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Electrochemical and EQCM investigation of L-selenomethionine in adsorbed state at gold electrodes

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Abstract

Selenomethionine (SeMet) adsorbs irreversibly from an aqueous solution to the gold surface. The resulting surface layer has a composite character and consists of SeMet and selenohomocysteine (SeHcy), which forms by the hydrolytic cleavage of the first one. The occurrence of these compounds was demonstrated by cyclic voltammetry and EQCM investigations. An anodic scan results in two poorly separated peaks corresponding to the oxidative desorption processes ($E_{1/2}$ about 0.70 V and E_p about 0.92 V *vs.* the Ag|AgCl (3 M KCl) electrode, respectively). The first one corresponds to the oxidation of SeHcy to $RSeO_2H$ (where R stands for $HO_2CCH(NH_2)(CH_2)_2-$) whereas the second results from the anodic conversion of SeMet to $RSeO_3H$ with $RSeO_2H$ as a possible intermediate. SeMet oxidation may continue in the region of gold oxide formation if not completed in the pre-oxide region. Partial decomposition of $RSeO_2H$ gives rise to H_2SeO_3 which was evidenced by its reduction reaction to Se(0) at about 0.25 V. In turn, Se(0) can be oxidized back to H_2SeO_3 at about 0.83 V. Surface Se(0) inhibits the electron transfer reaction of the $Fe(CN)_6^{3-/4-}$ redox couple. Ionization of the amino acid functions in the adsorbed state was investigated by capacitance *vs.* pH determinations. It was thus found that the carboxyl ionization constant (pK_{a1}) shifts from 2.19 in the aqueous solution to 5.1 in the adsorbed state whereas the adsorption has almost no effect on the ionization constant of the amino group ($pK_{a2} = 9.05$ in the adsorbed state *vs.* 9.15 in the solution form). Adsorption effect on the ionization constants was accounted for by the interplay of the effect of the surface charge on the local activity of the hydrogen ion, on one had, and intramolecular hydrogen bonding, on the other hand. A SeMet modified electrode can bind reversibly the copper(II) ion in the same way as cysteine and homocysteine proving that the amino acid functions are not involved in surface interactions. Selenium head group forms therefore the link between the adsorbate and the gold surface.

Keywords: L-Selenomethionine; Amino acids adsorption; Surface ionization; Selenium electrochemistry; Monoselenides

1. Introduction

Self-assembly of sulfur derivatives (mostly thiols) on metals is a convenient method for surface modification and functionalization [1]. In accord with the similarity of sulfur and selenium, selenols can also give rise to self-assembled monolayers (SAMs) by chemisorption at metal surfaces [2]. Self assembly of selenium derivatives is of interest from the standpoint of molecular electronics as the Se termination provides better electronic coupling to Au than the sulfur head group [3]. Either alkane selenols [4], aromatic selenols [5] or diselenides [6] can be used as starting materials. Diselenides split out by adsorption and the resulting SAM consists of selenols as well. There are however very few reports on self assembly of monoselenide derivatives [7,8]. In this respect, it is important to mention a difference between organic sulfides and monoselenides as far as adsorption to the gold surface is concerned. Whereas the sulfide-gold bonding strength is quite low [9], monoselenides give rise to rather stable surface layers. The difference may arise from the higher strength of the Se-Au

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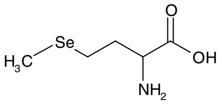
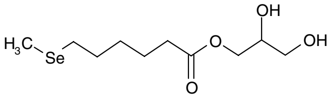
bond, which was recently documented by *ab initio* calculations [10].

