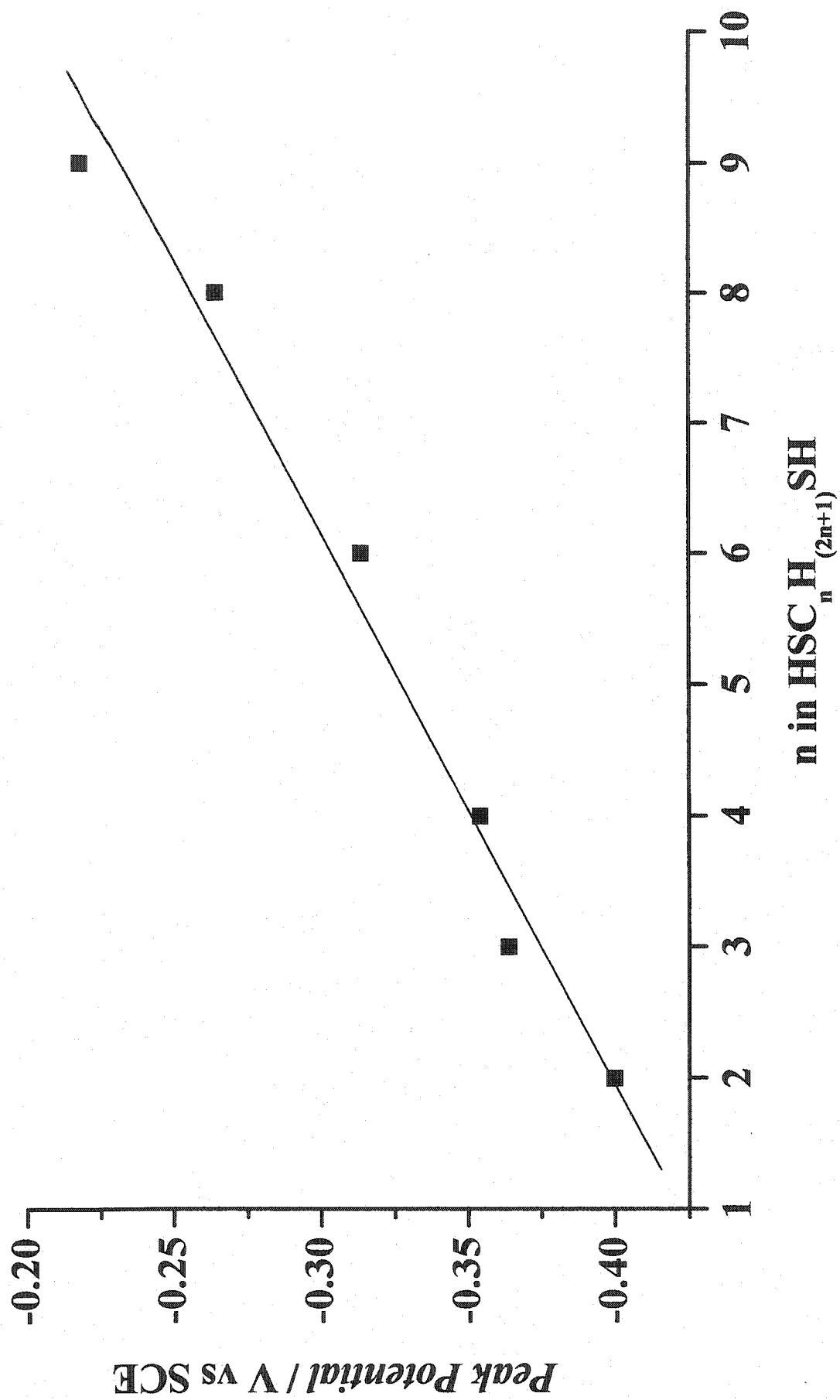


Figure 5.3: Potential of peak B as a function of alkanedithiol chain length.

standard deviations for these data (on at least five measurements) are comparable to or less than the size of the symbols. There is a linear variation and a shift of about 24 mV per CH<sub>2</sub> unit (towards more positive potentials) is obtained from the slope.

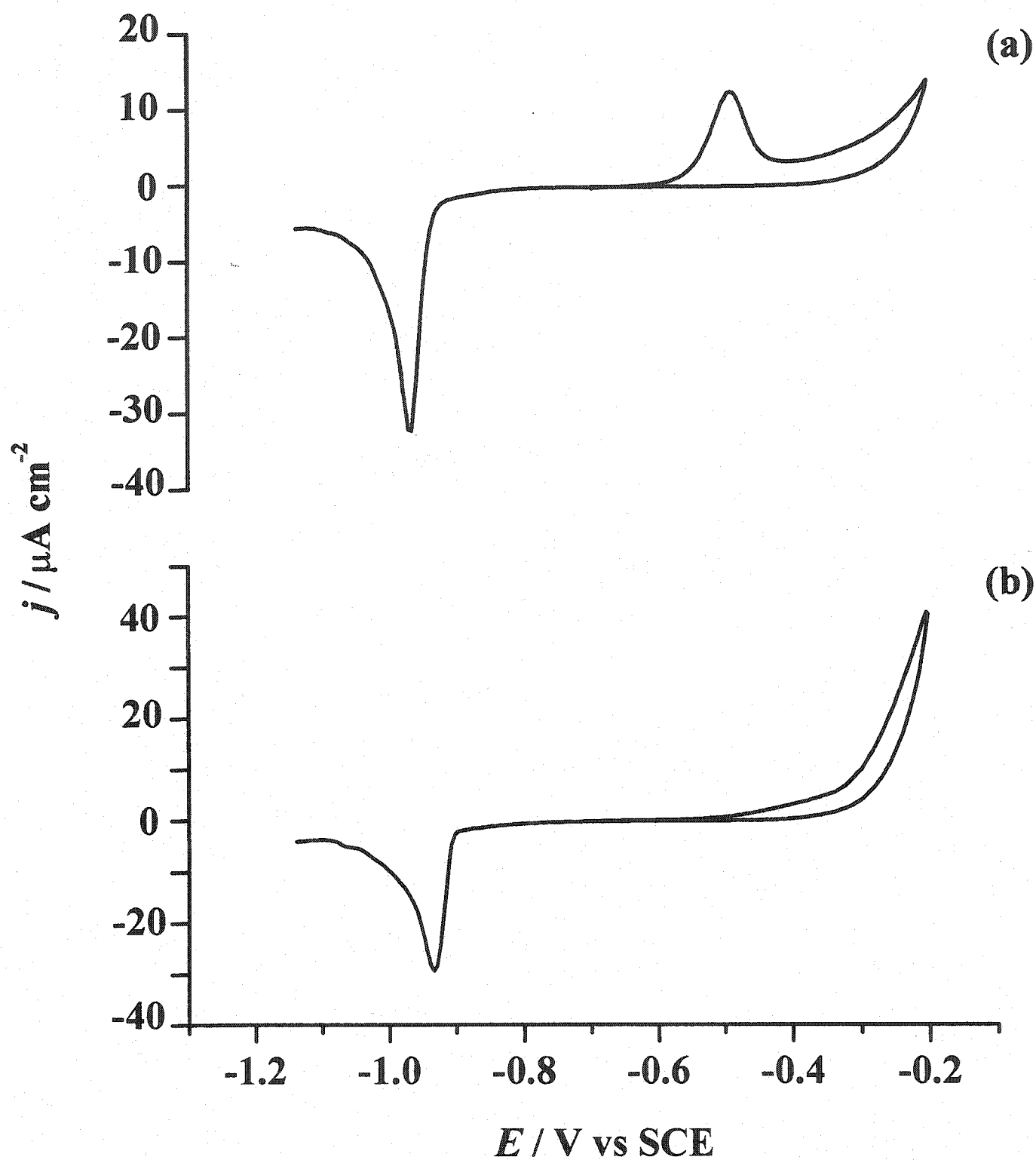
The separation between the two anodic peaks A and B, or C is 430, 550, and 640 mV for 1,2-EDT, 1,6-HDT, and 1,9-NDT respectively. This large separation implies that peak A and the new peak (B for the medium and long chain length dithiols, and C for the short chain dithiols) correspond to two separate oxidative processes. The increasing separation between the two peaks for longer chain lengths is as a result of the shifting second peak, since the position of peak A remains essentially the same for all of the dithiols (Table 5.1). The origin of the second oxidative peak was examined to see if it corresponds with the bilayer formation reported in Chapter 4 for the BDMT isomers.

Similar transfer experiments on the alkanedithiols were performed as those done on the BDMT isomers (section 4.2.2). After electrodepositing a monolayer (conditions same as in Figure 5.1, section 5.2.1) of each of the alkanedithiols, the coated electrode was transferred to a solution of pure 0.5 M KOH. Upon scanning towards more positive potentials, a second oxidative peak was not observed. This suggests that neither peak B nor C originate from dimerization between adsorbates, since this should occur whether or not there is dithiol in solution. In contrast, when the respective monolayers were transferred to 1 mM hexanethiol solutions and the potential was scanned towards more positive values, a second oxidative peak was observed. This implies that B results from a reaction between adsorbed dithiolates and dithiolates in solution. This also suggests that C is representative of a surface and/or solution process, as was the case with 1,2-BDMT (section 4.2.2b).

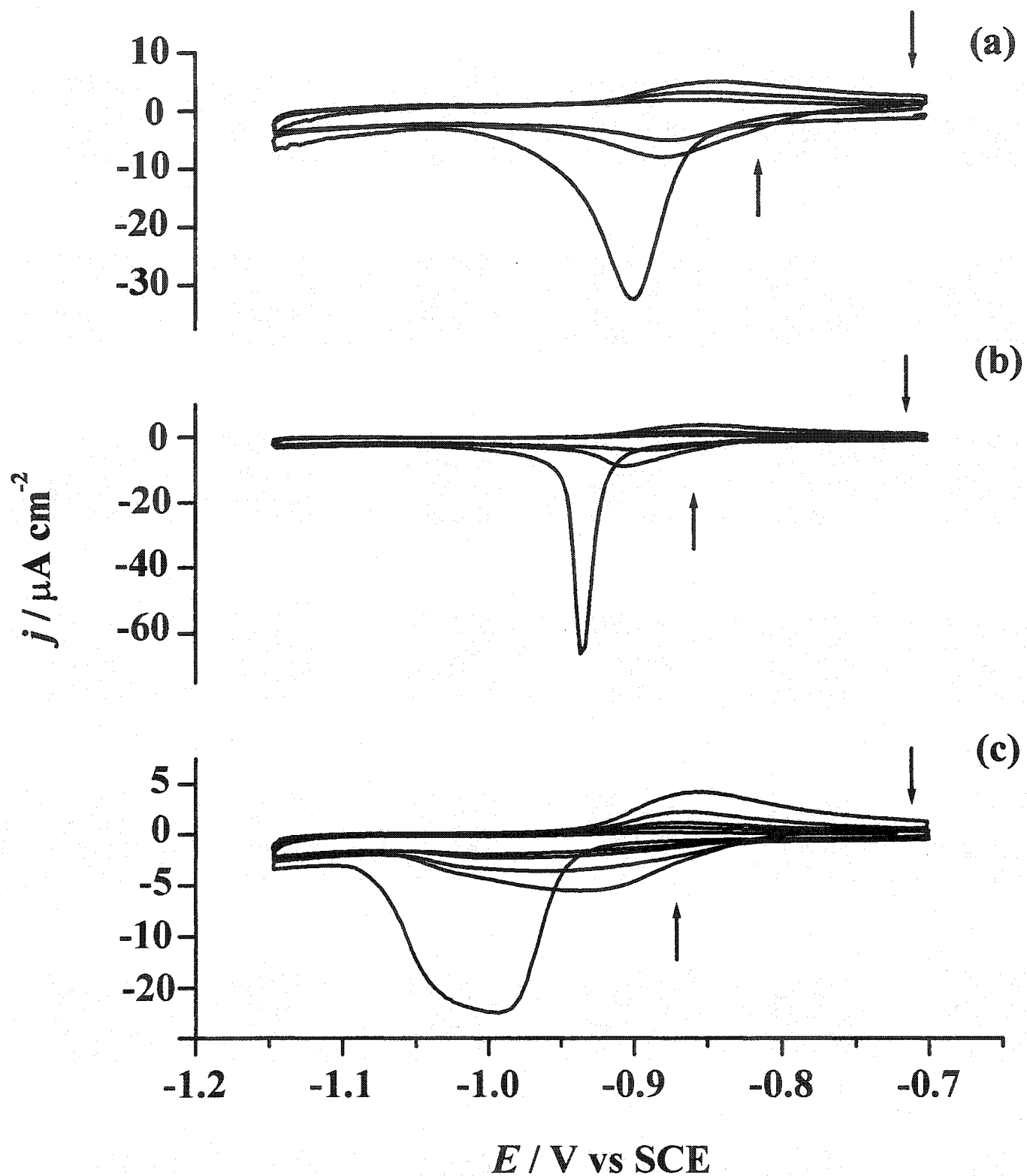
Figure 5.4 shows the abrupt change in reactivity of the monolayers with hexanethiol observed between 1,4-BDT (Figure 5.4a) and 1,6-HDT (Figure 5.4b). Surprisingly, the short chain dithiols reacted with the hexanethiol through formation of a well defined anodic peak at potentials very similar to those of the respective peak C. In contrast, the medium to long chain length dithiols resulted in an increased current, but no resolved peak. This could be due to the fact that the peak current occurs at more positive potentials because of the increased thickness. However, the gold oxide formation restricts the range of potentials accessible for further reactivity.

Further evidence to support that peaks B and C result through formation of disulfide linkages between an adsorbed dithiolate and one in solution comes from transfer experiments into pure 0.5 M KOH followed by continuous cycling of the potential. Figure 5.5 presents the transfer of a monolayer to pure electrolyte and cycling several times between  $-0.70$  V and  $-1.15$  V, starting in the cathodic direction. It is clear that the monolayers are relatively soluble for all of the dithiols, and diffuse into the solution. However, more cyclic voltammograms were required to remove the 1,9-NDT monolayer (Figure 5.5c) from the surface. This corresponds well with the fact that a longer chain alkanethiol is less soluble than a shorter one and therefore remains longer at the surface [22,23].

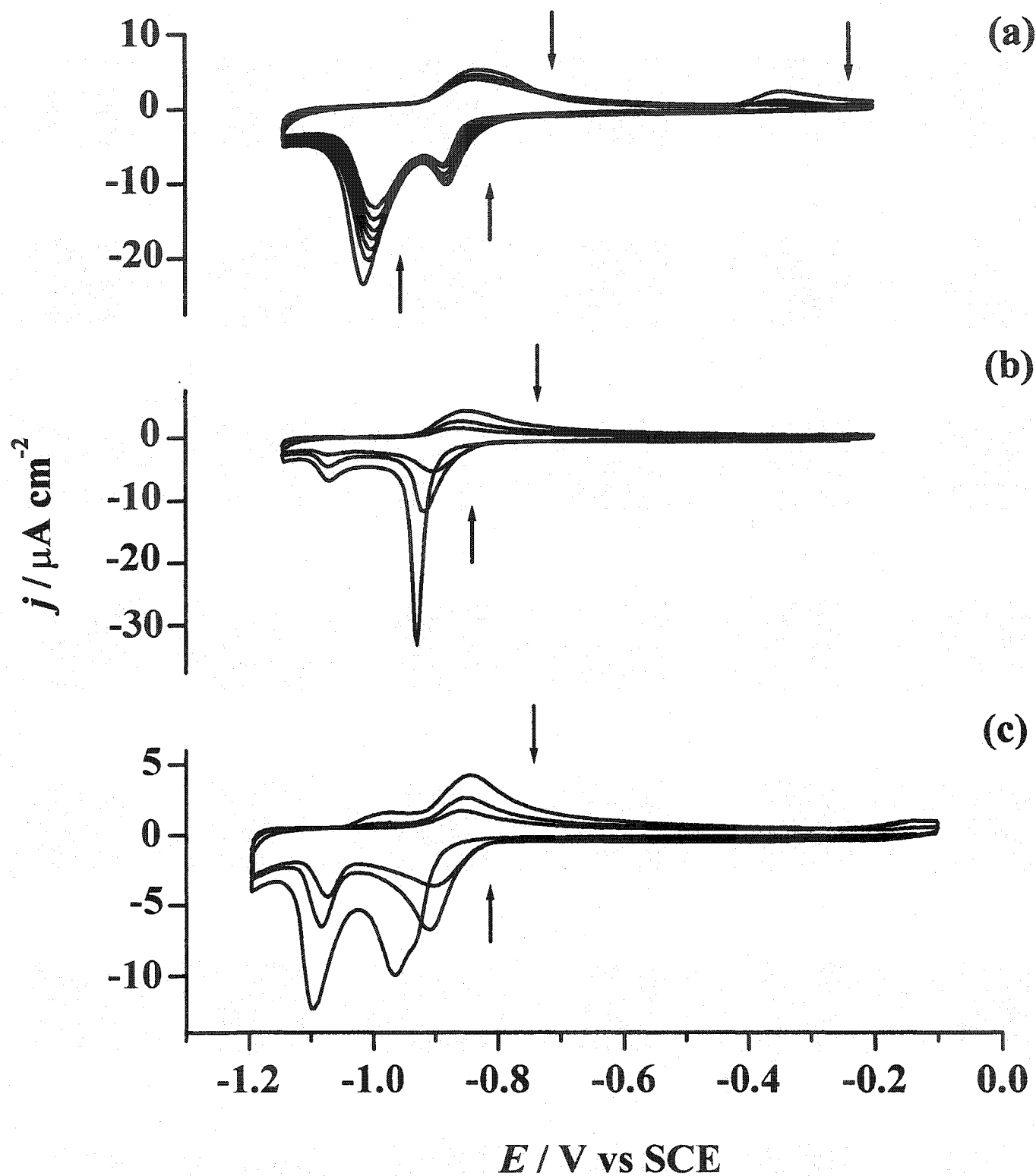
This chain length dependence of the electrodeposition presents itself more clearly after scanning through both anodic peaks and transferring to pure 0.5 M KOH. Figure 5.6 depicts the resulting cyclic voltammograms for (a) 1,2-EDT, (b) 1,6-HDT, and (c) 1,9-NDT. Only the even cycles are shown for clarity. In general, all of the alkanedithiols remain longer at the surface than their respective monolayers. This implies that less soluble species are generated upon scanning through the second anodic peak [7]. This supports dimer formation,



**Figure 5.4:** Cyclic Voltammograms of a Au(111) surface coated with a monolayer of (a) 1,4-BDT and (b) 1,6-HDT transferred into a 1 mM hexanethiol solution in 0.5 M KOH. Potential scan rate:  $20 \text{ mV s}^{-1}$ . See text for details.



**Figure 5.5:** Cyclic voltammograms of a Au(111) surface covered with a monolayer of (a) 1,2-EDT, (b) 1,6-HDT, and (c) 1,9-NDT in a 0.5 M KOH solution. The arrows indicate the increasing number of cycles. Potential scan rate:  $20 \text{ mV s}^{-1}$ . See text for details.



**Figure 5.6:** Cyclic voltammograms of a Au(111) surface covered with a bilayer of (a) 1,2-EDT (even cycles 2-14), (b) 1,6-HDT (cycles 2,4,6), and (c) 1,9-NDT (cycles 2,4,6) in a 0.5 M KOH solution. The arrows indicate the increasing number of cycles. Potential scan rate:  $20 \text{ mV s}^{-1}$ . See text for details.

which results in desorption of a thicker (less soluble) film. In particular, the 1,2-EDT remained longest at the gold surface. This suggests the possibility of multilayer formation in the case of 1,2-EDT. Dimerization between adsorbates could also be used to explain the above observation, however it has already been ruled out based on the first two transfer experiments described.

