THE EFFECT OF GOLD OXIDE ON ELECTROOXIDATION OF ALIPHATIC AMINES

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The electrooxidation of aliphatic amines ranging from ethylamine to butylamine at the gold electrode in contact with an alkaline electrolyte solution has been described. The adsorptive behaviour of substrate molecules was identified by changes in the differential capacitance of the double layer at the electrode/solution interface. Subsequent stages of the oxidation process are proposed.

Keywords: Amines; Gold electrode; Electrochemistry; Electrocatalysis; Tensammetry; Voltammetry; Oxidations; Adsorption.

Among the noble metals, platinum and gold are the most active catalysts. Platinum has the highest catalytic activity in acid solution, whereas gold is the most active in alkaline media[1–6]. The organic compounds selected for our study are aliphatic amines, widely used as starting or intermediate reagents in production of various chemical compounds such as polymers, corrosion inhibitors, pesticides as well as medicines. In spite of the unquestionable significance of aliphatic amines in industrial, clinical and environmental applications[7], their electrochemical behaviour has been scarcely examined. For platinum electrode in acetonitrile, Mann et al.[8,9] have proposed the dual mechanism of the oxidation of aliphatic amines depending on the electrode potential. The low-potential mechanism involves a one-electron transfer to form a cation radical, while at higher potentials iminium salts are formed. Horányi et al.[10,11] have concluded that the oxidation of methylamine and butylamine at the platinized platinum electrode in acid or alkaline medium produces adsorbed cyanide species. This conclusion has been confirmed by voltammetric and spectroscopic results obtained by Huerta et al.[12,13] on the oxidation of methylamine and ethylamine at monocrystalline Pt electrodes. Studies on the gold electrode have been limited to the voltammetric response of ethylamine upon anodic oxidation in aqueous alkaline media. Luo et al.[14] observed a significant oxidation cur-

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rent of ethylamine at electrode potentials more positive than 200 mV vs saturated calomel electrode (SCE). The results obtained by Johnson et al.[15–17] showed that the oxidation of $C_2H_5NH_2$ on gold occurred concomitantly with the formation of surface oxide (AuO). In view of poor experimental evidence published on aliphatic amines oxidation, more work is needed to draw any definite conclusions about the electrooxidation mechanism of this class of organics.

The subject of the study reported here is the oxidation of aliphatic amines on the gold electrode in an alkaline supporting electrolyte solution. Additional information on adsorption of the molecules under investigation was obtained.

EXPERIMENTAL

Cyclic voltammetric and tensammetric studies were performed in a conventional three-compartment cell separated by glass frits using a gold bead (99.999% purity) as a working electrode and a gold sheet as a counter-electrode. A hydrogen electrode (RHE) in the supporting electrolyte solution as proposed by Will[18,19] was used as a reference electrode. For easier comparison with published data, all the potentials are quoted versus SCE.

The solutions were prepared using water purified in a Millipore Milli-Q system, ethylamine, propylamine and butylamine of Aldrich analytical grade quality and NaOH of Merck analytical grade quality. The measurements were performed at 295 K. All solutions under investigation were purged with high-purity argon.

The experimental setup used to record cyclic voltammograms (j–E curves) and differential capacitance of the electric double layer versus electrode potential curves (C–E) was described previously[20]. The C–E curves were obtained by superimposing ac sinusoidal voltage signal (15 Hz, 5 mV) on a slow linear electrode potential scan (dE/dt = 5 mV s^{-1}). A slower scan rate of 2 mV s^{-1} did not affect the tensammetric curves observed. The equilibrium of the adsorption/desorption was checked in additional experiments at different frequencies. For the frequencies in the range from 5 to 40 s^{-1} no frequency dispersion of the differential capacity has been observed in the potential range between E = –1000 mV and E = 100 mV vs SCE, in the supporting electrolyte solution. This potential range narrows (E = –400 to 100 mV) in the solution containing amine in concentrations between 5×10^{-2} and 1×10^{2} mᴍ. Stirring of the solutions had no effect on the course of the tensammetric curves, which indicated that the mass transport did not limit the rate of adsorption/desorption processes of amine at the bulk concentrations studied. The above experimental findings allow the conclusion that the differential capacity data in the above-mentioned potential range can be considered at equilibrium.

