

The influence of aliphatic amines on the potential of the structural transition (hex) \rightarrow (1 \times 1) for Au (100) electrode

Piotr Skołoduda

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Abstract The impact of the aliphatic amines on the potential (E_T) of the structural transition (hex) \rightarrow (1 \times 1) for Au (100) electrode was investigated. This potential was shifted to more negative values as the concentration of a given amine increased. As E_T depends linearly on the log of the bulk concentration for each amine it was suggested to use this relationship for quantitative determination of the amines. Moreover, it was shown that the presence of amines reduced the stability range of the (hex) structure in the following sequence methylamine < ethylamine < propylamine < butylamine due to their increasing adsorbability. Furthermore, for a given concentration the introduction of each subsequent $-\text{CH}_2-$ group into the carbon chain of an amine is accompanied by the reduction of the stability range of ca. 23 mV.

Keywords Single crystal Au(100) electrode · Surface reconstruction · Aliphatic amines

1 Introduction

At present short-chain aliphatic amines can be often met in the aquatic environment which is a consequence of their widespread use in production of polymers, dyes, pharmaceuticals, corrosion inhibitors, fuel additives, and explosives [1–3].

Aliphatic amines are also common components of biological systems as they are degradation products of organic materials such as amino acids and proteins [4]. Most

amines are toxic and can react with nitrogen-containing compounds to form nitrosamines, which are carcinogenic substances. Therefore, to reduce the risk of the exposure to them, their detection and monitoring have become of great interest for the natural environment protection [5].

However, in general only chromatographic techniques have been used for determination of these compounds because of their little, if any, ultraviolet or visible light absorption and fluorescence [6]. Recently, also an attempt was made to use electrochemical methods with employment of polycrystalline gold electrode but the results were unsatisfactory [7, 8].

Unexpectedly, in the course of our electrochemical study of the reconstruction phenomenon at Au(100) electrode in the presence of amines, we obtained some data that could be useful for their quantitative determination.

The Au (100) surface undergoes a reconstruction of its outermost atomic layer from the (1 \times 1) bulk termination structure to a rotated hexagonal (hex) structure, which has an atomic density that is $\sim 25\%$ greater than that of the bulk-terminated (1 \times 1) surface layer. The reconstruction of Au (100) has been studied intensively by electrochemical measurements [9], in ultra high vacuum condition [9], scanning tunnelling microscopy [9] and by in situ surface X-ray scattering [10]. This phenomenon has been also the subject of theoretical consideration where the density functional theory [11] has been applied.

As follows from the hitherto data, a flame-annealed Au(100) electrode is reconstructed and stable in electrochemical environment. The reconstruction is lifted due to adsorption of anions and organic molecules and the surface structural transition (hex) \rightarrow (1 \times 1) takes place at the so-called transition potential (E_T) yielding the unreconstructed surface. Usually the occurrence of surface reconstruction has a marked impact on electrochemical

P. Skołoduda (✉)
Zakład Chemii Fizycznej, Wydział Chemii, Uniwersytet
im.A.Mickiewicza, ul.Grunwaldzka 6, 60-780 Poznan, Poland
e-mail: pskoluda@main.amu.edu.pl

processes, e.g., adsorption and phase transition in organic adlayer [12–14].

As follows from the general approach to the stability of the reconstructed Au (100) electrode in the presence of organic compounds these adsorbates alone do not necessarily lift the reconstruction as have been revealed for, e.g., coumarin [15] or propanal [16]. As evident from the energy diagram (see, e.g., Fig. 3 in [9]), the reason for this is that the difference in adsorption energy of the adsorbate on the (hex) and (1×1) structure has to exceed the difference in surface energy for both structures. On the other hand, the organic molecules for which the lifting of the reconstruction of the Au(100) electrode was documented [17–19] are mainly heterocycles with one or two nitrogen atoms in the ring.

In order to pursue the investigations, in the present article we have chosen another type of molecules containing nitrogen, i.e., aliphatic amines in order not only to probe but mainly to explain the impact of molecular structure or more precisely the length of the carbon chain in the amine molecule on the potential of structural transition at the Au (100)-(hex) electrode. These short-chain amines were methyl- (Me), ethyl- (Et), propyl- (Pr), and butyl-amine (Bu), respectively. Finally, we propose to apply the concentration dependence of E_T obtained for the above-mentioned amines in their quantitative determination.