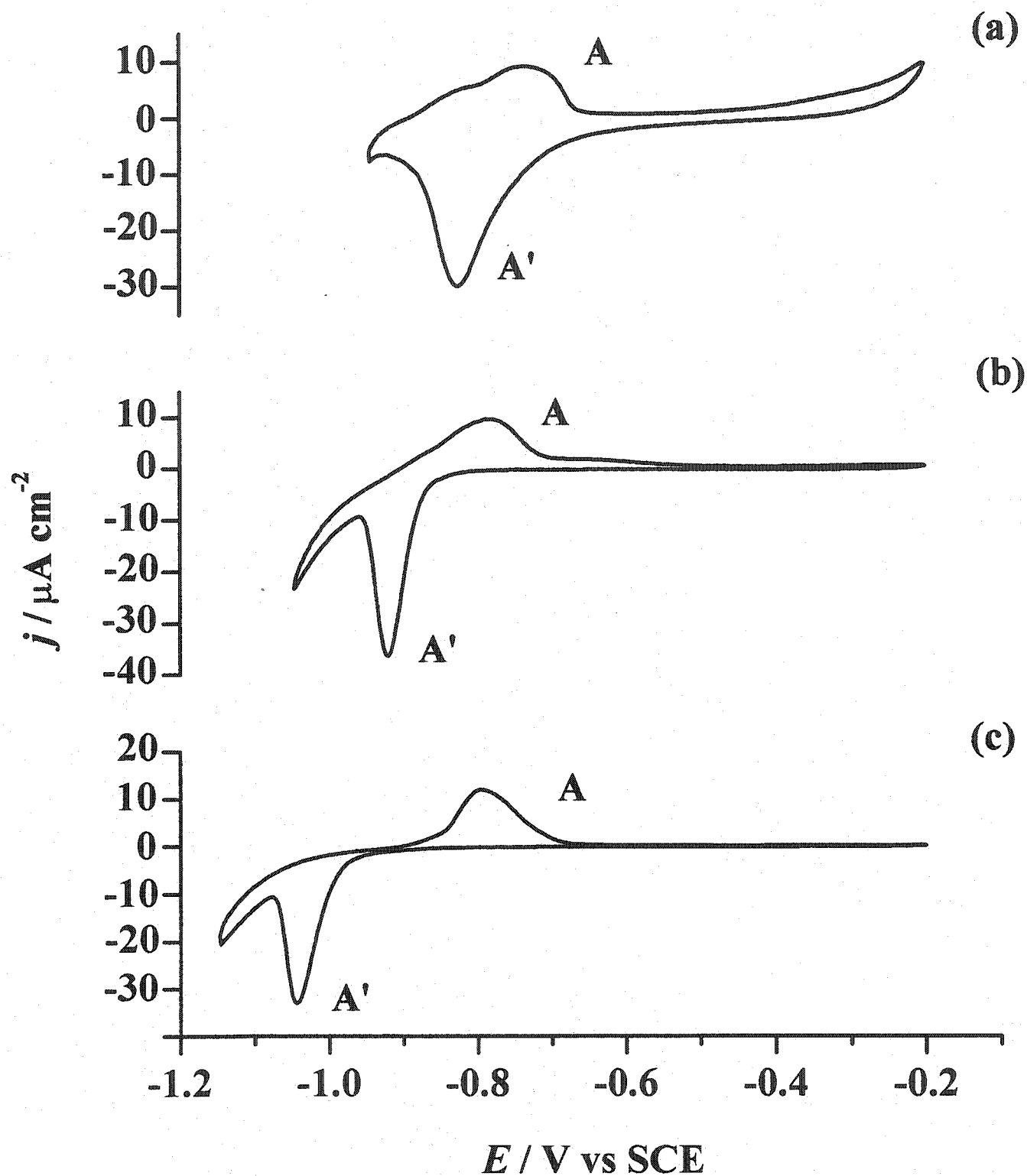
This increase in film thickness is also reflected in the cathodic scans of Figure 5.2. The integrated charges and peak positions of the reductive current peak B'' are summarized in Table 5.2. The charges are all slightly larger than those obtained for A'. The integration of peak B'' is difficult due to the presence of the hydrogen evolution current. Because the values for  $Q_{B''}$  are not significantly larger than those for  $Q_{A'}$  (except for 1,2-EDT), the desorption associated with B'' is assigned to the reduction of a S-Au bond. Peak B'' shifts towards more negative potentials when compared with the reductive removal of a monolayer (peak A'). This shift is as large as 180 mV for 1,2-EDT, 110 mV for 1,6-HDT, and 200 mV for 1,9-NDT. This implies that ion penetration is more difficult upon scanning through peaks A and B, or C. In turn, this makes the reduction more difficult. This is evidence of a thicker film (with fewer defects) at the electrode surface [22,24,25].

The alkanedithiols were also deposited from 0.1 M NaF over the same potential range used to deposit peaks A and B, or C in 0.5 M KOH. The resulting voltammograms are presented in Figure 5.7. There is no peak B for the medium to long chain length dithiols. This confirms that the surface process related to peak B results directly from reactivity of dithiols in the deprotonated form. There is a small peak C for the short chain dithiols. However, the process contributing to peak C occurs to a much lesser extent in the neutral electrolyte. The dithiols behave more like alkanethiols (i.e. monofunctional compounds) in



**Table 5.2:** Data obtained from cyclic voltammograms upon reactivity of monolayers deposited onto Au(111) from 1 mM alkanedithiol solutions in 0.5 M KOH, where  $Q_{B''}$  represents the charge of the reductively removed multilayer peak B'', and  $E_{B''}$  represents its reductive peak position. Each value is an average of at least three measurements.

| dithiol | $Q_{B''} / \mu\text{C cm}^{-2}$ | $E_{B''} / \text{V vs SCE}$ |
|---------|---------------------------------|-----------------------------|
| 1,2-EDT | $107 \pm 8$                     | -1.01                       |
| 1,3-PDT | $85 \pm 5$                      | -0.89                       |
| 1,4-BDT | $80 \pm 5$                      | -0.91                       |
| 1,6-HDT | $90 \pm 9$                      | -0.97                       |
| 1,8-ODT | $73 \pm 8$                      | -1.01                       |
| 1,9-NDT | $73 \pm 5$                      | -1.06                       |



**Figure 5.7:** Cyclic voltammograms of the oxidative deposition and reductive desorption of (a) 1,2-EDT, (b) 1,6-HDT, and (c) 1,9-NDT from a 1 mM dithiol solution in 0.1 M NaF at the Au(111) surface. Potential scan rate:  $20 \text{ mV s}^{-1}$ .

0.1 M NaF. The shape of peak A follows a similar trend as the one from 0.5 M KOH, in that it sharpens on going from the 1,2-EDT to 1,9-NDT. The charges for the oxidative peak A from 0.1 M NaF solution are tabulated in Table 5.3. Even though peak A is broader than its respective deprotonated A, the charges are similar to those obtained for peak A from 0.5 M KOH. On the other hand, the potential for peak A shifts towards more positive values for all of the alkanedithiols when compared with the deprotonated monolayers. This is expected, since there is an additional energy requirement in the breaking of the S-H bond [22].

**Table 5.3:** Data obtained from cyclic voltammograms of monolayers deposited onto Au(111) from 1 mM alkanedithiol solutions in 0.1 M NaF, where  $Q_A$  represents the charge of the oxidatively deposited monolayer,  $E_A$  represents its peak potential,  $Q_{A'}$  represents its reductive charge, and  $E_{A'}$  represents the reductive peak position. Each value is an average of at least three measurements.

| dithiol | $Q_A / \mu\text{C cm}^{-2}$ | $E_A / \text{V vs SCE}$ | $Q_{A'} / \mu\text{C cm}^{-2}$ | $E_{A'} / \text{V vs SCE}$ |
|---------|-----------------------------|-------------------------|--------------------------------|----------------------------|
| 1,2-EDT | $62 \pm 6$                  | -0.73                   | $52 \pm 5$                     | -0.82                      |
| 1,3-PDT | $54 \pm 4$                  | -0.76                   | $54 \pm 5$                     | -0.83                      |
| 1,4-BDT | $59 \pm 4$                  | -0.77                   | xxx (see text)                 | -0.87                      |
| 1,6-HDT | $60 \pm 6$                  | -0.78                   | $52 \pm 6$                     | -0.91                      |
| 1,8-ODT | $54 \pm 5$                  | -0.78                   | $52 \pm 4$                     | -1.01                      |
| 1,9-NDT | $55 \pm 3$                  | -0.80                   | xxx (see text)                 | -1.05                      |

The cathodic limit for both 1,2-EDT (Figure 5.7a) and 1,6-HDT (Figure 5.7b) was slightly less negative than that for 1,9-NDT (Figure 5.7c) due to onset of hydrogen evolution. There is a single reductive peak labeled A', whose charge is similar to that of the oxidative peak A for most of the dithiols. Peak A' was difficult to integrate because it was close to the onset of hydrogen evolution. This was the case for 1,4-BDT and 1,9-NDT, so we do not report values for them. The position of A' shifts towards more negative potentials by 230 mV from 1,2-EDT to 1,9-NDT. This is typical for thicker films (having fewer defects) and is analogous to what has already been reported on alkanethiols [7,23].

#### 5.2.2a 1,2-EDT and 1,2-BDMT

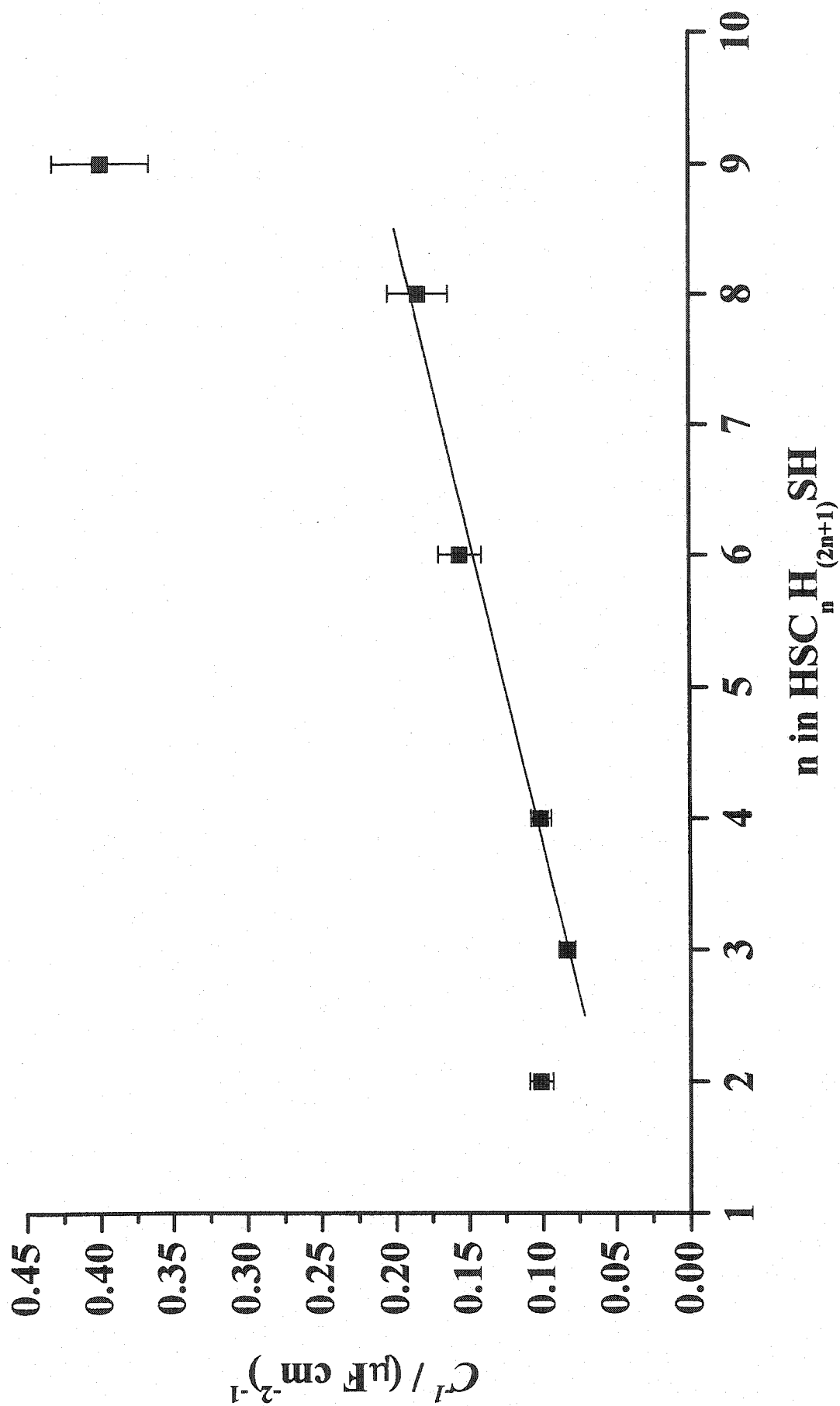
The electrodeposition of 1,2-EDT is compared with that of *ortho*-BDMT (Figure 4.3c). The reactivity of the monolayer of 1,2-EDT differs from that of the other alkanedithiols. In Figure 5.2a, peak C decreases in intensity with each consecutive cycle (all even cycles from 2-10 are shown), and finally stabilizes. Simultaneously, peak A' decreases and peak B'' grows until only B'' is observed and constant. The large oxidative peak C in the first cycle of Figure 5.2a is characteristic of a solution process. However, the various electrochemical experiments presented above suggest that it also originates from a surface process. We believe that the reactivity of the 1,2-EDT layer occurs inhomogeneously, i.e. multilayer formation does not occur completely in a single deposition cycle.

On the first reductive cycle there are two cathodic peaks A' and B'', representing removal of a monolayer and multilayer film respectively. The changes in voltammetry upon continuous cycling are attributed to the fact that with each oxidative deposition we are generating a more uniform multilayer surface. Hence, the ease of the solution process decreases, since the dithiolates in solution cannot approach the surface as closely as a result

of the increasing film thickness. Eventually, even multilayer growth is limited by the increasing distance of the unreacted sulfur from the electric field at the gold surface. This suggests that multilayers remain physisorbed at the surface and are being redeposited. This fits well with the voltammetry in the transfer experiments. This inhomogeneous multilayer growth of 1,2-EDT on gold has recently been reported in a SERS study, whereby they observed up to four layers forming from *n*-hexane [12].

### 5.3 Differential Capacitance Measurements

Differential capacitance measurements were performed on the monolayers of the alkanedithiols electrodeposited from 0.5 M KOH. The potential was cycled from  $-0.70$  V to  $-1.15$  V twice, starting with the cathodic scan and ending with the anodic scan. The hanging meniscus was then broken under potential control at  $-0.70$  V. The electrode was rinsed with water and transferred to a solution of pure 0.5 M KOH, where the capacitance was measured between  $-0.30$  V and  $-0.50$  V. The results are graphed in Figure 5.8 and summarized in Table 5.4. Figure 5.8 depicts the reciprocal capacitance as a function of the chain length. The 1,2-EDT and 1,9-NDT display a behavior different than the rest of the dithiols. The inverse of the capacity of the four chain lengths in between 1,2-EDT and 1,9-NDT varies linearly. From the slope of this graph ( $0.022 \pm 0.002 \text{ cm}^2 \mu\text{F}^{-1}$ ) and by rearranging equation 2.7, the relative dielectric constant of the separation medium ( $\epsilon_r$ ) is calculated. If it is assumed that the change in thickness for these films as a function of chain length equals 1.3 to 1.1 Å per CH<sub>2</sub> group (the value for an all trans alkyl chain packed perpendicular to the surface or inclined at 30° from the surface normal respectively), then  $\epsilon_r$  is calculated to be between  $6.8(\pm 0.6)$  to  $5.7(\pm 0.5)$ . This value is much higher than the range of values (2.2 –



**Figure 5.8:** Reciprocal capacitance vs.  $n$  for  $\text{HSC H}_n(2n+1)\text{SH}$  monolayer coated Au(111) surfaces deposited from 0.5 M KOH. The line represents a linear regression. See text for details.

3.0) that has been reported for alkanethiols [14,26-29] or the dielectric constant of 2.3 for polyethylene [30]. Therefore, it is indicative of monolayer films having defects.

**Table 5.4:** Capacity values taken after deposition of alkanedithiol monolayers onto Au(111) from 0.5 M KOH ( $C_{A(KOH)}$ ), and from 0.1 M NaF ( $C_{A(NaF)}$ ). In addition, the capacity values after reacting the monolayer deposited from 0.5 M KOH are presented  $C_{A+B(KOH)}$ . Each value is an average of at least three measurements. See text for details.

| dithiol | $C_{A(KOH)} / \mu\text{F cm}^{-2}$ | $C_{A(NaF)} / \mu\text{F cm}^{-2}$ | $C_{A+B(KOH)} / \mu\text{F cm}^{-2}$ |
|---------|------------------------------------|------------------------------------|--------------------------------------|
| 1,2-EDT | $9.9 \pm 0.8$                      | $10.3 \pm 1.0$                     | $1.4 \pm 0.1$                        |
| 1,3-PDT | $12.0 \pm 0.8$                     | $10.2 \pm 0.7$                     | $8.3 \pm 0.7$                        |
| 1,4-BDT | $9.9 \pm 0.7$                      | $7.3 \pm 0.7$                      | $5.2 \pm 0.3$                        |
| 1,6-HDT | $6.4 \pm 0.6$                      | $3.3 \pm 0.3$                      | $3.0 \pm 0.3$                        |
| 1,8-ODT | $5.4 \pm 0.6$                      | $2.2 \pm 0.1$                      | $2.3 \pm 0.2$                        |
| 1,9-NDT | $2.5 \pm 0.2$                      | $2.0 \pm 0.1$                      | $1.8 \pm 0.1$                        |

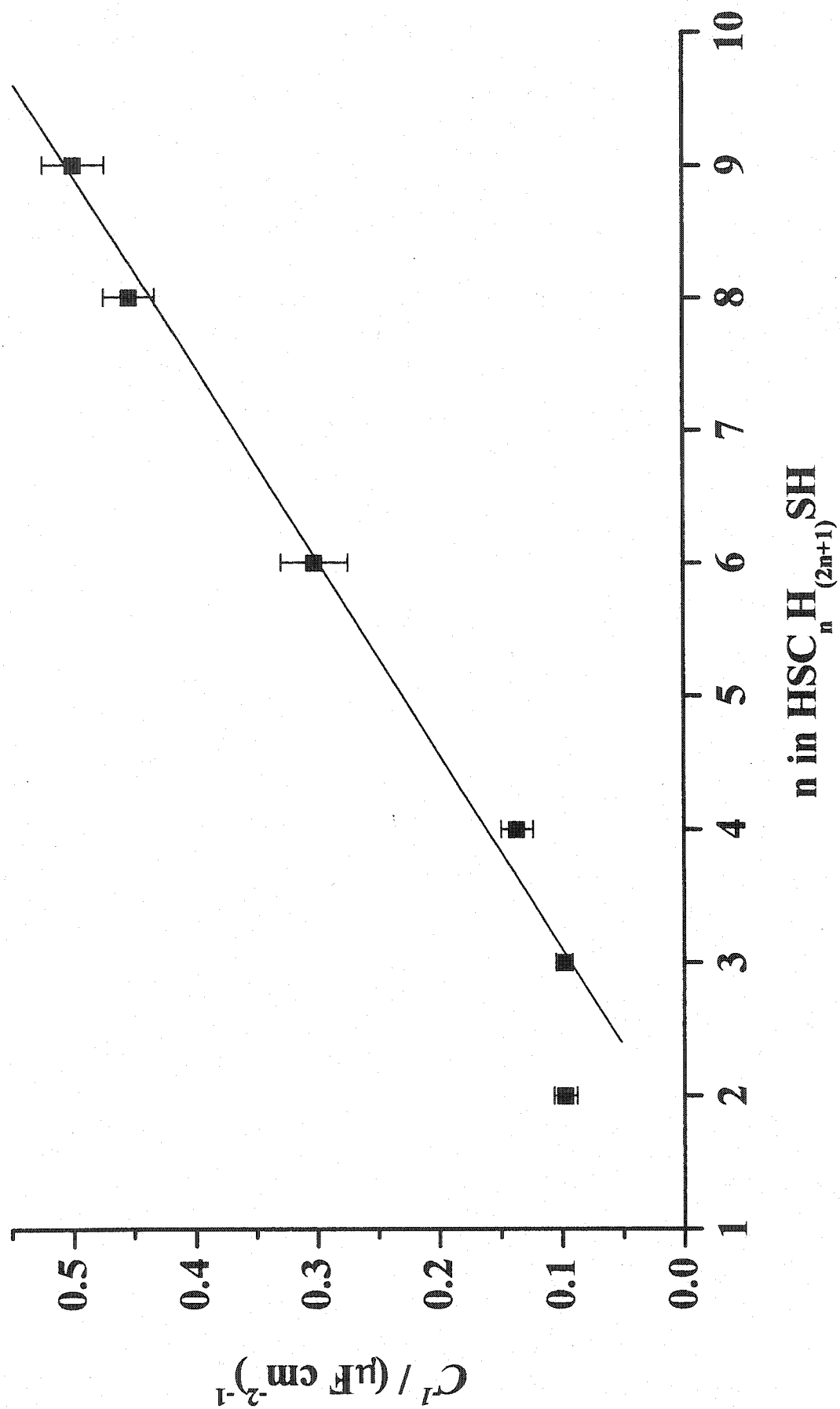
The large capacity obtained for a monolayer of 1,4-BDMT electrodeposited from 0.5 M KOH decreased both upon protonation and bilayer formation [1,2]. The former observation was assigned to the effect of the negatively charged sulfur end group. The latter observation was attributed to an increase in film thickness upon scanning from monolayer to bilayer. To confirm that the charged interface plays a significant contribution in the monolayer film capacitance, the dithiols were electrodeposited from 0.1 M NaF and the capacitance was measured in pure 0.1 M NaF between  $-0.30$  V and  $-0.40$  V. Except for the

1,2-EDT, a decrease in capacity was observed for all of the dithiols. The results are tabulated in Table 5.4 and graphed in Figure 5.9. The 1,2-EDT data point was excluded from the linear regression in Figure 5.9. A value for  $\epsilon_r$  between  $2.1(\pm 0.1)$  to  $1.8(\pm 0.1)$  was calculated from the slope of the graph ( $0.069 \pm 0.004 \text{ cm}^2 \mu\text{F}^{-1}$ ). This value is now equivalent to the dielectric constant previously reported for alkanethiols [14,26-29] and polyethylene [30]. This pH dependence in the capacitance also verifies that between  $-1.15 \text{ V}$  and  $-0.70$  or  $-0.65 \text{ V}$  (depending on the dithiol), the alkanedithiols adsorb to gold with one sulfur atom.