Prior to each series of measurements with amines, the working electrode was electrochemically activated by cycling (dE/dt = 100 mV s^{-1}) in the potential range between E = –1100 and 0 mV vs SCE in the supporting electrolyte solution (1×10^{2} mᴍ NaOH), where no faradic reactions occur on the gold surface. This procedure allows avoiding structural changes on the gold surface. Furthermore, the roughness factor remains constant. When reproducible values of the differential capacitance of the double layer (C) were achieved, a roughness factor of 1.1 was calculated assuming the differential double layer capacitance of a smooth gold electrode 22 μF cm^{-2} at E between –1000 and –850 mV vs SCE [21,22].

At the end of each series of experiments, the gold electrode was rinsed with water and the j–E and C–E curves were recorded again in a fresh supporting electrolyte solution. The shapes of j–E and C–E curves in each series of experiments were the same as those taken before the measurements. This means that the surface of the working electrode did not change during the experiment.

For identification of the electrooxidation products, the controlled potential electrolysis of 1×10^2 mM ethylamine as an example in 1×10^2 mM NaOH solution was carried out at a potential in the Tafel region. The samples of electrolysed solution were analysed by ^1H and ^{13}C NMR. The spectra were recorded using a Varian Gemini 300VT spectrometer, operating at 300.07 and 75.46 MHz for ^1H and ^{13}C, respectively.

RESULTS AND DISCUSSION

Figure 1 shows the cyclic voltammograms recorded at the gold electrode in the supporting electrolyte solution, 1×10^2 mM NaOH (curve 1), and in this solution in the presence of 1 mM ethylamine, propylamine and butylamine (curves 2–4).

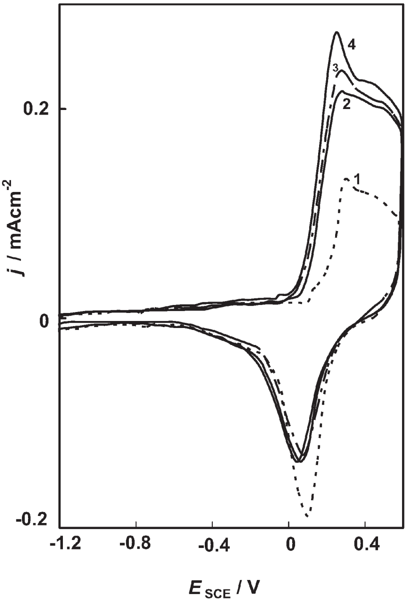


FIG. 1
Cyclic voltammograms of the gold electrode in 1×10^2 mM NaOH (1), with 1 mM ethylamine (2), propylamine (3), butylamine (4); dE/dt = 100 mV s^{-1}

A well-defined anodic peak at E = 300 mV vs SCE and a cathodic peak at E = 80 mV vs SCE visible in the j–E curve of the bare electrode is assigned to the gold oxide formation and to its reduction, respectively[23]. According to Newman et al.[23] the bare gold surface in alkaline solution might be covered by different species depending on the electrode potential. In the potential range between –440 mV vs SCE and 40 mV vs SCE the $AuOH_{ad}$ species are formed in the reaction: $Au + OH^- \rightarrow AuOH_{ad}$ and the gold surface coverage by adsorbed species, $\Theta_{AuOH_{ad}}$ is less than 1. The reaction $2\ Au + 3\ H_2O \rightarrow Au_2O_3 + 6\ H^+ + 6\ e$ is responsible for production of the Au_2O_3 monolayer with $\Theta_{Au_2O_3} \le 1$ at 40 mV < E < 390 mV vs SCE and multilayer of the Au_2O_3 at E > 390 mV vs SCE, respectively. In the latter electrode potential region the oxygen evolution occurs also via the electrochemical decomposition of water molecules.

As follows from the cyclic voltammograms obtained, aliphatic amines are inactive at the gold electrode potentials below $E \approx 0.0$ mV vs SCE. The organics oxidation proceeds irreversibly only in parallel with the gold oxide formation and the anodic peaks with the maximum at $E \approx 275$ mV vs SCE appear on the cyclic voltammograms. The shape of j–E curves for all amines studied is similar (curves 2–4 in Fig. 1).