2 Experimental

The working electrode was an Au(100) single crystal disc, 4 mm in diameter and 4 mm thick, and oriented to $<1^\circ$ (MaTeck, Jülich). Before each experiment the electrode was prepared according to the well-known procedure for preparation of well-ordered gold surfaces [20]. Namely, the crystal was annealed for 3 min in a Bunsen burner flame, then cooled down to room temperature in a stream of nitrogen. Contact with the electrolyte was achieved by the hanging-meniscus method [21]. The counter electrode was a Pt wire. The reference electrode was a saturated calomel electrode (SCE) and throughout this work all potentials are reported versus SCE. The voltammetric measurements were performed using an AUTOLAB system (Eco Chemie). All the voltammograms were obtained at a scan rate of 10 mV s^{-1} .

The supporting electrolyte solution ($2 \times 10^{-2} \text{ M NaClO}_4$) was prepared from doubly recrystallised NaClO_4 (analytical grade, Merck). Amines were of Aldrich analytical grade quality. All solutions were prepared from Milli-Q water.

All electrolytes were deaerated (for 50 min) by nitrogen. Nitrogen was allowed to flow over the solution at all times.

All experiments were carried out at room temperature $25 \pm 1^\circ \text{C}$.

3 Results and discussion

Shown in Fig. 1 are two cyclic voltammograms (CV's) obtained for Au(100) single crystal electrode in the absence or presence of propylamine. The cyclic voltammogram presented for the supporting electrolyte alone, at potentials more positive than 0.650 V, correspond to the formation of surface oxides and is characteristic of the Au(100) surface, as reported in independent studies [22]. This oxide formation region is preceded by a much smaller peak (r_S), which occurs at 0.496 V. The addition of Pr, as follows from Fig. 1, has a significant influence on the oxidation of gold as indicated by the differences between the two oxidation regions. Moreover, CV recorded in the presence of Pr also exhibits a small peak (r_A) in the double layer region but at negative (-0.116 V) value of potential. This peak as well as the peak recorded in the supporting electrolyte is associated with the lifting of the reconstruction because as follows from [9] this surface process is clearly seen in the cyclic current–potential curve as a small and sharp current peak on the positive-going potential scan. The potential of such a peak was called the potential of structural transition [9] and although depends somewhat on the scan rate, is a convenient indicator of the stability of the (hex) structure, which exists only on its negative side.

Figure 2 shows the cyclic voltammograms for a thermally prepared Au(100)-(hex) electrode with the (hex) \rightarrow (1×1) structural transition in the supporting electrolyte ($2 \times 10^{-2} \text{ M NaClO}_4$) and with various additions (from

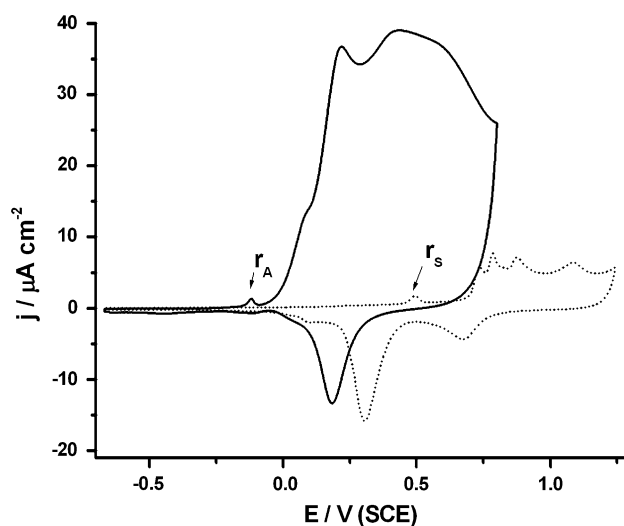


Fig. 1 Cyclic current–potential curves for thermally prepared Au(100)-(hex) in $2 \times 10^{-2} \text{ M NaClO}_4$ (dotted line) and with addition of $2 \times 10^{-2} \text{ M}$ propylamine (continuous line)

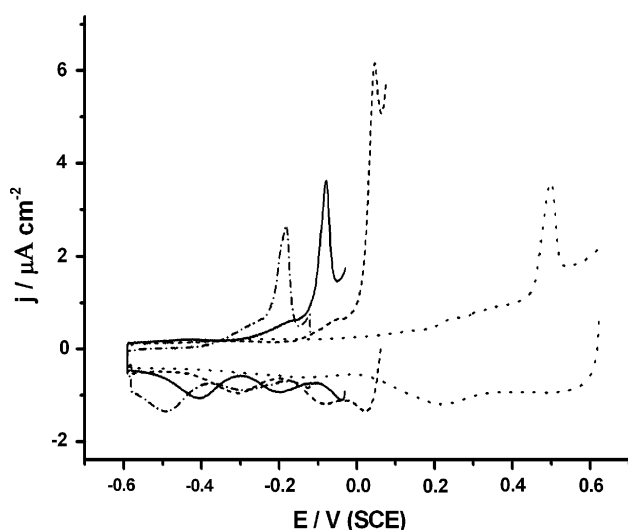


Fig. 2 Cyclic current–potential curves for thermally prepared Au(100)-(hex) with the (hex) \rightarrow (1 \times 1) structural transition in 2×10^{-2} M NaClO₄ (dotted line) and with increased propylamine concentration: 10^{-3} M (dashed line), 10^{-2} M (continuous line) and 10^{-1} M (dotted dashed line)