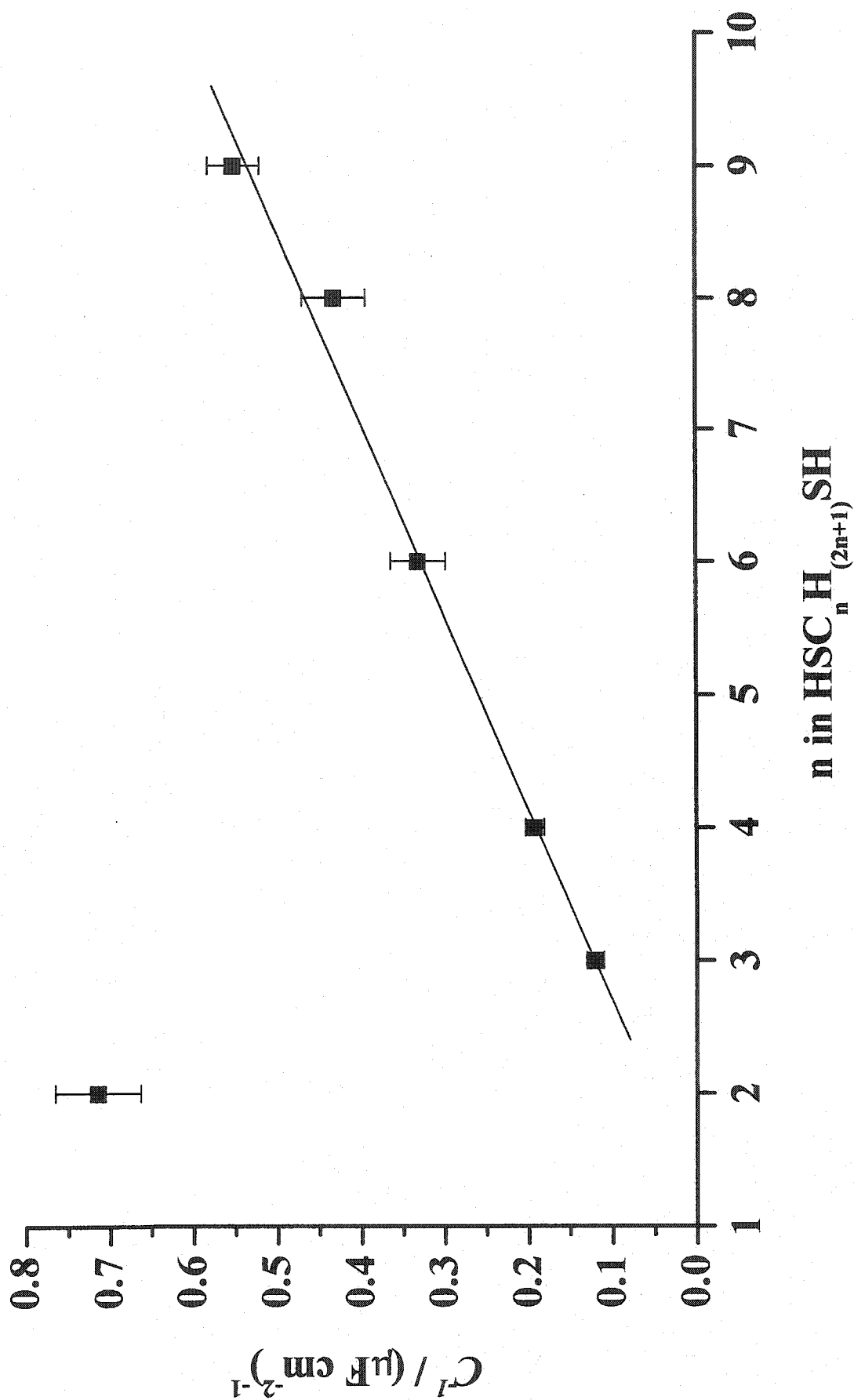
The capacitance was measured after scanning through peaks A and B, or C of the dithiol solutions in  $0.5 \text{ M KOH}$  between  $-0.30 \text{ V}$  and  $-0.50 \text{ V}$ . The results are graphed in Figure 5.10 and summarized in Table 5.4. Again, with the exception of 1,2-EDT, all of the dithiols show a similar trend in the capacitance. The large decrease in the capacity of 1,2-EDT from  $9.9 \pm 0.8$  to  $1.4 \pm 0.1 \mu\text{F cm}^{-2}$ , supports the multilayer formation suggested by the voltammetric experiments. Therefore, this data point was not used in the linear regression plot in Figure 5.10. From the slope of the graph ( $0.070 \pm 0.003 \text{ cm}^2 \mu\text{F}^{-1}$ ), a  $\epsilon_r$  between  $2.1(\pm 0.1)$  to  $1.8(\pm 0.1)$  was calculated. This value is the same as the one we obtained from the protonated monolayer data in Figure 5.9.

The capacitance decreases by approximately a factor of two for 1,4-BDT, 1,6-HDT, and 1,8-ODT versus the monolayer. The 1,4-BDMT displayed similar results and the decrease was attributed to bilayer formation [1,2]. A decrease in capacitance is expected for longer alkyl chains because of the more cohesive interchain interactions. This generates a larger diffusion barrier for the ion flux through the dithiol film towards the electrode [23,24,26,31-33]. There is a smaller decrease in capacitance for both 1,3-PDT and 1,9-NDT, suggesting partial bilayer formation. The monolayer of 1,3-PDT might have more defects to





**Figure 5.9:** Reciprocal capacitance vs.  $n$  for  $\text{SH C H}_{n(2n+1)}\text{SH}$  monolayer coated  $\text{Au}(111)$  surfaces deposited from  $0.1 \text{ M NaF}$ . The line represents a linear regression. See text for details.



**Figure 5.10:** Reciprocal capacitance vs.  $n$  for  $\text{SHC H}_n(2n+1)\text{SH}$  measured at the  $\text{Au}(111)$  surface after scanning through peak B in 0.5 M KOH. The line represents a linear regression. See text for details.

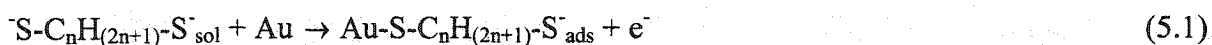
begin with. The bilayer growth of 1,9-NDT may be limited due to the distance of the unreacted sulfurs from the gold surface. These changes in capacitance upon formation of peak B, or C gives us a qualitative idea about the extent of the respective monolayer's reactivity.

## 5.4 Mechanism for the Oxidative Adsorption of the Alkanedithiols onto Au(111)

### 5.4.1 Monolayer Formation

The electrochemical measurements suggest that all of the alkanedithiols oxidatively adsorb via single S-Au bond formation, with the exception of 1,2-EDT. Some of the 1,2-EDT molecules might bind via both sulfurs to the gold surface. The potential and charge of peak A are compatible with the one-electron process reported for the oxidative deposition of a monolayer of alkanethiols on gold [21,22]. The pH effect observed in the capacitance measurements, and the transfer experiments performed on all of the dithiols clearly support the presence of unreacted thiolates. These results are similar to those reported for the isomers of BDMT in Chapter 4.

The following expression describes monolayer formation of the alkanedithiols [1,2]:



The oxidative deposition of a monolayer of alkanedithiols from aqueous electrolyte differs from a monolayer deposited from the vapor phase where they bind via both sulfurs to the gold surface [3-7]. In contrast, when deposited from organic solution (under open circuit conditions), the alkanedithiols adsorbed to the Au(111) surface [3,7-11,13] and to colloidal gold [12,14,15] vertically (with one sulfur and with their molecular axes relatively normal to

the metal surface). However, the structure of the monolayers was under speculation in most of these studies. For instance, 1,6-HDT was reported to adsorb upright onto Au(111), but no ordered structure was imaged with STM [3,7]. Only after annealing of the sample (resulting in desorption of some of the 1,6-HDT) were striped phases observed, corresponding to the remaining 1,6-HDT lying prone to the surface [3]. Similarly, upon partial electrochemical desorption, a striped pattern of 1,6-HDT emerged [7]. Other studies reported inhomogeneous multilayer formation for 1,2-EDT [12] and for 1,6-HDT, 1,8-ODT, and 1,9-NDT [13]. The origin of these different orientations was discussed in sections 3.4.1 and 4.4.1, and they were attributed to the difference in deposition times and solvation.

It is well known that longer chain alkanethiols (versus shorter chains) typically form well-packed monolayers, due to their increased Van der Waals interactions [23,24,26]. This trend is also evident with the alkanedithiolate monolayers. The attractive behavior is reflected in the shape of peak A, as well as in the capacitance measurements. Peak A was broader for the short chain alkanedithiols (Figure 5.1). In fact, there was a significant current over the entire potential range for 1,2-EDT, suggesting that there is no fine distinction between monolayer and multilayer formation of 1,2-EDT. Quite possibly, the 1,2-EDT monolayer might even deposit with some of the molecules bound through both sulfurs to the gold surface. The capacitance values, measured for peak A in 0.5 M KOH, were relatively high for most of the dithiols. Upon protonation, a decrease in the capacitance for all of the dithiols was observed except for 1,2-EDT. The medium chain length dithiols showed the most significant decrease in the monolayer capacitance, whereas 1,9-NDT showed a slight decrease. Notwithstanding these differences, there is a decrease in the capacitance as the chain length increases in both sets of data (Table 5.4).

These changes in the monolayer capacitances may be explained by the various interactions dictating film formation (section 2.2). Here, they are considered in more detail. Three regimes of electrodeposition were observed: (a) 1,2-EDT, (b) a trend for 1,3-PDT to 1,8-ODT, and finally (c) 1,9-NDT. These exemplify the numerous interactions taking place. For instance, the distance of the unreacted sulfur from the gold surface influences dimer formation. This results in a very reactive thin film of 1,2-EDT from both alkaline and neutral mediums. As a result, a disorganized monolayer is formed whose capacity remains the same in 0.5 M KOH and 0.1 M NaF. The reactivity of 1,2-EDT is very different than the other alkanedithiols. It is for this reason that it was not included in the linear regressions of the plots in Figures 5.8 and 5.9.

A trend in the capacity as a function of chain length is observed starting with 1,3-PDT to 1,8-ODT. The elevated capacitances in 0.5 M KOH (versus those measured in 0.1 M NaF) were attributed to the negatively charged dithiol/solution interface. More specifically, the interactions between the negatively charged end groups (related to solvation, ion pairing, and repulsion) and the lack of more predominant chain-chain interactions prevent the shorter dithiols (i.e. 1,3-PDT and 1,4-BDT) from forming monolayers with few defects. If the charge on the unbound sulfur was the only factor influencing the capacitance measurements, a more significant decrease would have been expected upon protonation. The small Van der Waals interactions between alkane chains results in monolayers having defects when deposited from either electrolyte.

The capacitance of the medium chain length dithiols (1,6-HDT and 1,8-ODT) decreases by a factor of two in 0.5 M KOH versus 0.1 M NaF. The capacity for 1,6-HDT in NaF compares well with the reported value of  $2.5 - 3.5 \mu\text{F cm}^{-2}$  for a 1,6-HDT and

hexanethiol monolayer deposited from organic solution through chemical incubation [7]. This implies that the chain-chain interactions are adequate in forming monolayers with fewer defects, and that the larger capacitances measured in 0.5 M KOH for 1,6-HDT and 1,8-ODT are caused mostly by the effect of the thiolate end groups. There is a sharp decrease in the capacitance (in 0.5 M KOH) through addition of an extra methylene unit from 1,8-ODT to 1,9-NDT. Therefore, 1,9-NDT was excluded from the linear regression in the plot of Figure 5.8. However, there is little effect (if any) on the charge of the thiol end groups on the assembly of the 1,9-NDT film. The Van der Waals attractions are important and the presence of a negatively charged sulfur does not influence the assembly of 1,9-NDT from either electrolyte.

The above discussion illustrates the difficulty in separating the contribution of the various factors influencing dithiol monolayer formation. Although a relative dielectric constant  $\epsilon_r$  was calculated from Figures 5.8 (0.5 M KOH) and 5.9 (0.1 M NaF), the difference in the  $\epsilon_r$  values cannot directly be ascribed to the change in charge on the unreacted sulfur atoms. It is for this reason that the total capacitance was not separated into individual capacitances, as was done in previous studies [24,27]. The linear dependence of the inverse capacitance as a function of dithiol length (excluding 1,2-EDT) in Figure 5.9, and the  $\epsilon_r = 2.1(\pm 0.1)$  to  $1.8(\pm 0.1)$  confirm that the protonated monolayer assemblies behave as a homogeneous dielectric medium. Qualitatively, it can be inferred that the ensemble of densely packed and solvated  $S^-$  groups could create defects.

#### 5.4.2 Bilayer Formation

All of the dithiol monolayers (peak A) were found to react with dithiolates in solution upon oxidation (peak B and C). This is supported by the various monolayer transfer

experiments, as well as the decrease in capacitance upon scanning towards more positive potentials. There was no evidence of a second oxidative peak when electrodeposited from 0.1 M NaF. The dimer formation in 0.5 M KOH is described by the following expression, which was discussed in sections 3.4.2 and 4.4.2 [1,2]:



The short chain alkanedithiols were more reactive than the longer chains, both in alkaline and neutral electrolytic solutions. They dimerized in solution and at the surface in 0.5 M KOH. There was some hint of dimer formation in 0.1 M NaF, which was attributed to a solution process since there was no major change in the capacitance measured directly after monolayer formation (peak A) or after scanning to  $-0.20$  V (Figure 5.7a). This increased reactivity at the surface (specifically the multilayer formation of 1,2-EDT in 0.5 M KOH) can be explained by the proximity of the unreacted thiolate to the gold surface. In the same respect, the solution process is promoted for the shorter chain dithiols since the dithiolates can approach the surface more closely and thus be activated (i.e. oxidized). The number of multilayers of 1,2-EDT was not quantified since the deposition occurred inhomogeneously.

The effect of chain length on dimerization is also demonstrated in the shift of the peak current potential of B or C to more positive values as the dithiol length increases (Figure 5.3). The farther away the unreacted thiolate group is from the surface, the more difficult it is for dimer formation to occur. A more subtle odd-even effect [34] is also observed in the data plotted in Figure 5.3. The odd-numbered carbon data points are above the regression line, whereas those corresponding to even-numbered carbon dithiols lie below

it. This implies that nucleophilic attack of the thiolate end group at the organic/solution interface occurs more readily (i.e. easily) for dithiols having an even number of carbons. Furthermore, this suggests that the unreacted thiolate end group of the monolayer is more accessible in the case of the even-numbered dithiols than the odd-numbered dithiols. These results further support the conclusions presented in section 4.5, whereby we suggested that bilayer formation depends on the accessibility and solvation of the adsorbed activated thiolate. Such an odd-even effect has been reported for alkanethiol monolayers from IR spectra and contact angle measurements [34].

The above chain-length dependence is also reflected in the monolayer transfer experiments into a 1 mM hexanethiol solution. A well-resolved peak was observed upon reactivity of the monolayer with hexanethiol for the short chain dithiols (Figure 5.4a). No complete peak was observed for the medium and long chain dithiols (Figure 5.4b).

The capacitance decreases even more so upon bilayer formation in 0.5 M KOH, than the decrease observed upon protonation (especially for the short chain dithiols). This confirms that the decrease is as a result of an increase in film thickness, and not simply dimerization between adsorbates. If the latter were the case, a decrease comparable to the one observed in 0.1 M NaF would have been expected. A relative dielectric constant of  $2.1(\pm 0.1)$  to  $1.8(\pm 0.1)$  was calculated from Figure 5.10. Again, this suggests that the inverse of the capacitance of the film scales with its thickness.

## 5.5 Summary

All of the alkanedithiols were found to oxidatively adsorb to the gold surface with one sulfur upon monolayer formation (excluding 1,2-EDT). The short chain dithiols formed monolayers containing more defects than the longer chains. Scanning towards more positive



potentials resulted in oxidation of the unreacted thiolate end groups and formation of a second layer. Significant multilayer formation for 1,2-EDT was observed. In addition, dimerization in solution occurred for all of the short chain alkanedithiols (1,2-EDT, 1,3-PDT, and 1,4-BDT). The ease of dimer formation decreased with increasing chain length. Our results suggest that the negatively charged thiolate groups and intermolecular interactions are influential in the packing of alkanedithiol films. Finally, we have demonstrated that the electrodeposition of both conjugated and fully saturated dithiols is possible. This could lead to the development of mixed dithiol films, which is discussed in Chapter 6.

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## Chapter 6: Rigid versus Flexible: A Comparison of 1,4-BDMT and 1,6-HDT.

### Electroformation of Mixed-Bilayer Films.

#### 6.1 Introduction

Evidence of bilayer formation for both 1,4-BDMT and 1,6-HDT has been presented in Chapters 3 and 5 respectively. Here, we compare the electrodeposition mechanism of monolayers and subsequent bilayers of rigid (1,4-BDMT) versus flexible (1,6-HDT) dithiols onto gold. The different molecular frameworks might shed more light on the interactions involved in assembling the dithiol films. For instance, the size of the dithiol might affect monolayer formation. Specifically, packing rectangular (1,4-BDMT) versus cylindrical (1,6-HDT) shaped dithiols could require different deposition conditions. In addition to Van der Waals interactions, the aromatic dithiol has electrostatic interactions (i.e.  $\pi$ - $\pi$  interactions). The aromaticity could also influence the dithiol's conducting behavior. Despite these structural differences, the separation between the sulfurs in both molecules is quite similar. The distance was calculated with *Gaussian*<sup>®</sup>, having a value of 8.4 Å in 1,4-BDMT and 9.2 Å in 1,6-HDT.

The effects of the molecular structure on the assembly can also be probed by varying the deposition time. The potential scan rate dependence of the oxidative deposition of both 1,4-BDMT and 1,6-HDT was used to provide qualitative information on their adsorption processes [1, p213]. In these experiments, cyclic voltammograms are cycled at various potential sweep rates, at least over three decades (i.e. over a range of 1 – 1000 mV s<sup>-1</sup>). The oxidative peak-current is then plotted as a function of the (scan rate)<sup>n</sup>. Depending on the value of n, we can suggest a possible model for the deposition process. For n = 1, the deposition is known to follow a Langmuir model [1, p523]. For n = 1/2 [1, p218], a

diffusion-limited process predominates, while for  $n = 3/5$  a nucleation and growth model dictates the adsorption process [2].