We have previously investigated the electrochemistry of a surface layer generated by the adsorption of a monoselenide derivative (O^1-[6-(methylselanyl)hexanoyl]glycerol, SeOG, Chart 1) [7] and demonstrated that this compound can function as a convenient anchor for attaching complicated molecules (like carotenoids) to the gold surface [7,11]. This paper reports on the behavior of a readily available monoselenide, namely the amino acid seleno-L-methionine (SeMet, Chart 1), a compound of a particular importance in nutrition and medicine [12]. Anodic reaction of the sulfur analogue (methionine, Met) was investigated at gold [13], carbon [13,14], platinum [15], and carbon paste electrodes including cysteamine-modified colloidal-gold [16].

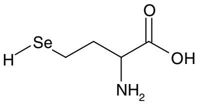
Until now, cysteine (Cys) and its derivatives have been the main candidates for preparing amino acid adsorbed layers at metal surfaces. Two main features can be distinguished in this respect. First, the thiol group forms a covalent bond with gold (Ref. [17] and references therein). Consequently, Cys and its derivatives in adsorbed state can undergo anodic [18] and cathodic [19] reactions alike to that of short-chain alkanethiol SAMs. Cys anodic desorption lifts the reconstruction of the gold surface [20]. Second, particular features result from the occurrence of amino acid groups that can be involved with electrostatic interactions and hydrogen bonds. Consequently, adsorbed Cys molecules are likely to form ordered aggregates [21,22] and perform chiral recognition [23]. Apparently, thermal activation is required in order to form covalent S–Au bonds after vapor deposition of a Cys layer on Au(111) [22] but strong interaction with the metal occurs immediately in the case of Au(110) [24]. Cys in the neutral form is abundant at low coverage on Au(110) but intramolecular interactions cause the zwitterionic form to be the dominant species at a high coverage degree [24]. A second, weakly adsorbed layer can also form [24]. Cys monolayers prepared in aqueous solution display various lattice structures according to solution pH and composition and the electrode potential of the metal substrate ([19] and references therein).



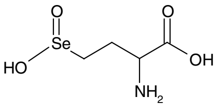
Selenomethionine (SeMet; $RSeCH_3$)



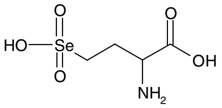
O^1-[6-(methylselanyl)hexanoyl]glycerol (SeOG)



Selenohomocysteine (SeHcy, RSeH)



4-selenino-2-aminobutiric acid ($RSeO_2H$)



4-selenono-2-aminobutiric acid ($RSeO_3H$)

Chart 1. Chemical structure of SeMet and related compounds.

Not only the thiol end group but also the amino acid functionalities can interact with the metal substrate. Theoretical approaches demonstrated that under sterically favorable conditions the amino group binds to either Au(111) [25] or Au(110) [23] along with the sulfur function. Amine blocking by acetylation (in *N*-acetyl-cysteine, NAC) allows carboxyl group to interact with gold in a surface layer formed by adsorption from solution [26], as it also occurs in a gluthatione surface layer [27]. Homocysteine (Hcy) layers on gold display most of the Cys typical features [28].

Amino acid behavior in the adsorbed state is dependent on the protonation degree. Ionization of organic acids and bases in the SAM state [29] is an active area of research and a worthwhile investigation approach in this field is based on capacitance measurements either in the absence [29,30] or in the presence of a redox couple [31]. On the other hand, the acid–base properties of the adsorbate are strongly influenced not only by the distribution of the electric charge at interface but also by molecular interactions (such as hydrogen bonds and electrostatic forces) and metal surface topography [32]. It was already demonstrated that the supply of an appropriate environment to the target molecule allows tuning the p*K* value and eventually impart the amino acid residue catalytic activity [33]. Self-assembly of amino acid at metal surfaces can be a fruitful approach in this connection and contribute to the field of artificial enzymes [34].

It is also worth mentioning the application of chemisorbed amino acids as ion receptors in voltammetric sensors for ion metals like copper [35] and zinc [36]. Amino acid surface layers can also perform as catalyst for electrochemical reactions of organic derivatives [37] or as promoters for electron transfer reactions of metallo-proteins [38].