10^{-4} M till 10^{-1} M) of Pr (for the sake of clarity only three selected voltammograms for 10^{-3} , 10^{-2} , and 10^{-1} M are depicted). The presence of a well-developed peak on the positive-going scan of the voltammograms indicates that the adsorption of these organic molecules lifts the reconstruction. The influence of the Pr molecules is further seen as a shift of the transition peak towards more negative values of potential as the concentration increases, thus decreasing the stability range of the (hex) structure. Such a considerable reduction of the stability range (ca. 0.450 V) upon addition of a small amount of Pr (10^{-3} M), being almost 1.2 and 3 times larger than for pyridine and pyrazine, respectively [18] is quite remarkable.

We mentioned in passing that the subsequent increase in the density of the current found to occur for positive values of potential greater than E_T is connected with the oxidation of Pr. The overlapping of the reconstruction peak and the oxidation wave, however, does not obscure the observation that the charge under the peak decreases with increasing bulk concentration of Pr. Nevertheless, due to the coincidence of both processes we had to perform our measurements in solutions containing not less than 10^{-4} M of Me, Et, Pr, and 5×10^{-4} M of Bu.

The current–potential dependencies obtained for the other amines under investigation are similar and therefore are not shown. Instead, the expanded section of CV for thermally prepared Au(100)-(hex) in electrolyte solutions containing the same amount (10^{-3} M) of the amines under consideration are presented in Fig. 3. As follows from this figure the reconstruction peak shifts to more negative values of potential as the amine is changed from Me to Et and

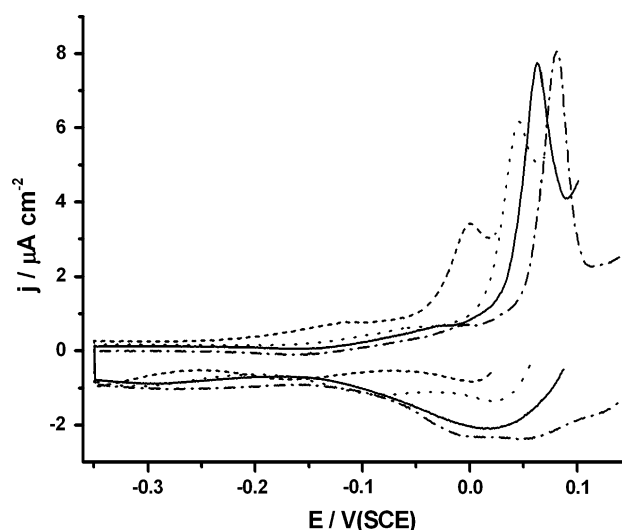


Fig. 3 Expanded section of the cyclic current–potential curves for thermally prepared Au(100)-(hex) with the (hex) \rightarrow (1 \times 1) structural transition in 2×10^{-2} M NaClO₄ and with 10^{-3} M addition of Me (dotted dashed line), Et (continuous line), Pr (dotted line), and Bu (dashed line) amines

then successively to Pr and Bu. Besides, the charge under each peak decreases in the same sequence. It means that the presence of amines in the supporting electrolyte reduces the stability range of the (hex) structure in the following sequence Me < Et < Pr < Bu. In other words, the strongest impact on the stability range of the reconstructed surface was found for Bu, the least for Me. As pH of these solutions is similar and equal 10.3 ± 0.2 such different influence of amines on E_T can be attributed to their increasing adsorbability. Increasing adsorbability means that the adsorbate–gold interaction determining the interfacial energetics, i.e., the Gibbs energy of adsorption (ΔG_{ads}) increases in the same order. The Gibbs energy of adsorption for the amines studied is available from literature, however, only for polycrystalline gold [7]. Nevertheless, we attempted to correlate these values of ΔG_{ads} (keeping in mind that the difference in adsorption energy of the admolecule on the (hex) and (1 \times 1) structure is decisive for lifting of the reconstruction) and the shift in transition potential for (hex) \rightarrow (1 \times 1) due to adsorption for the amines studied. ΔG_{ads} values are equal to: -30.46 , -33.19 , -35.52 , -37.90 kJ mol⁻¹ for methyl-, ethyl-, propyl-, and butylamine, respectively [7] and these sequence implies the following order of the amines according to the interaction with gold electrode Me < Et < Pr < Bu. As can be seen, at least from Fig. 3 or 4 (see below) the shift in transition potential to more negative values follows this trend very clearly. In other words the reduction of the stability range for a given amine is accompanied by a progressive increase in the absolute values of ΔG_{ads} , i.e., its higher adsorbability.