The nucleation and growth model has been used previously to describe the electrodeposition and electrodesorption process of alkanethiolate monolayers [3-5]. It occurs when adsorbates have stabilizing interactions between them. This model suggests that the oxidative deposition begins at some defect sites on the metal surface called nucleation centers. The activation energy,  $\Delta G^\ddagger$ , required for the formation of these nucleation centers and subsequent growth are dependent on the applied overpotential (section 2.2.2). The rate of growth  $k_{N-G}$  in the nucleation and growth model is given by the following expression:

$$k_{N-G} = A_{N-G} \exp(-\Delta G^\ddagger/RT) \quad (6.1)$$

where  $A_{N-G}$  is a pre-exponential factor,  $R$  is the gas constant, and  $T$  is the absolute temperature. There are two limiting cases in the nucleation and growth model, instantaneous nucleation and progressive nucleation. The former of the two is characterized by formation of all nuclei at the beginning, followed by rapid growth only from these sites. In chronoamperometric experiments the current transient is described by the following equation:

$$I/I_m = t/t_m \exp[-(t^2 - t_m^2)/2t_m^2], \quad (6.2)$$

Where  $I$  is the current at time  $t$ , and  $I_m$  is the maximum current that occurs at time  $t_m$ . The latter case corresponds to similar rates of creation of nucleation centers and growth and is represented by the following equation:

$$I/I_m = t^2/t_m^2 \exp[-(t^3 - t_m^3)/3t_m^3], \quad (6.3)$$

In cyclic voltammetry measurements, both instantaneous and progressive nucleation and growth have the same dependence on the scan rate [2]. The Langmuir model is based on

the assumption that every adsorption site is equivalent and that the adsorption is occurring randomly. If the adsorption process were diffusion-limited, the rate of the reaction is governed by the rate at which the molecules diffuse to the surface. We are confident that the oxidative deposition of our dithiols is not driven by diffusion alone, even though the bulk dithiol concentration is low. This is explained by the hanging meniscus method used in their electrodeposition. The low solubility of the dithiols results in an accumulation of molecules at the electrolyte solution's surface, analogous to a Langmuir-Blodgett film.

An alternate approach to varying the deposition time is through holding the potential. It has been reported that monolayer formation of thiols onto gold occurs in two steps. The first step involves rapid adsorption [3,4,6], whereas the second step involves the slower reorganization of the alkane chains to maximize the Van der Waals interactions [3,4,6]. This has also been demonstrated in a recent study on the oxidative deposition of alkanethiolates on gold, whereby the reorganization is a slow, potential independent process [3]. In other words, longer deposition times allow this second step to occur and a more homogeneous film with fewer defects is obtained. This approach will be applied to dithiol bilayer formation.

Establishing the conditions to form a compact monolayer and bilayer of dithiols, as well as better understanding the interactions involved in their formation are key to the development of a device. Depositing mixed bilayers of, e.g. a monolayer of a conducting dithiol reacted with an insulating dithiol (or in the reverse order) could display switching characteristics. That is, one mixed bilayer may promote electron conductivity more readily than the other. Here, we test the efficiency of our electrodeposition scheme to see if it can be used in making mixed-bilayer films involving 1,4-BDMT and 1,6-HDT.

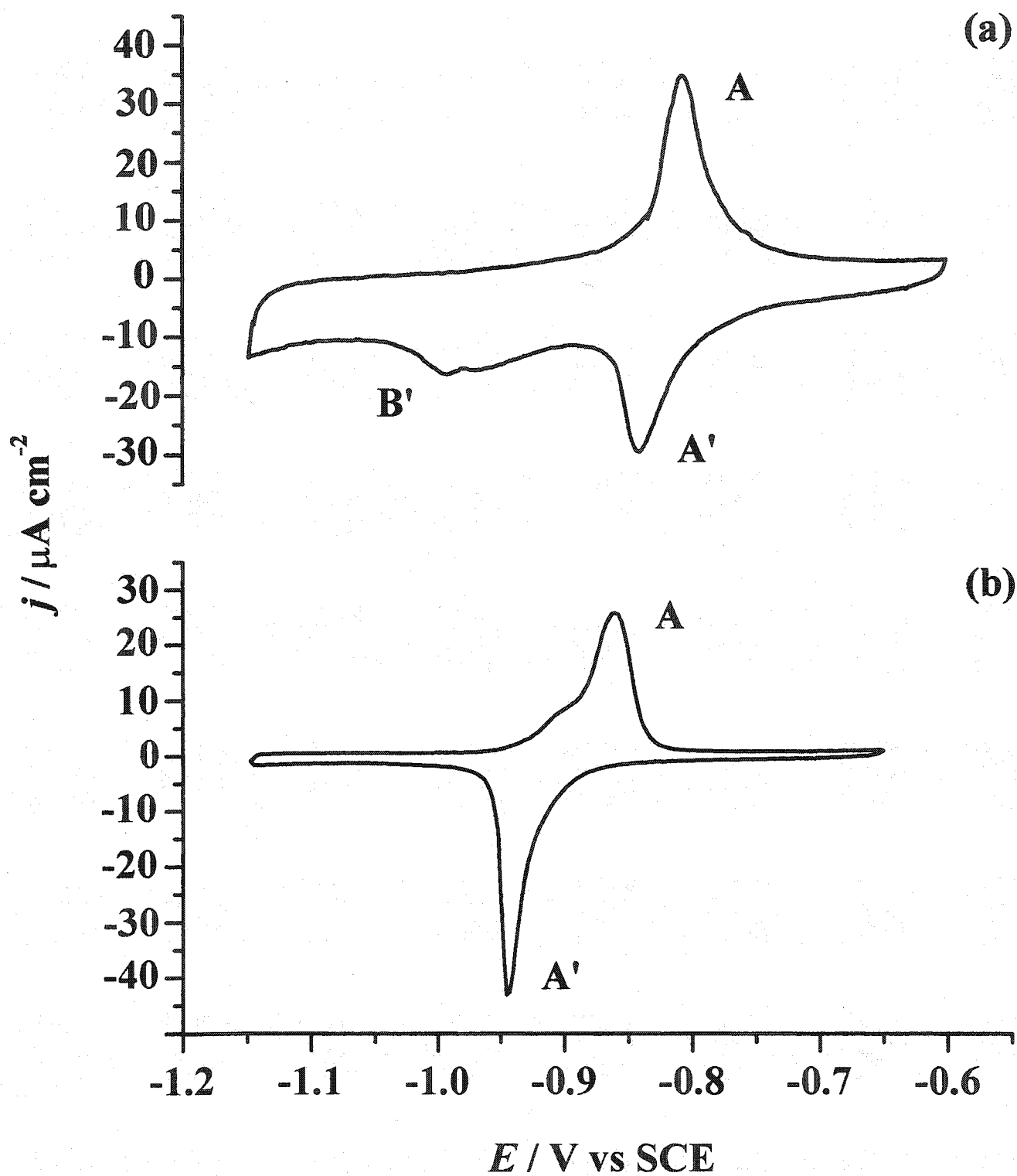
## **6.2 Oxidative Deposition of Bilayers of 1,4-BDMT and 1,6-HDT**

The oxidative deposition of a monolayer of 1,4-BDMT and 1,6-HDT from 0.5 M KOH is presented in Figure 6.1. The peak current is located at  $-0.81$  for 1,4-BDMT and  $-0.86$  for 1,6-HDT. The oxidative current is larger over the entire potential range for the aromatic dithiol. A surface concentration of  $7.5(\pm 0.4) \times 10^{-10} \text{ mol cm}^{-2}$  for 1,4-BDMT and  $6.3(\pm 0.4) \times 10^{-10} \text{ mol cm}^{-2}$  for 1,6-HDT was calculated from the corresponding charges of  $73 \pm 4 \text{ } \mu\text{C cm}^{-2}$  and  $61 \pm 4 \text{ } \mu\text{C cm}^{-2}$ . The asymmetric shape of the oxidative peak A for 1,6-HDT is similar to the electrodeposition of a typical alkanethiol [3]. On the cathodic scan, there are two reductive peaks for 1,4-BDMT, and only one for 1,6-HDT. Peak A' was attributed to the reduction of a monolayer and B' to the reduction of a bilayer in section 3.2.1. The position of A' is approximately 110 mV more negative for 1,6-HDT. This suggests that the electrodeposited 1,6-HDT monolayer is a better ion blocking film than that of 1,4-BDMT. The 1,6-HDT film is deposited via a more homogeneous process, and this is inferred by the single reductive peak.

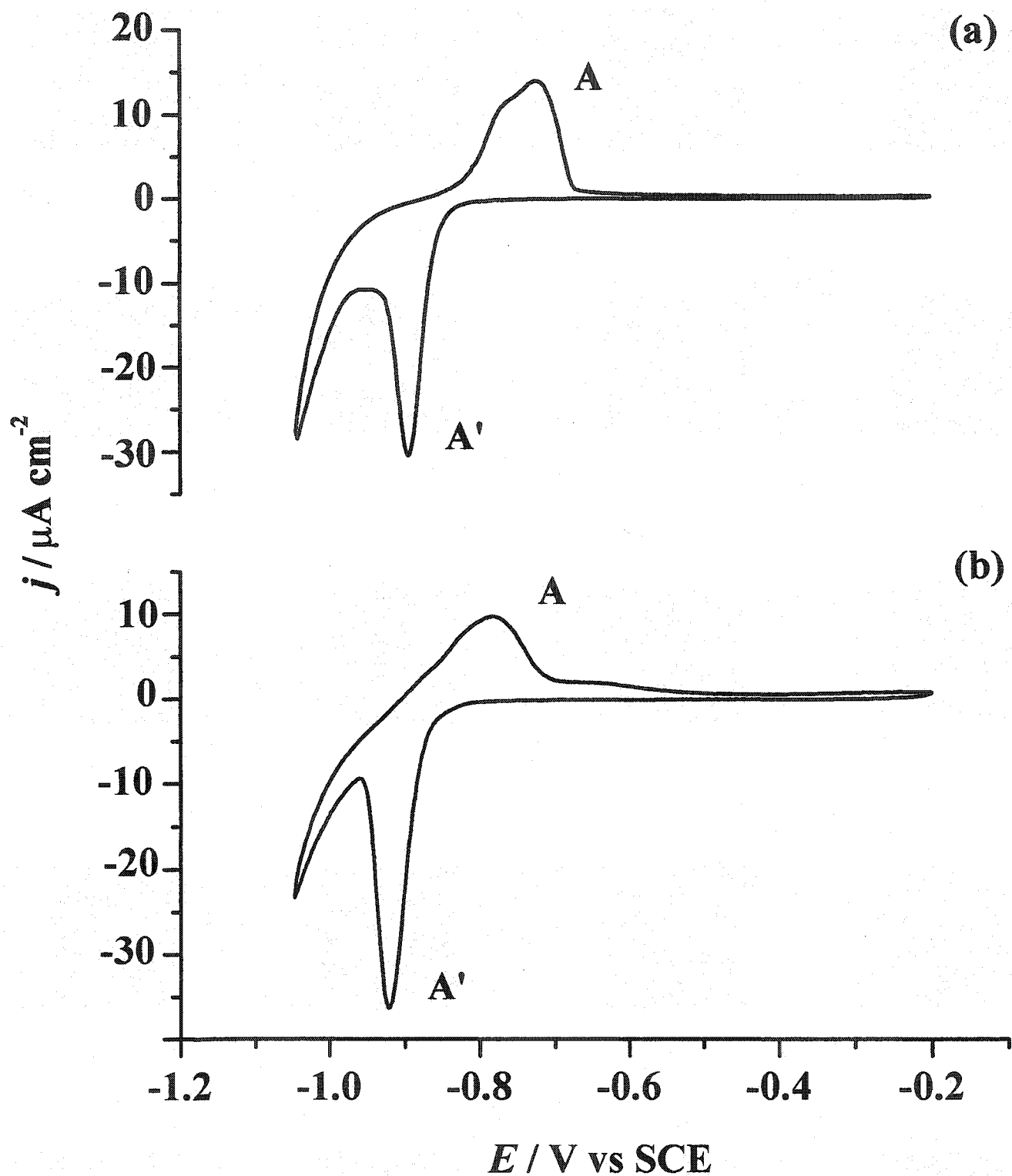
The cyclic voltammograms of the two dithiols deposited from neutral electrolyte (0.1 M NaF) are shown in Figure 6.2. Both oxidative peaks are broader and located at more positive potentials,  $-0.74 \text{ V}$  for 1,4-BDMT and  $-0.78 \text{ V}$  for 1,6-HDT. However, the charges remain the same, with a value of  $73 \pm 5 \text{ } \mu\text{C cm}^{-2}$  for 1,4-BDMT and  $60 \pm 6 \text{ } \mu\text{C cm}^{-2}$  for 1,6-HDT. On the negative-going scan, there is only one reductive peak A' at  $-0.92 \text{ V}$  for 1,4-BDMT and  $-0.91 \text{ V}$  for 1,6-HDT. They behave more like monofunctional thiols in 0.1 M NaF solution.

Figure 6.3 displays bilayer formation upon extending the anodic limit in 0.5 M KOH. There is always a significant current for 1,4-BDMT, whereas there is a clearer separation between monolayer formation and the onset of bilayer formation for 1,6-HDT. The oxidative

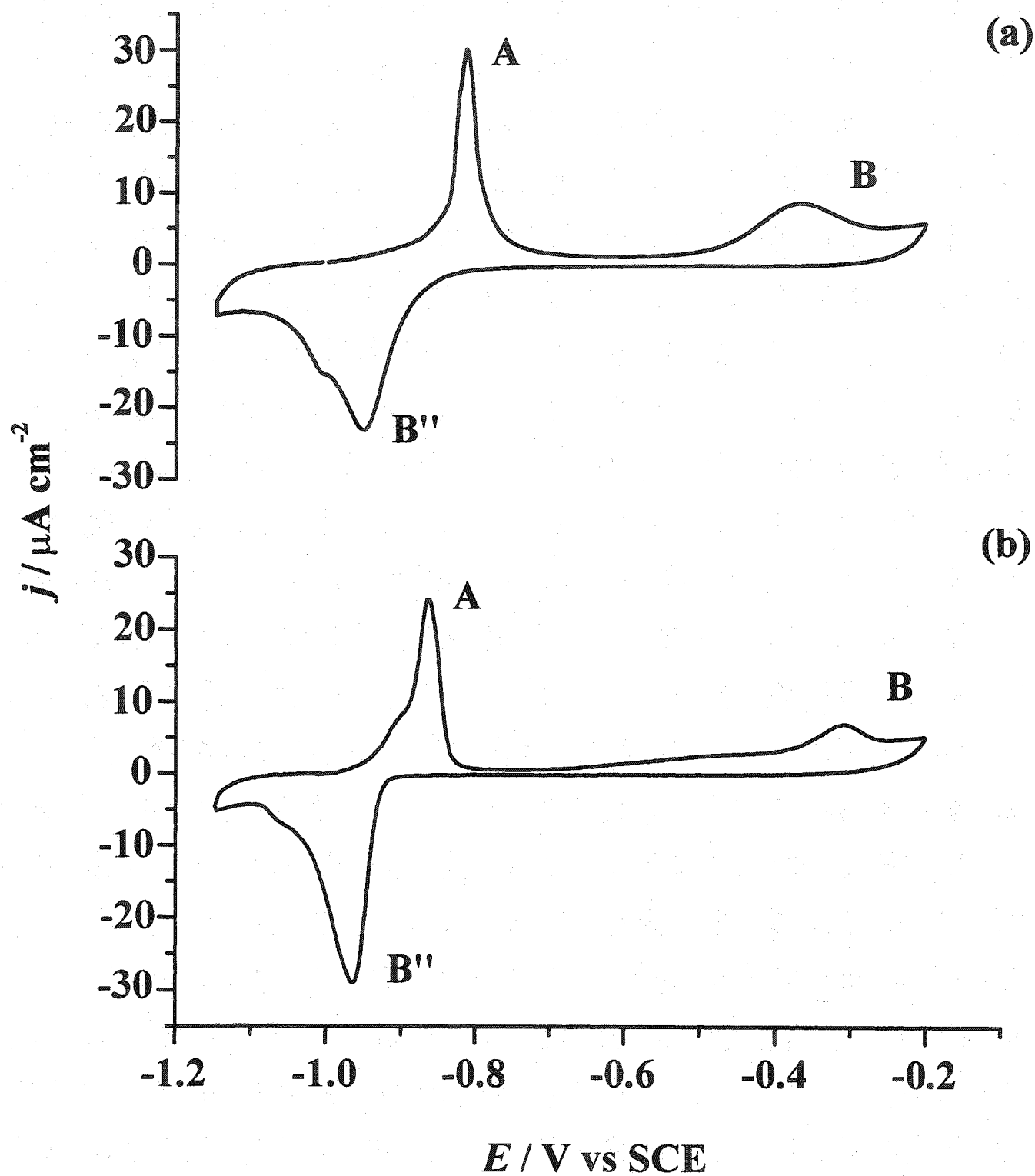




**Figure 6.1:** Cyclic Voltammograms of the oxidative adsorption and reductive desorption of monolayers of (a) 1,4-BDMT and (b) 1,6-HDT from 0.5 M KOH at the Au(111) surface. Potential scan rate: 20 mV s<sup>-1</sup>.



**Figure 6.2:** Cyclic Voltammograms of the oxidative adsorption and reductive desorption of monolayers of (a) 1,4-BDMT and (b) 1,6-HDT from 0.1 M NaF at the Au(111) surface. Potential scan rate: 20 mV s<sup>-1</sup>.



**Figure 6.3:** Cyclic Voltammograms of the oxidative adsorption and reductive desorption of bilayers of (a) 1,4- BDMT and (b) 1,6- HDT from 0.5 M KOH at the Au(111) surface. Potential scan rate: 20 mV s<sup>-1</sup>.

peak position of B is at  $-0.36$  V for 1,4-BDMT and  $-0.31$  V for 1,6-HDT. Similar potential step experiments were performed on 1,6-HDT, as previously described for 1,4-BDMT in section 3.2.2. The results are plotted in Figure 6.4, displaying charge density as a function of time. The charges obtained for A are similar to those from the corresponding voltammetry, with a value of  $70 \pm 7 \mu\text{C cm}^{-2}$  for 1,4-BDMT and  $66 \pm 4 \mu\text{C cm}^{-2}$  for 1,6-HDT. The charges for B are  $133 \pm 8 \mu\text{C cm}^{-2}$  and  $125 \pm 10 \mu\text{C cm}^{-2}$  for 1,4-BDMT and 1,6-HDT respectively. The longer time scale required for the charge of B to plateau reflects that bilayer growth is a slower process than monolayer formation (A). Both compounds have the same charge ratio  $Q_B/Q_A$  of  $1.9 \pm 0.2$ . On the reductive scan in Figure 6.3 there is a peak B'' at about the same potential for both dithiols,  $-0.96$  V for 1,4-BDMT and  $-0.95$  V for 1,6-HDT. The shape of peak B'' is broader for 1,4-BDMT than for 1,6-HDT.

### 6.3 Differential Capacitance Measurements

The differential capacitance was measured after monolayer deposition from 0.5 M KOH. A capacity of  $10.4 \pm 0.8 \mu\text{F cm}^{-2}$  for 1,4-BDMT and  $6.4 \pm 0.6 \mu\text{F cm}^{-2}$  for 1,6-HDT was obtained. As described previously (section 2.3.3), a higher capacity was expected for the dithiols deposited from basic solution than from 0.1 M NaF. However, it is surprising that the capacities are different, since both dithiols have a similar molecular length and monolayer coverage. The discrepancy must either reflect on the conducting ability of the aromatic ring (higher  $\epsilon_r$ ) versus the saturated alkane chain or on the ion blocking properties (i.e. homogeneity and defects) of the monolayers.

Capacitance measurements were also performed on monolayers deposited from 0.1 M NaF. The capacities decreased to similar values of  $3.8 \pm 0.3 \mu\text{F cm}^{-2}$  for 1,4-BDMT and  $3.3 \pm 0.3 \mu\text{F cm}^{-2}$  for 1,6-HDT. This implies that from neutral solution, better ion blocking

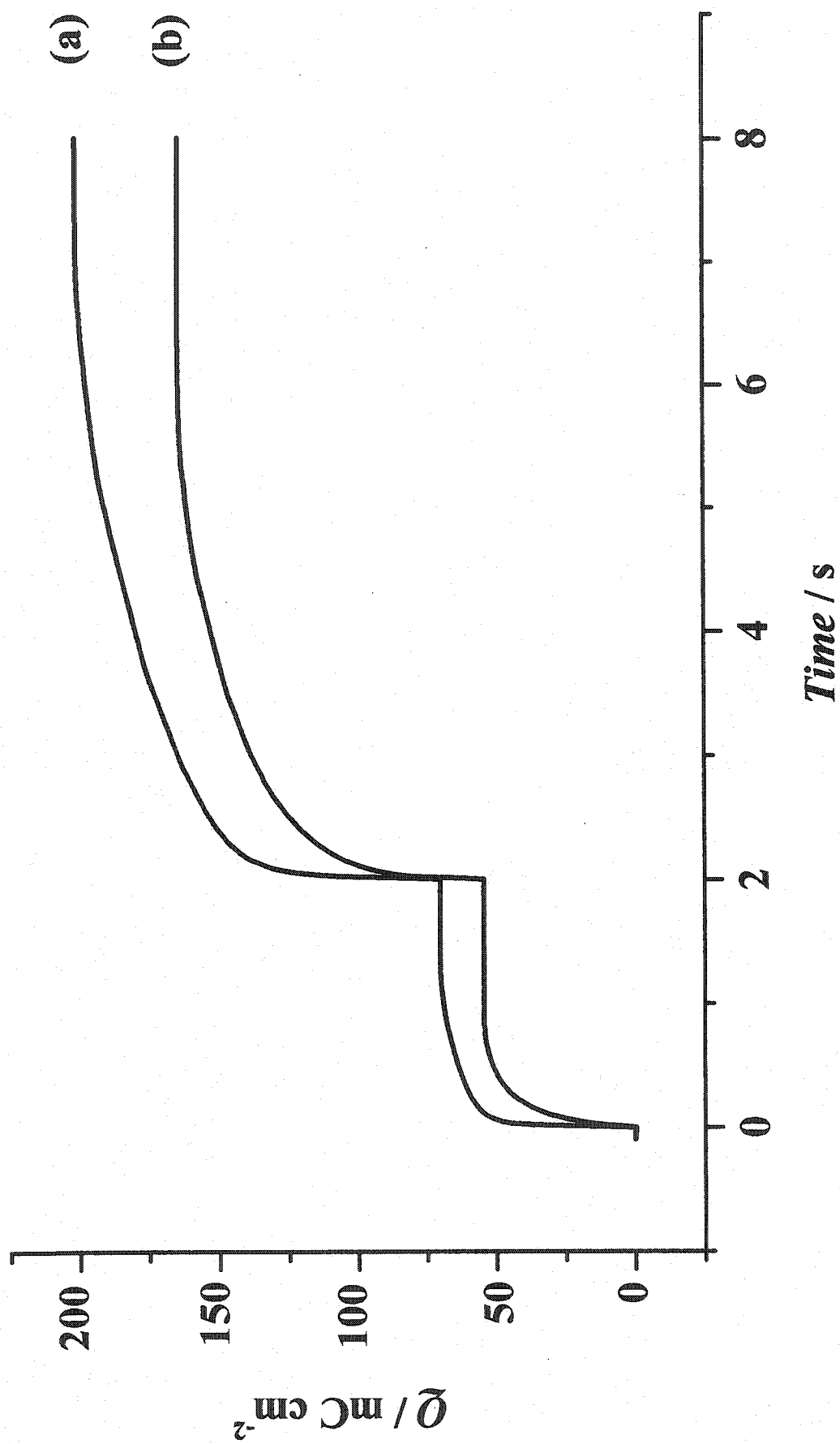


Figure 6.4: Chronocoulometric measurements of (a) 1,4-BDMT and (b) 1,6-HDT deposited on Au(111) from 0.5 M KOH. See text for details.

monolayers are formed. In addition, this suggests that the dielectric constant of both organic films is essentially the same. This is supported by the fact that the dielectric constant of polyethylene (a conjugated molecule) [7] is comparable to the one reported for alkanethiol films (fully saturated compounds) [8-12]. The higher capacitance for 1,4-BDMT in 0.5 M KOH indicates a monolayer having more defects than that of 1,6-HDT. This corresponds well with the voltammetric results and may be explained by the flexibility of the alkyl chains. 1,4-BDMT is limited by its rigid frame, and likely requires more time to orient in such a way as to maximize the intermolecular interactions and to decrease the repulsion of the S<sup>-</sup> groups.

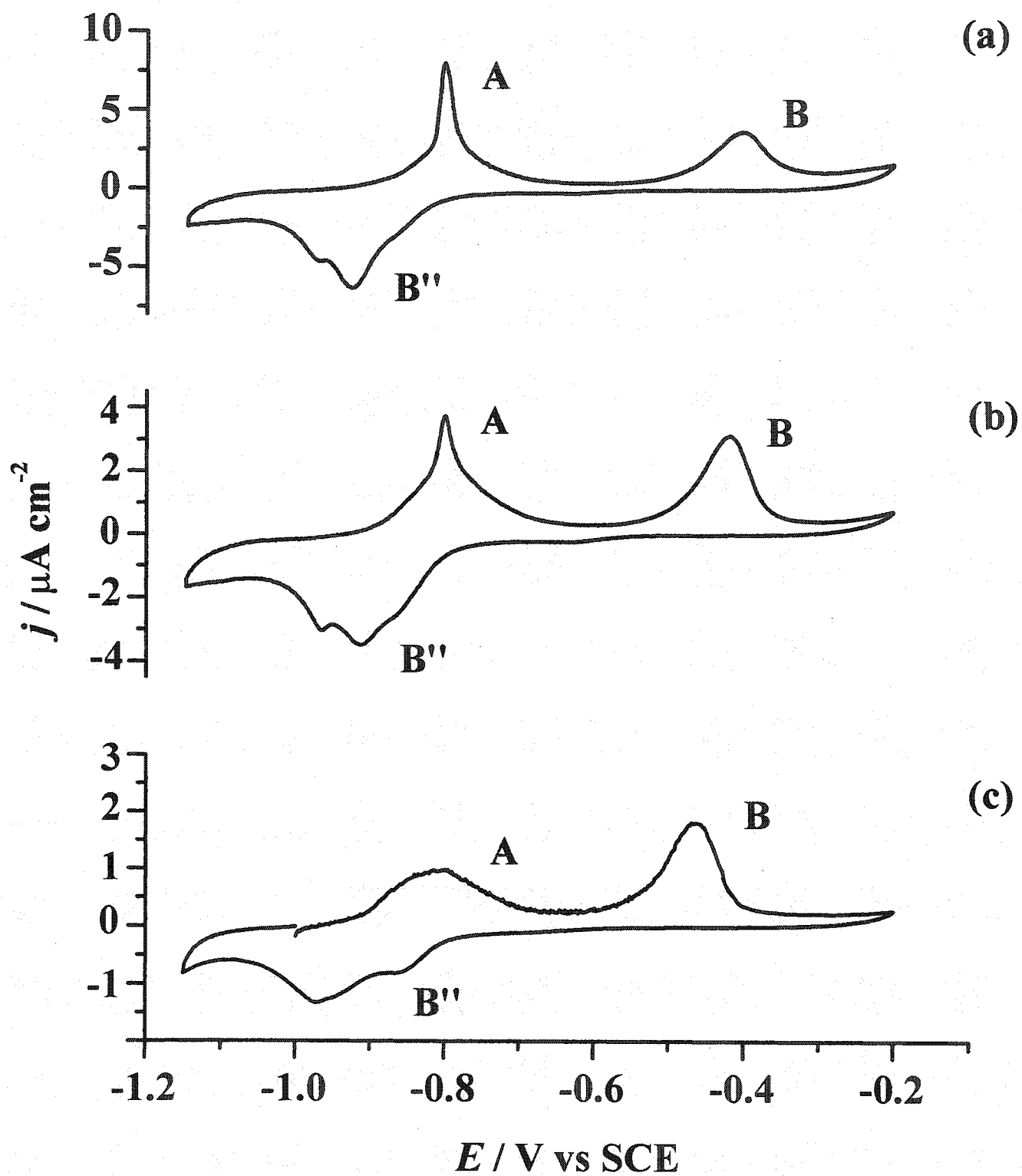
The capacitance was also measured after bilayer formation, and a value of  $4.6 \pm 0.5$   $\mu\text{F cm}^{-2}$  for 1,4-BDMT and  $3.0 \pm 0.3$   $\mu\text{F cm}^{-2}$  for 1,6-HDT was obtained. This decrease in capacity by approximately a factor of two for both dithiols was ascribed to an increase in film thickness (sections 3.2.2 and 5.3). The longer the chain length, the stronger the intermolecular interactions [9,13,14]. The decrease is comparable (within error) to the decrease in capacitance upon protonation. This illustrates the importance of the negatively charged end group and its effect on orienting the organic films (section 4.4.2).

## **6.4 Effect of Deposition Time on Bilayer Formation**

### **6.4.1 Scan Rate Dependence**

#### **6.4.1a Oxidative Deposition of Bilayers of 1,4-BDMT**

Figure 6.5 presents the voltammetry of bilayer formation for 1,4-BDMT at sweep rates of (a) 5, (b) 3, and (c) 1  $\text{mV s}^{-1}$ . Voltammograms taken at faster scan rates were similar to the one presented for bilayer formation at 20  $\text{mV s}^{-1}$  in Figure 6.1a. However, the shape of peak A (monolayer) changed significantly upon decreasing the scan rate to values below 5  $\text{mV s}^{-1}$ . At 5  $\text{mV s}^{-1}$ , there is a hint of tailing on either side of peak A, which becomes even



**Figure 6.5:** Cyclic voltammograms of the oxidative deposition and reductive desorption of 1,4-BDMT onto Au(111) at potential scan rates of (a) 5, (b) 3, and (c)  $1 \text{ mV s}^{-1}$  from 0.5 M KOH.

more prominent at  $3 \text{ mV s}^{-1}$ . Although A broadens and is asymmetric, it still maintains a particular sharpness near the peak-current potential. At  $1 \text{ mV s}^{-1}$ , peak A completely broadens and has decreased significantly in peak current. Even though the shape changes, the position of peak A remains essentially the same. There is a total change in peak potential of only about 50 mV over the entire potential scan range (i.e. three decades). Overall, this is indicative of a relatively fast deposition process. In contrast, peak B sharpens and shifts to more negative potentials upon decreasing the scan rate. The shift in peak potential for B is much more significant and measures about 350 mV over the entire scan range. Even upon decreasing the scan rate from 20 to  $1 \text{ mV s}^{-1}$ , there is a shift in peak B towards more negative potentials by 120 mV. This implies that bilayer formation is a slower process than monolayer formation. This was also observed in the chronocoulometry (Figure 6.4).

The capacitance was measured in pure 0.5 M KOH after electrodeposition of the monolayer and bilayer at  $1 \text{ mV s}^{-1}$ . The capacity of the monolayer deposited at  $1 \text{ mV s}^{-1}$  is approximately double that obtained at  $20 \text{ mV s}^{-1}$ , measuring  $19.4 \pm 1.2$  and  $10.4 \pm 0.8 \mu\text{F cm}^{-2}$  respectively.

Surprisingly, the rate of monolayer deposition does not compromise the capacity of the bilayer. The capacitance results are (within error) the same after depositing both peaks A and B at 1 and  $20 \text{ mV s}^{-1}$ . The capacity obtained at  $1 \text{ mV s}^{-1}$  measured  $5.1 \pm 0.6 \mu\text{F cm}^{-2}$ , while the value at  $20 \text{ mV s}^{-1}$  measured  $4.6 \pm 0.5 \mu\text{F cm}^{-2}$ . In addition, the charge ratio  $Q_B/Q_A$  remains the same at both scan rates.

Recalling the discussion on the monolayers of the BDMT isomers (section 4.2.1), the broad peak A and the large capacity at  $1 \text{ mV s}^{-1}$  can be attributed to a less homogeneous deposition process than at  $20 \text{ mV s}^{-1}$ . Moreover, a previous study on chemisorbed ferrocene-



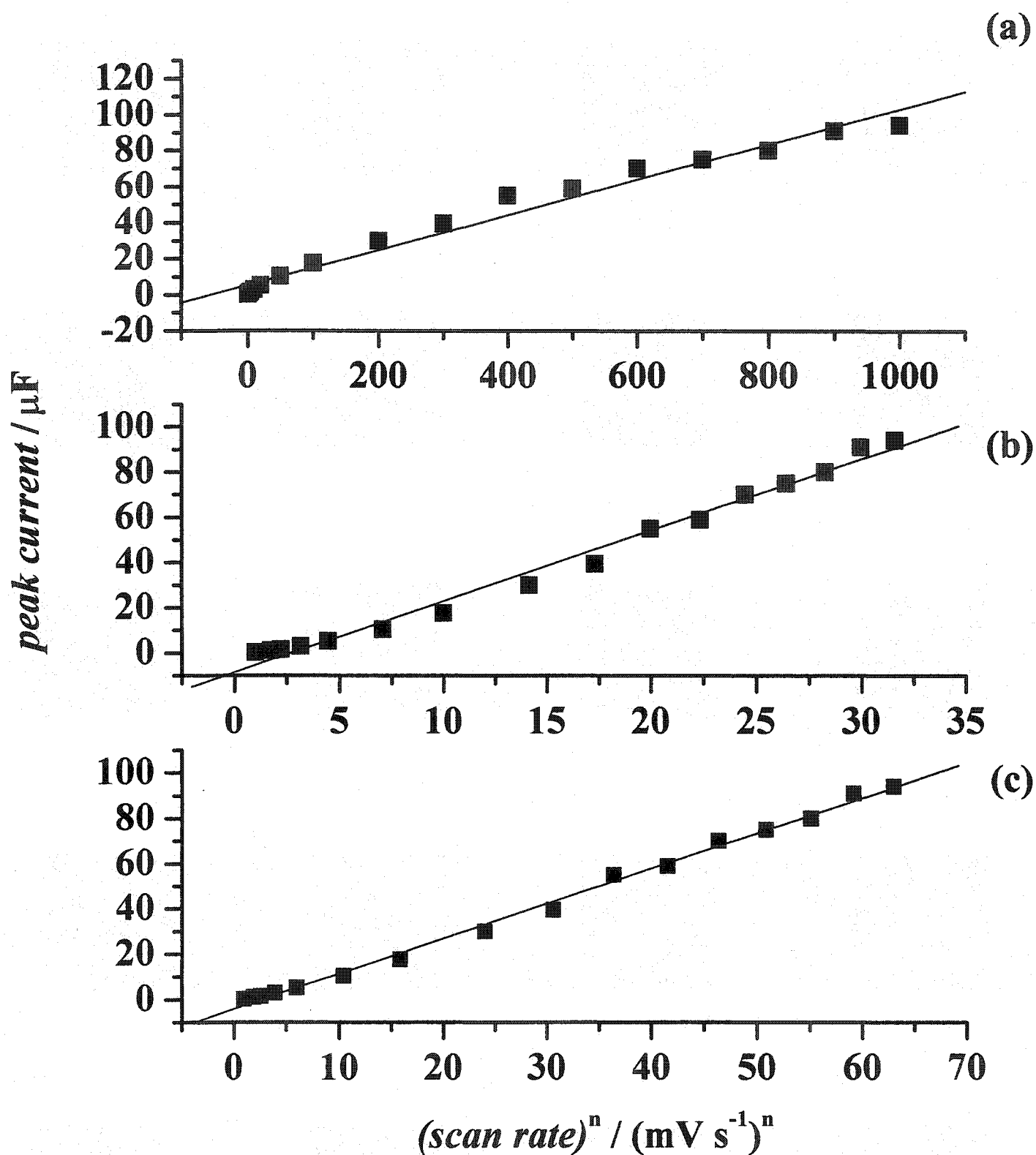
terminated alkanethiols of chain lengths  $C_8$  and  $C_{11}$  reported broad, asymmetric peaks with a narrowing of the I-E curves (i.e. cyclic voltammograms) near the peak-current [15]. It was suggested that the sharpness was due to the presence of attractive interactions between neighboring groups within a portion of both layers. The changes in 1,4-BDMT monolayer peak shape may then be attributed to more repulsive interactions experienced by neighboring groups at slower deposition rates.

The rate at which the monolayer is deposited plays an important role in its formation. The effect of adsorption rate in the comparison of chemical incubation versus electrodeposition was described in sections 3.4.1 and 4.4.1. At slower deposition rates, it is possible that the thiolate end groups have more time to reorient via both sulfurs towards the gold surface. The charge of A is (within error) the same at both 1 and 20  $\text{mV s}^{-1}$ , having a value for  $Q_A$  of  $82 \pm 9$  and  $73 \pm 4 \mu\text{C cm}^{-2}$  respectively. However, vertical adsorption via a single S-Au bond cannot be inferred from the charge alone (section 3.2.1). It is possible that some of the dithiols adsorb with both sulfurs to the gold electrode at slower deposition rates, and that the deposition process results in a less homogeneous film.

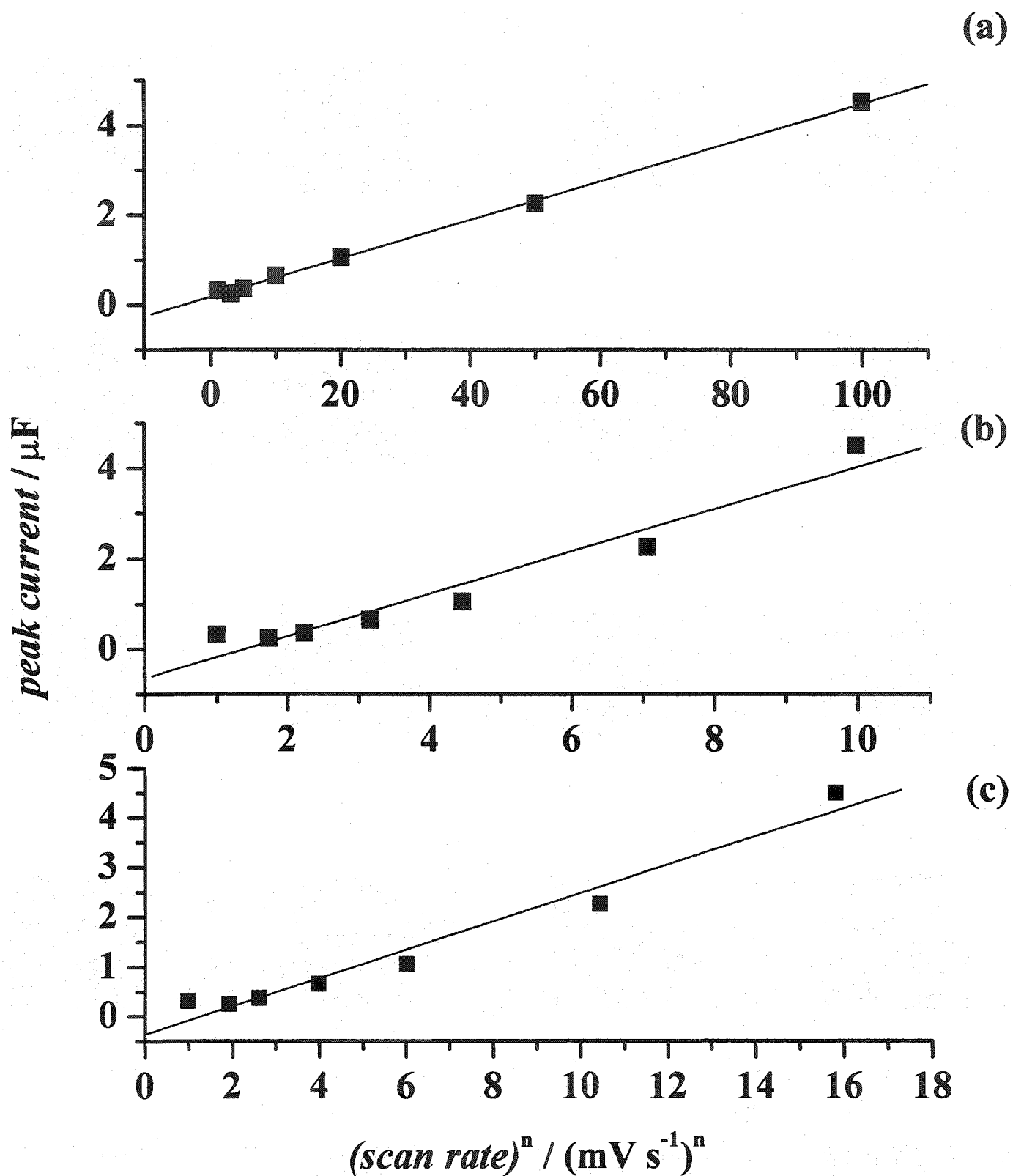
If the monolayer has more defects at slower deposition rates, it is not clear as to how bilayer formation occurs just as readily at both 1 and 20  $\text{mV s}^{-1}$ . A more compatible explanation with the results is discussed here. The large capacitance could result from a highly organized film with a few defects. At longer deposition times, the rigid frame of 1,4-BDMT could organize in such a way as to maximize the interadsorbate interactions. This is supported by the fact that peak B occurs at more negative potentials for deposition at 1  $\text{mV s}^{-1}$ ; the ease of bilayer formation will be dependent on the template for reactivity (i.e. the accessibility of the S<sup>-</sup>).