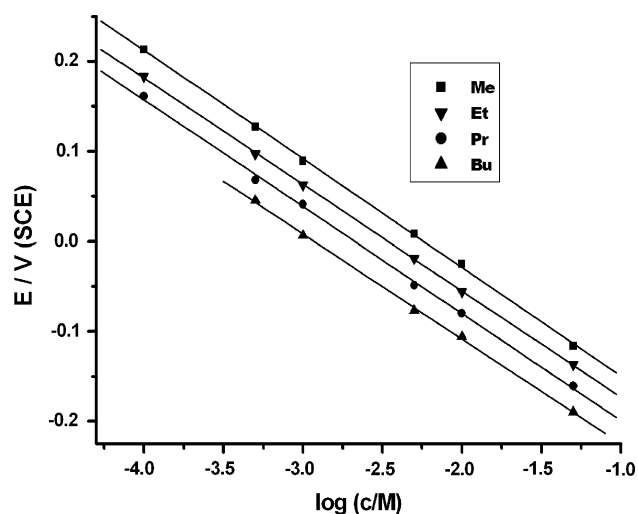


Fig. 4 Dependence of the peak potential for the (hex) \rightarrow (1 \times 1) transition of Au(100) on the concentration of Me (filled square), Et (filled inverted triangle), Pr (filled circle), and Bu (filled triangle) amines added to 2×10^{-2} M NaClO₄

Finally, it is worthwhile to mention a few interesting observations following from a detailed study of the concentration dependence of the potential of the structural transition (hex) \rightarrow (1 \times 1) for the amines considered. This concentration dependence depicted in Fig. 4 shows the transition potentials, as derived from CV curves for thermally prepared Au(100)-(hex) in various solutions, as a function of the logarithm of the amines concentration. As can be seen for each amine E_T changes linearly with log of the amine concentration similarly as already observed for thiourea but in contrast to pyridine and pyrazine for which this relationship was nonlinear [18]. The slope and correlation coefficient calculated for the lines depicted in Fig. 4 are -0.121 ± 0.001 V ($R^2 = 0.9995$, $n = 6$), -0.118 ± 0.0006 V ($R^2 = 0.9998$, $n = 6$), -0.119 ± 0.002 V ($R^2 = 0.994$, $n = 6$) and -0.116 ± 0.002 V ($R^2 = 0.999$, $n = 5$) per decade for Me, Et, Pr, and Bu, respectively. Thus, taking into account both the linear relationship between E_T and log of concentration and the well-known reproducibility and stability of the measurements with single crystal electrodes [22–24], the reconstructed Au(100) electrode could have potential application for quantitative determination of aliphatic amines in the above-mentioned concentration range.

The observed relationship (Fig. 4) is presented by a series of not only straight but also nearly parallel lines. The parallelism of the lines shows a qualitatively similar impact of the amines studied on the stability range of the reconstructed surface. In addition, this parallelism is associated with almost equal distance separating the lines. As follows from Fig. 4, the intersect is shifted towards more negative values by about 23 mV as Me is replaced by Et and then

subsequently by Pr and Bu, respectively. A linear reduction of the stability range as results of increasing carbon chain of the amine could therefore be postulated. In other words for a given concentration the introduction of each subsequent $-\text{CH}_2-$ group into the carbon chain of the amine is accompanied by the reduction of the stability range by ca. 23 mV.

4 Conclusions

The influence of aliphatic amines molecules on the potential of structural transition (hex) \rightarrow (1 \times 1) at Au(100) electrode has been investigated over a wide concentration range. The data obtained indicate that adsorption of these organic compounds lifts the reconstruction and in consequence shifts the potential of structural transition in the negative direction. It was shown that the presence of amines in the supporting electrolyte reduces the stability range of the (hex) structure in the following sequence Me < Et < Pr < Bu due to their increasing adsorbability.

Moreover, detailed concentration investigation has shown that:

- (i) for each amine under study E_T changes linearly with log c
- (ii) for a given amine concentration, gradual introduction of $-\text{CH}_2-$ group into the carbon chain of the amine, is accompanied by reduction of the stability range by ca. 23 mV.

This former [i.e., (i)] finding was suggested to be tested as possible method for quantitative determination of the aliphatic amines under consideration.

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