To identify the type of growth associated with monolayer formation, the peak current was plotted as a function of the (scan rate)<sup>n</sup>, where  $n = 1, 1/2$ , and  $3/5$  in Figure 6.6. The best fit is the one obtained with a (scan rate)<sup>3/5</sup>, which is representative of a nucleation and growth process [2]. This is in accordance with a recent kinetic study on the oxidative deposition of alkanethiolates on gold [3,4]. They reported that the electro-adsorption occurred in two steps: a fast instantaneous nucleation and growth process, followed by slow deposition via a Langmuir process. Since we are confident that at  $20 \text{ mV s}^{-1}$  a compact, vertically aligned monolayer of 1,4-BDMT is electrodeposited (section 3.2.1), we can compare our dithiol system with simple alkanethiols. The latter explanation for the broader peak A at  $1 \text{ mV s}^{-1}$  involved improved interactions between adsorbed BDMT molecules. Given that the nucleation and growth model involves the adsorbates having attractive interactions between them, this is a suitable growth process for 1,4-BDMT monolayer formation.

To identify a growth mechanism for bilayer formation is more challenging. Our template for reactivity is no longer the gold surface, but rather the organic/solution interface of the monolayer. In Figure 6.5, peak B becomes sharper and shifts to more negative potentials as the scan rate is decreased. A total shift of  $-340 \text{ mV}$  occurs upon decreasing the scan rate from  $1000 (-0.15 \text{ V})$  to  $1 (-0.49 \text{ V}) \text{ mV s}^{-1}$ . This electrochemical behavior is typical of a slow deposition process. At scan rates greater than  $100 \text{ mV s}^{-1}$ , peak B is relatively broad and ill-defined. It is therefore difficult to give an exact value for the peak current at faster scan rates, especially since the peak is also located close to the gold oxide formation. Consequently, the peak current is plotted as a function of the (scan rate)<sup>n</sup>, where  $n = 1, 1/2$ , and  $3/5$  in Figure 6.7 only for rates below  $100 \text{ mV s}^{-1}$ . The best fit is obtained when  $n = 1$ , which is representative of a Langmuir deposition process. This is compatible with the



**Figure 6.6:** Peak current as a function of  $(\text{scan rate})^n$  for monolayer formation of 1,4-BDMT on Au(111) from 0.5 M KOH, where (a)  $n = 1$ , (b)  $n = 1/2$ , and (c)  $n = 3/5$ .



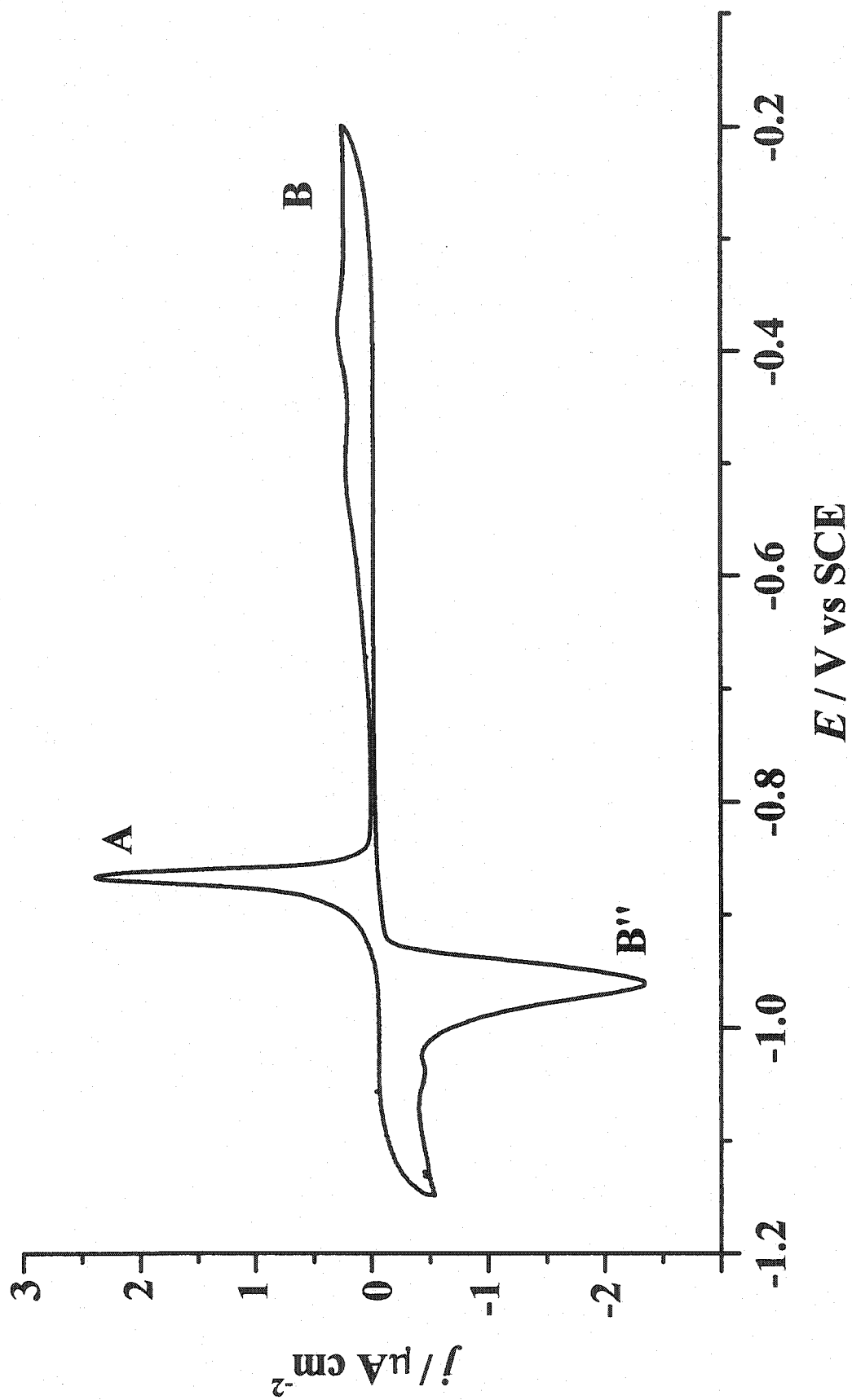
**Figure 6.7:** Peak current as a function of  $(\text{scan rate})^n$  for bilayer formation of 1,4-BDMT on Au(111) from 0.5 M KOH, where (a)  $n = 1$ , (b)  $n = 1/2$ , and (c)  $n = 3/5$ .

bilayer mechanism presented in section 3.4.2, whereby there is a nucleophilic attack of the adsorbed dithiolates in the monolayer by one from solution.

#### 6.4.1b Oxidative Deposition of Bilayers of 1,6-HDT

The scan rate dependence was also performed on bilayer deposition of 1,6-HDT. Figure 6.8 shows the cyclic voltammogram for the oxidative deposition of 1,6-HDT at  $1 \text{ mV s}^{-1}$ . Unlike 1,4-BDMT, there was no significant change in peak A upon decreasing the potential scan rate. Peak A is only slightly sharper at  $1 \text{ mV s}^{-1}$  than at  $20 \text{ mV s}^{-1}$  (Figure 6.1a) and remains at about the same potential ( $-0.87 \text{ V}$  and  $-0.86 \text{ V}$  respectively). There is only a shift of about  $60 \text{ mV}$  over the entire scan range ( $1 - 1000 \text{ mV s}^{-1}$ ). The charge of peak A does not change either, measuring  $60 \pm 6 \mu\text{C cm}^{-2}$  at  $1 \text{ mV s}^{-1}$  and  $61 \pm 4 \mu\text{C cm}^{-2}$  at  $20 \text{ mV s}^{-1}$ . Peak B remains relatively diffuse at all scan rates, with an overall shift of about  $-260 \text{ mV}$  from  $1000$  to  $1 \text{ mV s}^{-1}$ . These results are similar to those observed for 1,4-BDMT.

The capacitance was measured in pure  $0.5 \text{ M KOH}$  upon electrodeposition of the monolayer and bilayer at  $1 \text{ mV s}^{-1}$ . The capacity of the monolayer deposited at  $1 \text{ mV s}^{-1}$  is within error the same as that obtained at  $20 \text{ mV s}^{-1}$ , having values of  $6.9 \pm 0.4$  and  $6.4 \pm 0.6 \mu\text{F cm}^{-2}$  respectively. This is also the case for the capacitance upon bilayer formation, measuring  $2.5 \pm 0.2$  and  $3.0 \pm 0.3 \mu\text{F cm}^{-2}$  respectively. In contrast to 1,4-BDMT, the assembly of the 1,6-HDT films appears to be independent of deposition time. The behavior of 1,6-HDT at  $1 \text{ mV s}^{-1}$  helps to shed some light on the origin of the broader peak A of 1,4-BDMT. If the broadness corresponded to more repulsive interactions between adsorbates, a similar trend should have appeared in the voltammetry of 1,6-HDT. This further supports the fact that the broader A and higher capacity result from a better organized 1,4-BDMT monolayer at slow deposition rates.

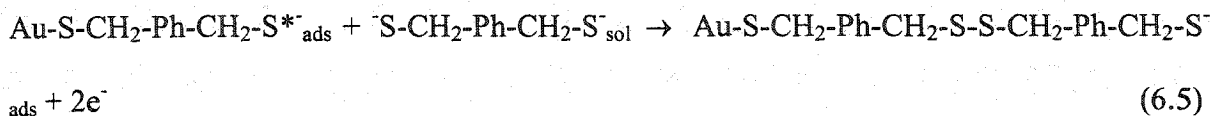
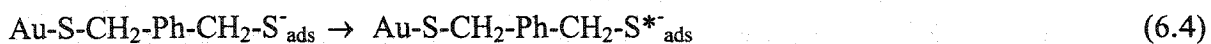


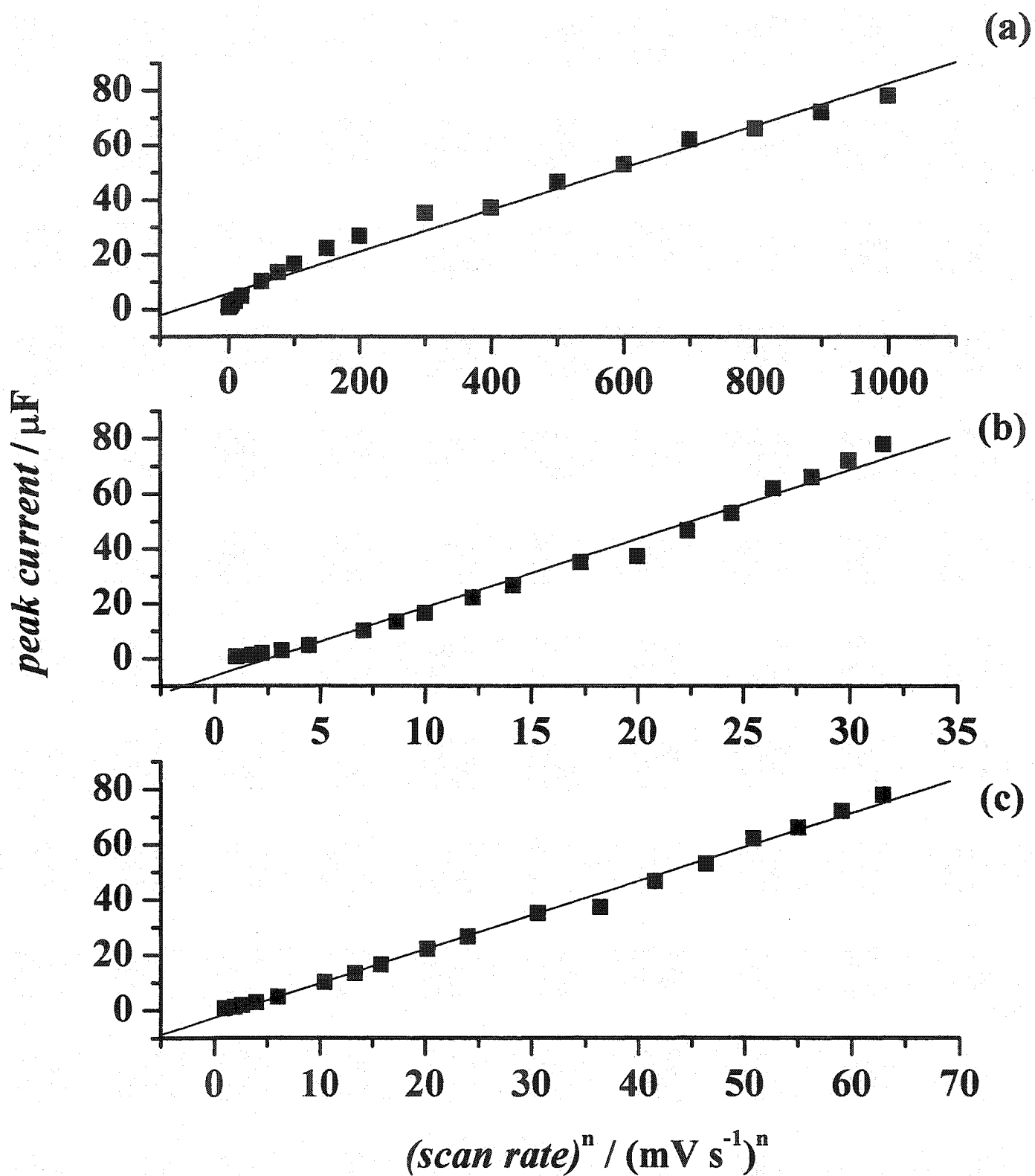
**Figure 6.8:** Cyclic voltammogram of the oxidative deposition of 1,6-HDT onto Au(111) at a potential scan rate of  $1 \text{ mV s}^{-1}$ .

To identify the type of growth associated with monolayer formation (peak A), the peak current was plotted as a function of the (scan rate)<sup>n</sup>, where n = 1, 1/2, and 3/5 in Figure 6.9. The best fit is the one obtained with a (scan rate)<sup>3/5</sup>, which is representative of a nucleation and growth process [2]. Figure 6.10 presents the peak current for B as a function of potential for scan rates ≤ 100 mV s<sup>-1</sup>, for the same reason described for 1,4-BDMT. The best fit is again obtained when n = 1, which is representative of a Langmuir deposition process.

#### 6.4.1c On the Mechanism of the Oxidative Deposition of Bilayers of 1,4-BDMT and 1,6-HDT

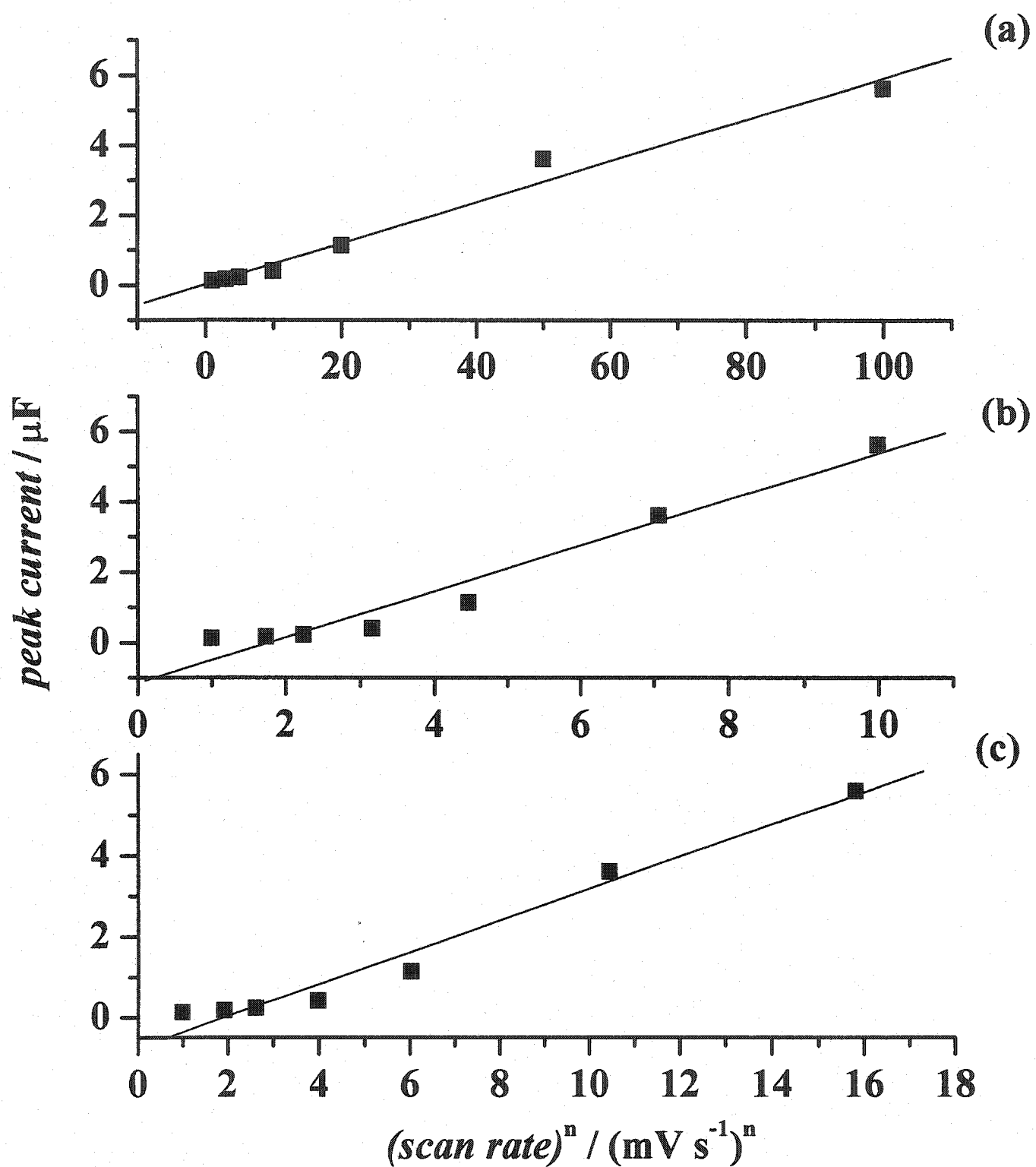
The potential scan rate dependence studies show a similar response by both of the dithiols. Monolayer formation was best described by a nucleation and growth process, while bilayer formation was governed by a Langmuir-like growth. Nucleation and growth is generally characterized by interactions between adsorbates, which fits well with the forces involved in the electrodeposition of rigid and flexible monolayers. The Langmuir growth process for bilayer formation corresponds well with the mechanism proposed in section 3.4.2:





**Figure 6.9:** Peak current as a function of  $(\text{scan rate})^n$  for monolayer formation of 1,6-HDT on Au(111) from 0.5 M KOH, where (a)  $n = 1$ , (b)  $n = 1/2$ , and (c)  $n = 3/5$ .





**Figure 6.10:** Peak current as a function of  $(\text{scan rate})^n$  for bilayer formation of 1,6-HDT on Au(111) from 0.5 M KOH, where (a)  $n = 1$ , (b)  $n = 1/2$ , and (c)  $n = 3/5$ .

The nucleophilic attack of the adsorbed and activated dithiol (equation 6.5) most likely occurs randomly. The interadsorbate interactions do not play an important role in this chemical reaction.

The reaction mechanism of bilayer formation corresponds to an ECE reaction [1, p.430]. E represents an electron transfer at the surface, while C represents a chemical reaction. The following equations describe the ECE process in bilayer formation:



Equation 6.6 represents the oxidative deposition of a monolayer (M) of dithiolates (DT). This is followed by a chemical step, which consists in first activating the thiolate end group of the M. There is then a nucleophilic attack of the activated M by a dithiolate (DT) in solution to form  $B^*$  (equation 6.7). Finally, there is a transfer of two electrons per adsorbate to form bilayer (B) in equation 6.8. It is difficult to identify when the actual transfer of both electrons occurs in the bilayer mechanism, since it is expected to be fast (section 3.4.2).

The resulting S-S dimerization (B) is not electroactive at potentials between  $-0.20$  V and  $-1.15$  V, where the reduction of the S-Au bond (initially formed upon monolayer formation) occurs. The S-S bond in the bilayer was found to be irreversible and compared to the irreversibility of dimerization of cysteine in solution [16] in section 3.4.2.

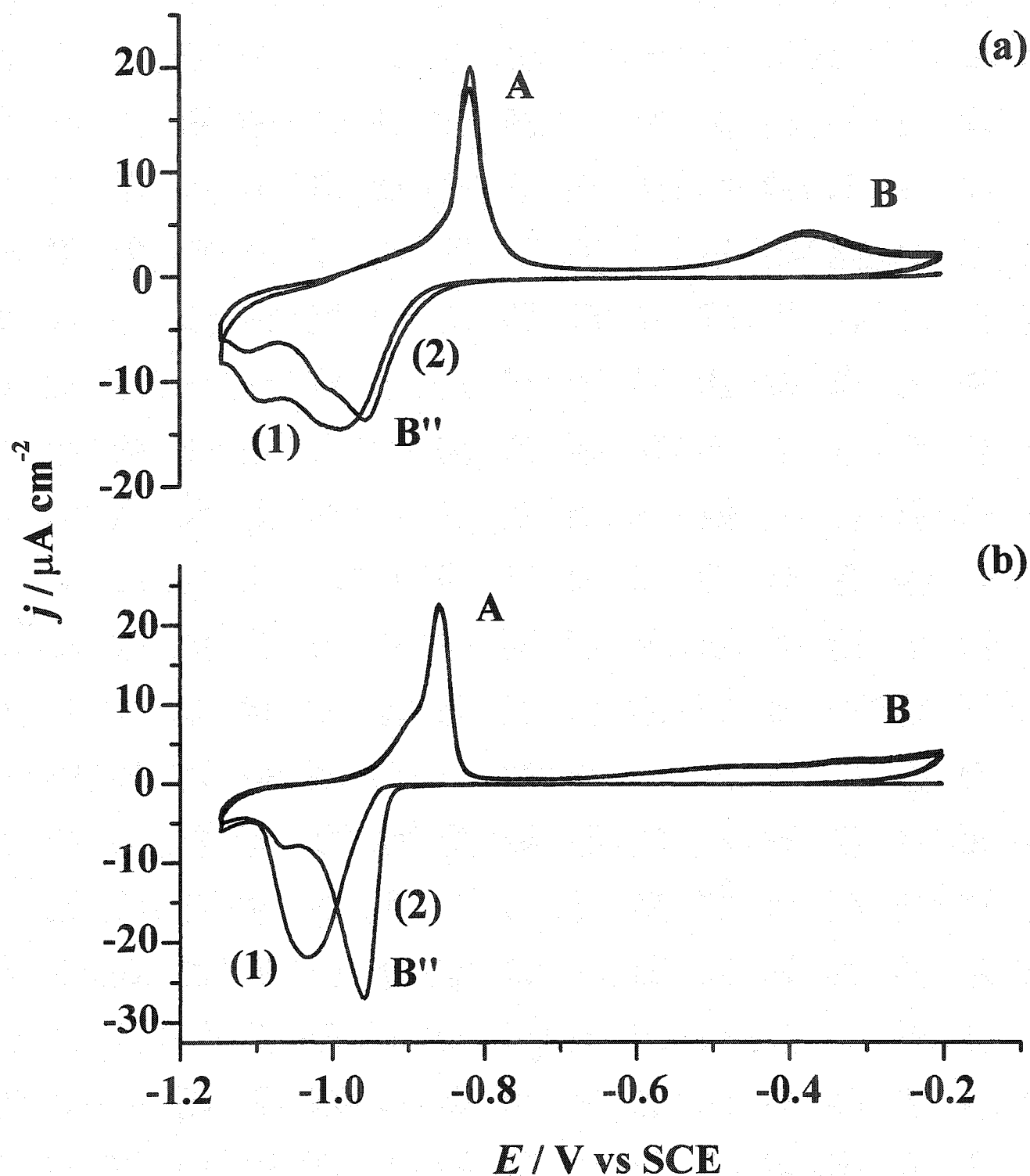
#### 6.4.2 Effect of Holding the Potential

The formation of a 1,4-BDMT monolayer at slow deposition rates suggests that a molecular reorganization occurs, which results in a more organized film with few defects. Given that a similar bilayer was formed upon direct scanning at  $1$  or  $20 \text{ mV s}^{-1}$ , we focus

attention on the effect of longer deposition times on bilayer formation. For the EQCM measurements presented in section 3.2.2, it was established that a complete bilayer could be generated if the potential was held for 10 minutes at  $-0.65$  V. Maintaining a similar holding time, but with a larger driving force (e.g. holding for 10 minutes at  $-0.20$  V) might allow for sufficient time for the molecules in the bilayer to better organize/pack. This experiment is different than scanning at  $1 \text{ mV s}^{-1}$  to form bilayer (between  $-1.00$  to  $-0.20$  V). The unreacted sulfurs will be activated (equations 6.4 and 6.5) during 10 minutes in the former experiment, whereas they will only be activated for about 2.5 minutes at  $1 \text{ mV s}^{-1}$ .

The potential was scanned from  $-1.00$  to  $-0.20$  V and then held at  $-0.20$  V for 10 minutes. The potential was then cycled twice starting at  $-0.20$  to  $-1.15$  V. The resulting cyclic voltammograms are presented in Figure 6.11a and 6.11b for 1,4-BDMT and 1,6-HDT respectively. The first reductive scan represents the reduction of the bilayer formed on holding the potential, whereas the second reductive scan represents bilayer formation made through direct scanning. The charge of  $B''$  on consecutive cycles remains the same for both dithiols, having values of  $69 \pm 6 \mu\text{C cm}^{-2}$  for 1,4-BDMT and  $80 \pm 5 \mu\text{C cm}^{-2}$  for 1,6-HDT. However, the  $B''$  on the first reductive scan is located at slightly more negative peak potentials than the  $B''$  on the second reductive scan. This suggests ion permeation is more difficult after scanning and holding the potential to form bilayer. The film is more uniform and has fewer defects when prepared in this way.

This observation is supported by the capacitance measurements performed after scanning through A and B, followed by holding the potential for 10 minutes at  $-0.20$  V. The capacity of  $4.6 \pm 0.5 \mu\text{F cm}^{-2}$  for 1,4-BDMT obtained through direct scanning decreased to  $1.5 \pm 0.1 \mu\text{F cm}^{-2}$ . A decrease was also observed in the capacitance of 1,6-HDT from  $3.0 \pm$



**Figure 6.11:** Cyclic Voltammograms of (a) 1,4-BDMT and (b) 1,6-HDT on Au(111) from 0.5 M KOH. The potential was held at -0.20 V for 10 minutes and then cycled between -0.20 V and -1.15 V twice, starting with the cathodic scan. The first (1) reductive peak is more negative than the consecutive one (2).

0.3 to  $2.0 \pm 0.2 \mu\text{F cm}^{-2}$ . These values are comparable to the capacitance measured for a hexadecanethiol monolayer ( $1.7 \mu\text{F cm}^{-2}$ ) formed through spontaneous adsorption [5] or by electrodeposition from 0.5 M KOH [17]. This is expected since the bilayers are of similar length to the hexadecanethiol monolayer. This value is approximated to be about 18.0 Å by assuming a thickness of 1.1 Å per  $\text{CH}_2$  (the value for an all trans alkyl chain inclined at  $30^\circ$  to the surface) [18]. The bilayers of 1,4-BDMT and 1,6-HDT are expected to have a film thickness of about 16.8 Å and 18.4 Å respectively. The decrease is not due to a thicker film forming, but rather to adequate time for the intermolecular interactions to organize the bilayer. This is evident in the more significant decrease in the capacitance of the 1,4-BDMT bilayer. The limitations in forming a third layer have already been discussed in section 3.4.2. In addition, the distance of the unreacted sulfur group has been shown to effect the dimerization (section 5.4.2).

It is important to differentiate between the longer time scale in our electrodeposition method (10 minutes) and the much longer time scale required for spontaneous adsorption (hours to weeks). Application of an electric field promotes deposition of a monolayer of dithiolates via a single S-Au bond in a few seconds. After the initial deposition of an almost complete layer, the adsorbed dithiolates orient in such a way so as to maximize their Van der Waals and electrostatic interactions, as well as to decrease their repulsion (e.g. 1,4-BDMT). In addition, there is more time for the holes to be filled. This results in a small capacitance, typical of a very low defect layer. This contrasts the suggestion that slower deposition times (in the absence of an electric field) would allow more time for both thiol groups to adsorb to the gold surface (sections 3.4.1 and 4.4.1). The reorientation of the second thiolate towards

the gold surface cannot happen while holding the potential, since an almost complete monolayer occupies the electrode surface in a few seconds.

### 6.5 Mixed Bilayers: 1,4-BDMT and 1,6-HDT

Having established that the quality of the bilayer improves upon holding the potential at  $-0.20$  V for 10 minutes, a similar method of depositing bilayers was employed in forming mixed-component bilayers. A monolayer of 1,4-BDMT was first deposited and the meniscus was broken under potential control at  $-0.70$  V. The electrode was rinsed with water and transferred to a solution of 1,6-HDT. The potential was scanned from  $-0.70$  V to  $-0.20$  V and held for 10 minutes. The meniscus was again broken under potential control and the electrode rinsed with water. Finally, the capacitance was measured between  $-0.30$  and  $-0.50$  V in pure  $0.5$  M KOH. A value of  $2.3 \pm 0.2 \mu\text{F cm}^{-2}$  was obtained for the capacitance of the mixed bilayer. The integration of the reductive peak B'' on stripping was similar to that of B'' obtained directly in the 1,4-BDMT solution through scanning ( $89 \pm 6 \mu\text{C cm}^{-2}$  and  $82 \pm 5 \mu\text{C cm}^{-2}$  respectively). Peak B'' was located at a potential of about  $-1.03$  V. The same experiment was performed starting with a monolayer of 1,6-HDT and reacting it with 1,4-BDMT. A capacity of  $1.6 \pm 0.1 \mu\text{F cm}^{-2}$  was measured for the mixed bilayer. The reductive peak B'' was located at  $-1.12$  V and had the charge ( $70 \pm 6 \mu\text{C cm}^{-2}$ ) expected for the reductive removal of a S-Au bond. These capacitance values are comparable to the ones obtained upon holding the potential in the same dithiol solution. It is difficult to comment on which monolayer template is better for reacting (i.e. 1,4-BDMT or 1,6-HDT) since the capacitance values are all very close. This also supports the suggestion made in section 6.3 that both compounds have similar  $\epsilon_r$ .

## 6.6 Summary

The electrodeposition of monolayers of rigid 1,4-BDMT and flexible 1,6-HDT occur via a nucleation and growth process. This type of deposition process requires that the adsorbed molecules interact with one another. The flexible and cylindrical framework of the alkanedithiol (assumed all trans) 1,6-HDT allows for optimal intermolecular interactions in its monolayer assembly at all deposition rates. The rigid 1,4-BDMT organizes more slowly than its alkyl counterpart 1,6-HDT. Bilayer growth for both dithiols follows a Langmuir process, which is characteristic of random adsorption. This is in agreement with the nucleophilic attack. Both bilayer films show improved ion blocking properties at longer deposition times, with a large driving force. A more significant improvement in the ion blocking properties was noted for 1,4-BDMT. Mixed-bilayer films can be formed using electrodeposition.

## 6.7 References

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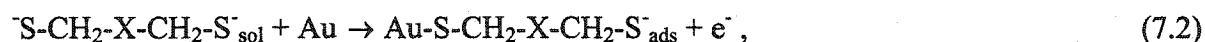
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## Chapter 7: Conclusions and Claims to Original Work

### 7.1 Mechanism for the Oxidative Adsorption of Dithiols onto Au(111)

#### 7.1.1 Monolayer Formation

We developed an original electrodeposition scheme, that allows for the formation of aromatic and alkyl dithiol monolayers via single S-Au bond formation from both pH neutral (equation 7.1) and basic (equation 7.2) aqueous electrolytes:

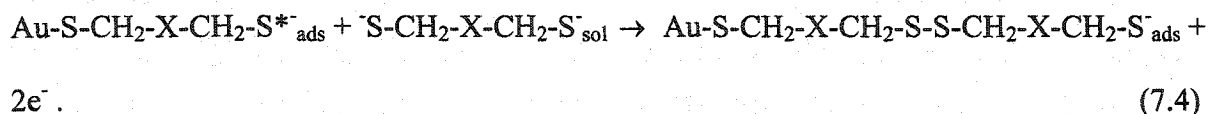
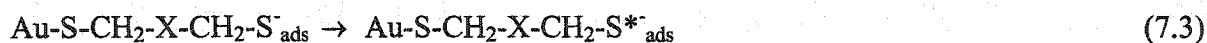


where X represents a phenyl group or methylene units. Monolayer formation occurs via a nucleation and growth process from alkaline solution, whereby the adsorbates experience stabilizing intermolecular interactions. The chain length dependence of the alkanedithiols demonstrates the importance of the Van der Waals interactions in forming monolayers having fewer defects. The interaction between the terminal thiolate end groups and the aqueous electrolyte also plays a role in the assembly of these compounds.

We have shown that the electrodeposition of dithiol monolayers results in reproducible coverages with adsorption through a single sulfur to the gold surface. This is not easily achieved through chemical deposition, i.e. in the absence of an applied electric field.

### 7.1.2 Bilayer Formation

The unreacted thiolate of the monolayer was oxidized by applying a more positive potential (i.e. a larger driving force) than that used in the deposition of the monolayer. Bilayer formation occurred between adsorbed dithiolates and dithiolates in basic aqueous solution according to the following mechanism:



The proposed mechanism occurs in two consecutive steps. The first step represents the activation of the free thiolate end group (equation 7.3). The second step involves the nucleophilic attack of the activated thiolate by a dithiolate in solution, followed by the transfer of two electrons (equation 7.4). Bilayer growth follows a Langmuir process, which is characteristic of random adsorption.

Bilayer formation was facilitated by a greater accessibility of the negatively charged end groups. In addition, the smaller the distance between the unreacted sulfur and gold surface, the more easily it was oxidized. In some cases, a thinner film (having more defects) resulted in a closer approach of the dithiolates in solution and therefore promoted intra- and intermolecular dimerization of solution dithiolates as well. Improved bilayer films were formed (i.e. films having better ion blocking properties) upon longer deposition times and at positive deposition potentials. This allowed for sufficient time for the dithiol molecules to

organize such that the intermolecular interactions, including Van der Waals interactions and electrostatic interactions (for the aromatic dithiols), were maximized. The deposition time had more of an effect on the aromatic (i.e. rigid) dithiols than on the alkyl (i.e. flexible) dithiols. Mixed-bilayers films were formed with aromatic and alkyl dithiols.

Our electrosynthetic approach to growing bilayers of dithiols at the Au(111) surface is an improvement over traditional incubation methods using oxygen as the oxidant. The electrodeposition of our dithiol films is time efficient, reproducible, and easily controlled. We have shown that the bilayer mechanism is applicable to aromatic and alkyl dithiols. It could be used to deposit more complex aromatic dithiols and to grow molecular wires at the gold surface. This electrochemical method can be extended to making new materials, e.g. by reacting the thiolate end group of the monolayer with other thiols or metals and making hybrid systems. These films have potential for applications in molecular electronics and chemical sensors.

## **Appendix A: More Than Just Ducks in Cyclic Voltammetry?!**

I was sure of only one thing upon starting graduate school:

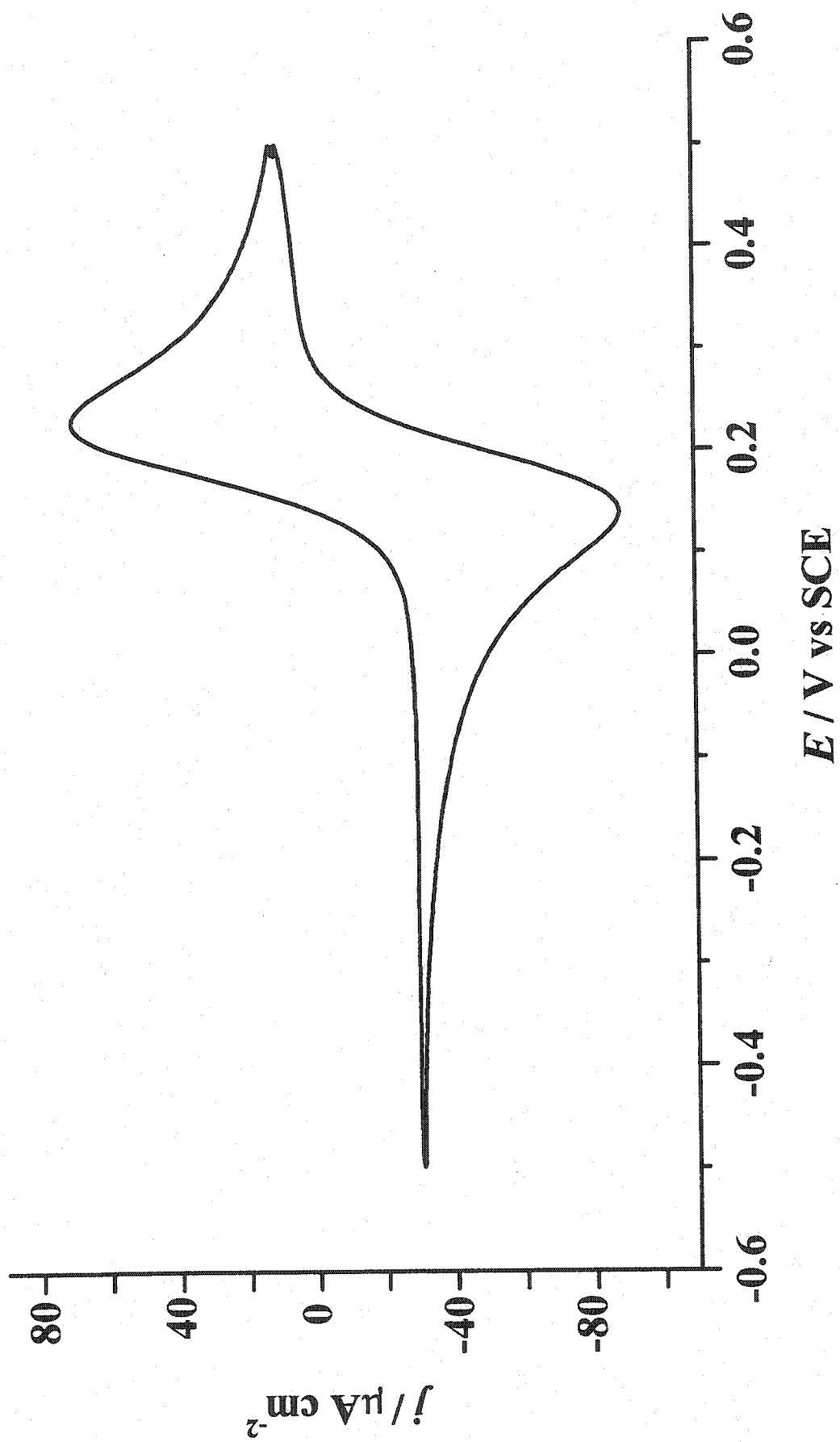
**GOLD + THIOLS = PROJECT.**

Somehow, all of the other research related words had not made much of an impact. So, it was with great surprise that I ran my first electrochemical experiment. A little panic went through me and I thought “Oh no, how did I miss this part of the project description?!” My undergraduate experience with electrochemistry had left me with

**CV = DUCK and DOUBLE DUCK.**

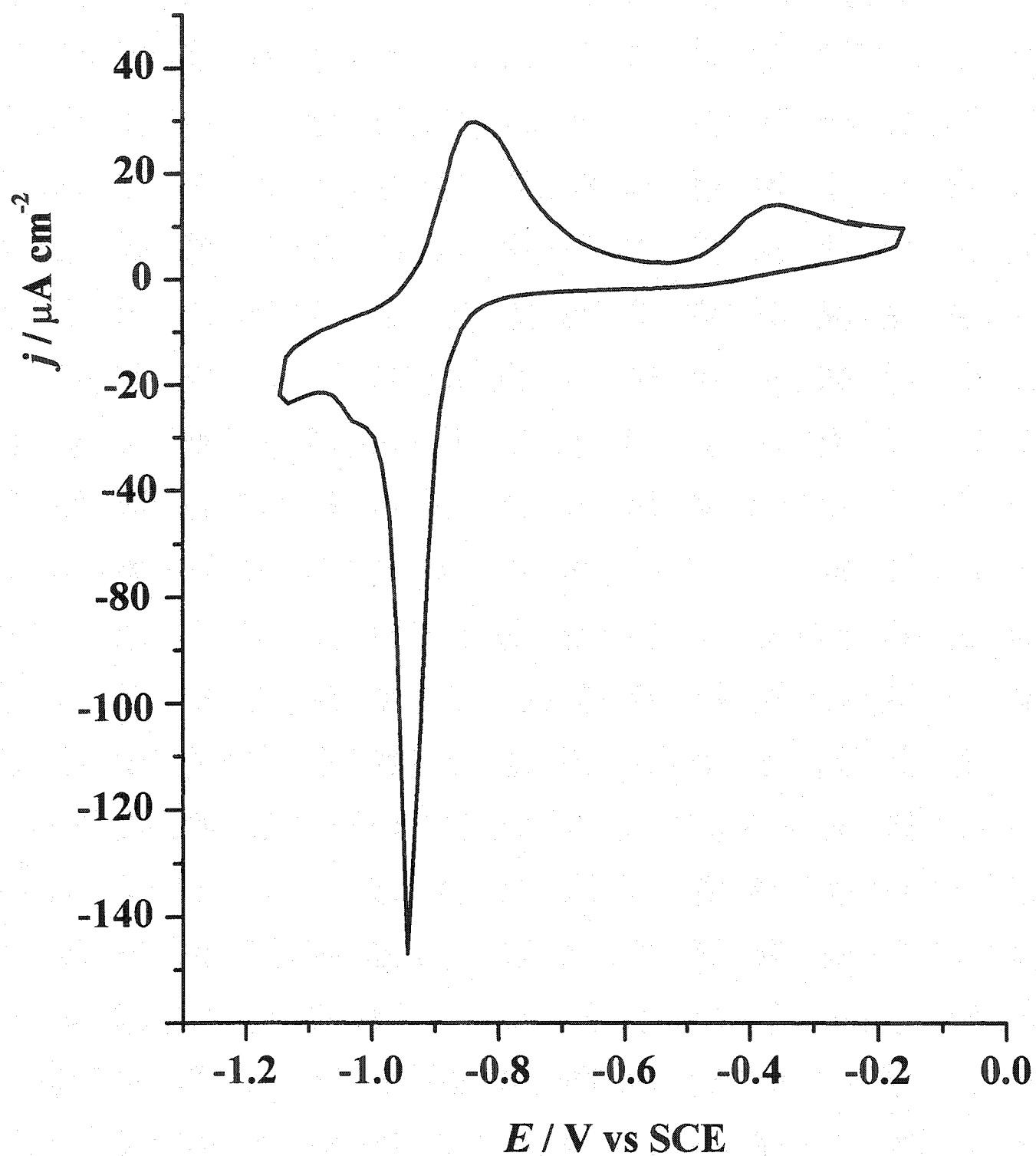
That is not very much to work with!

I have since learned that there is a lot more to cyclic voltammetry than just ducks, but my instinct is still to see the picture first and then the science.

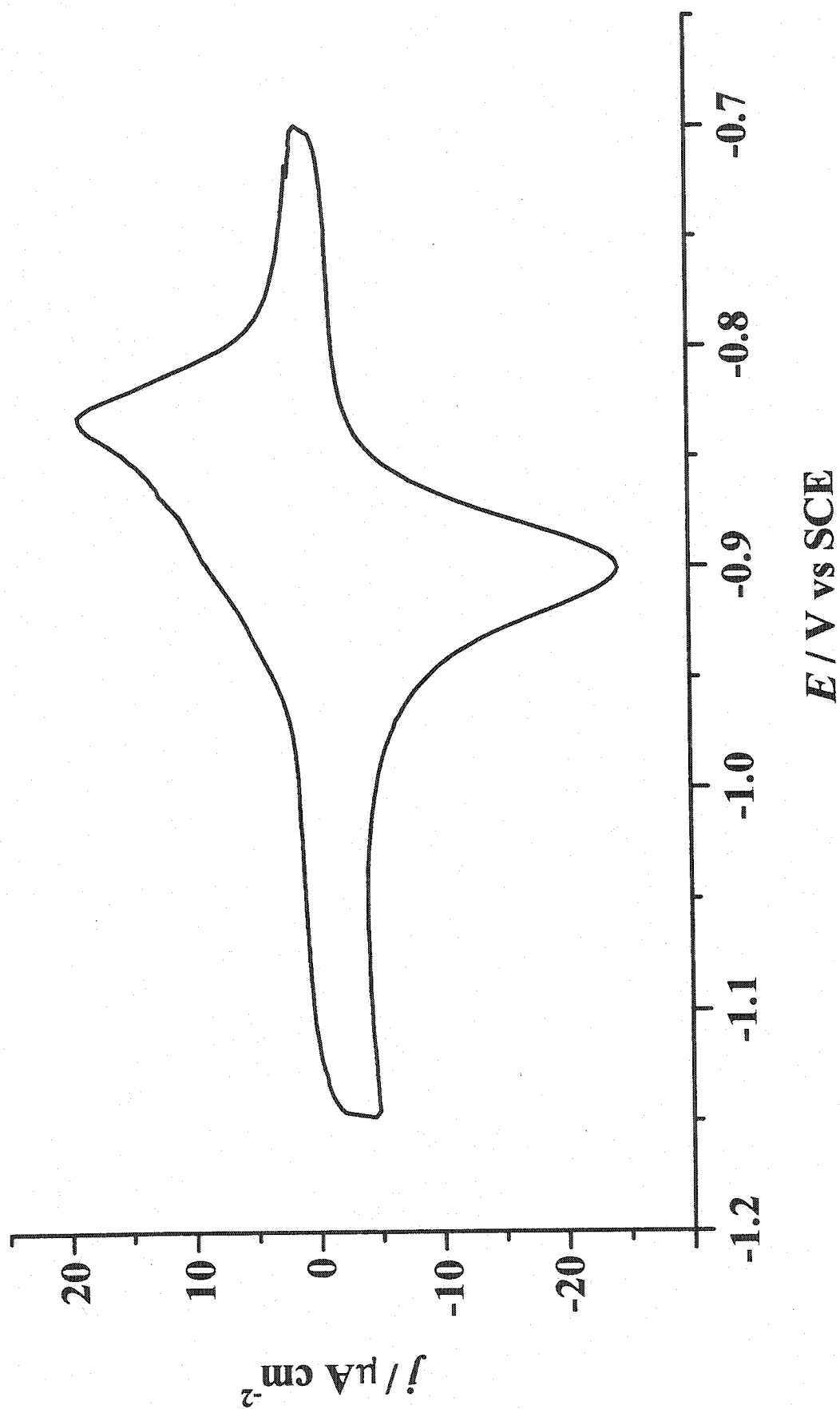


Cyclic voltammogram of 1.0 mM  $\text{K}_3\text{Fe}(\text{CN})_6$  in 0.1 M aqueous  $\text{KClO}_4$  at bare gold.

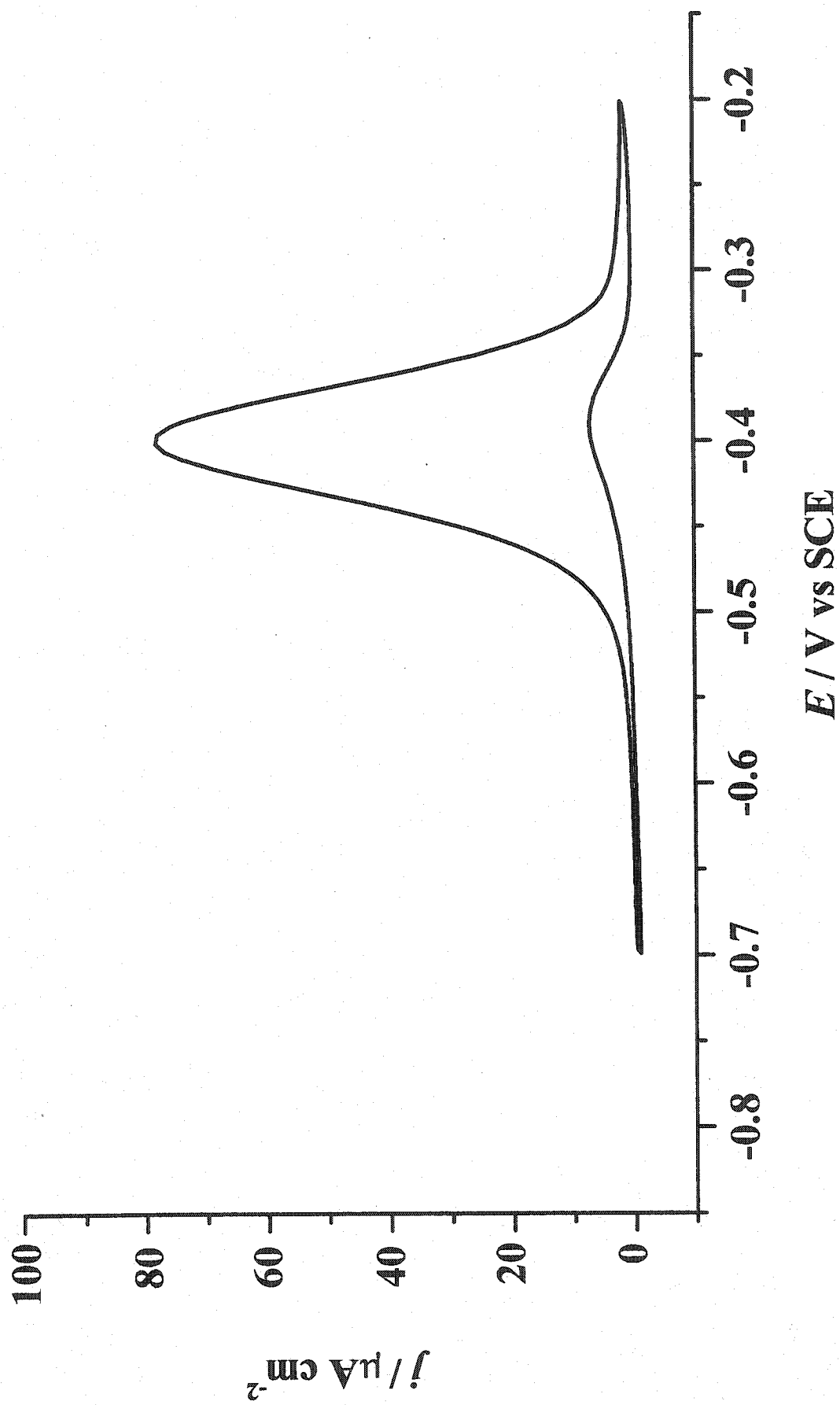
DUCK =

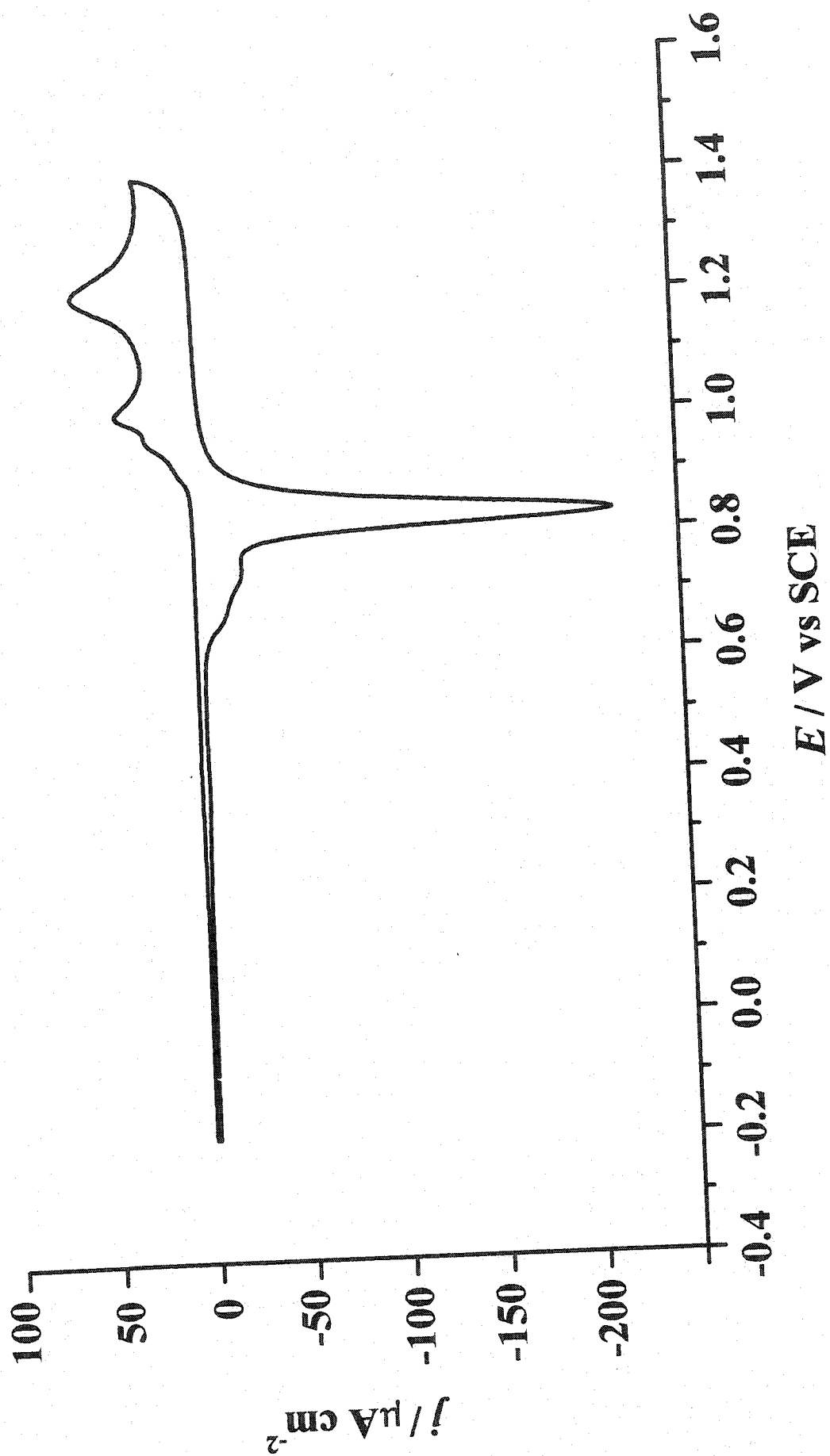


**CAMEL** = 1,2-EDT remains close to Au(111) surface in 0.5 M KOH.

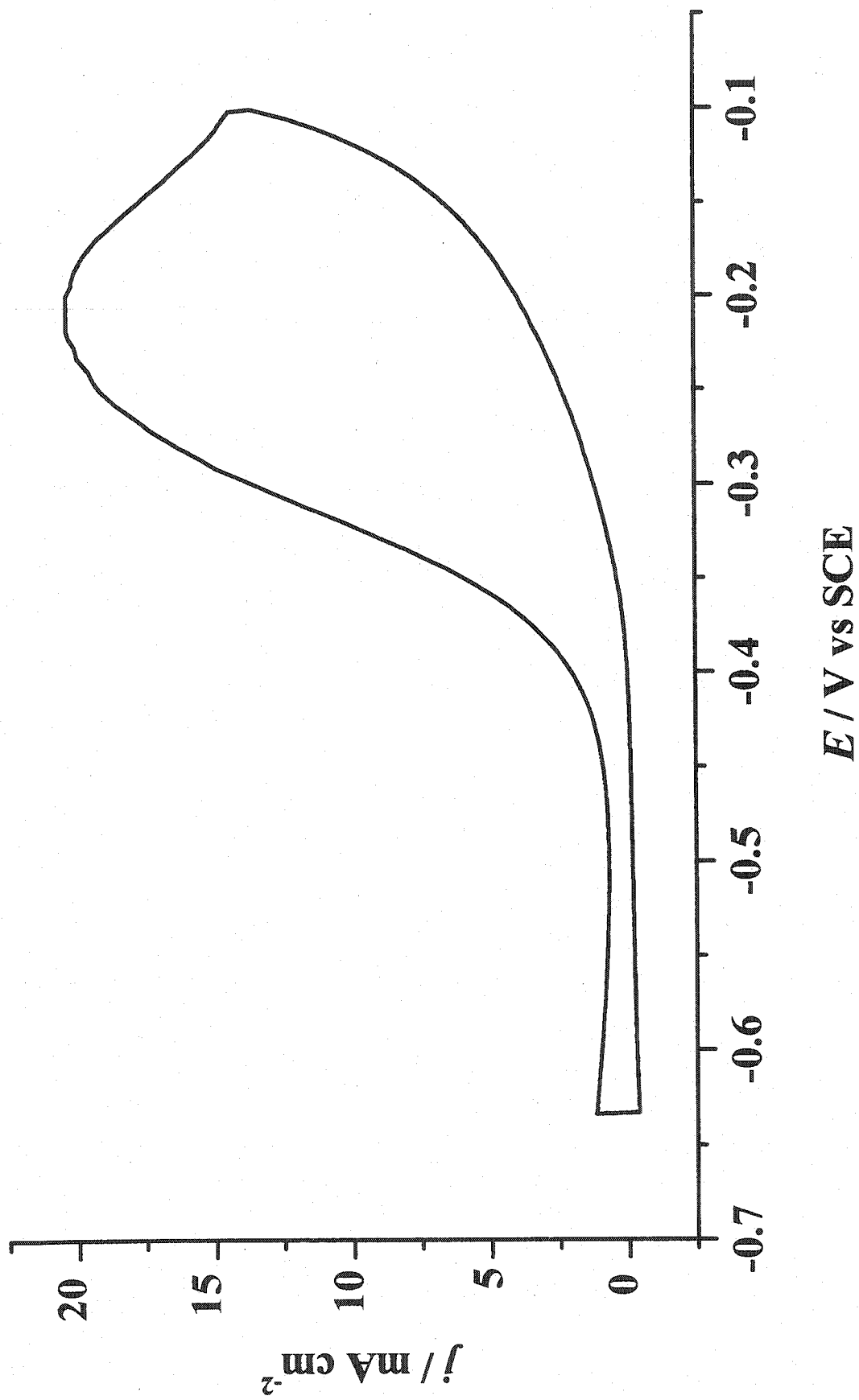








**RHINO** = Gold oxide formation in 0.1 M  $\text{HClO}_4$ .



WHALE = Contaminant!