When comparing the response of the gold electrode recorded in the supporting electrolyte solution (curve 1) with those obtained in the presence of amines (curves 2–4), one can find that the charge used for reduction of gold oxide in the presence of amines is smaller than that consumed in the solution without the solute. This observation points to participation of gold oxide in oxidation reaction of amines. The same conclusion was drawn for methanol oxidation on the polycrystalline gold electrode[24,25].

The Tafel analysis of the j–E relationships corresponding to the oxidation of 1 mM amines plotted in the log j–E coordinates gives the straight lines in the potential range between 50 and 200 mV vs SCE. Figure 2 gives the value of the Tafel slope, $dE/\log j = 2.303RT/\alpha nF$, equal to 200 ± 20 mV per decade of the current density. The electron transfer coefficient, $\alpha n = 0.30 \pm 0.02$, consistently lower than 0.5 and decreasing with an increase in the amine concentration support the assumption of an adsorption step preceding the first electron transfer step determining the overall reaction rate. Further steps proceed so fast that they have no influence on the rate of the amine oxidation. As expected in the case of oxidation of adsorbed amine molecules, stirring the solutions does not affect the current density. For all the amines studied in the pH range between 11 and 13.4 the E_p versus pH plots (Fig. 3) are linear with the slope of the $dE_p/dpH \approx 60 \pm 3$ mV, which suggests the participation of equal numbers of protons and electrons in the oxidation reaction.

An increase in the carbon chain length of the organic molecule is accompanied by some increase in the electrochemical activity of amine. However, this effect is significantly smaller when compared with that observed for example for aliphatic alcohols[5,6]. It can be a consequence of the relatively large standard Gibbs energy of adsorption ΔG^0_{ad} = –33.19, –35.52 and –37.90 kJ mol^{-1} for ethylamine, propylamine and butylamine, respectively[26].

With increasing potential sweep rates for all the amines studied, the oxidation peak potential is shifted towards more positive values, as typical for the irreversible processes. The log j_p versus log v plots are linear with the slope of the d log j_p/d log $v \approx 0.6$ (Fig. 4) which may indicate a mixed, i.e., diffusion–adsorption rate control.

For all the amines studied a characteristic feature is an increase in the anodic current density with increasing concentration of these compounds in the supporting electrolyte solution. As an example the cyclic voltammograms recorded at the gold electrode in 1 × 10^2 mM NaOH in the presence of

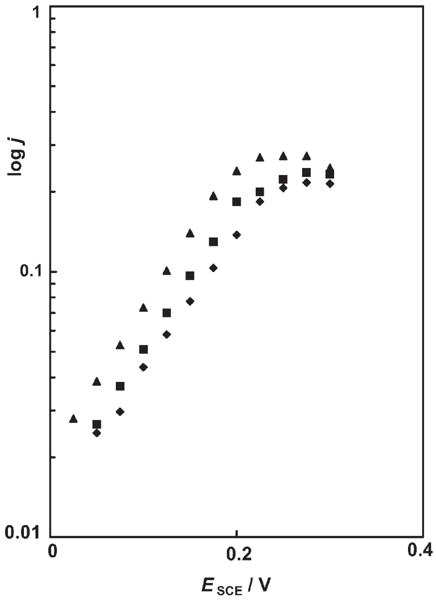


FIG. 2
The dependence of the current density on the gold electrode potential in 1 × 10^2 mM NaOH, with 1 mM ethylamine (◆), propylamine (■), butylamine (▲); dE/dt = 100 mV s^{-1}

propylamine of concentrations ranging from 1×10^{-1} to 1×10^{2} mM are presented in Fig. 5. The *j*–*E* curves move towards negative potentials when the bulk concentration of amines (c_A) increases. At the same time the maximum of the oxidation peaks is shifted towards positive potentials (Fig. 5). Such a shift is typical of the reactions involving the molecules adsorbed on the electrode surface. An increase in amine coverage may generate a decrease in the gold oxide coverage. This conclusion is supported by the fact that any increase in the anodic peak is accompanied by a decrease in the cathodic peak.

The decisive role of adsorption steps in the kinetics of aliphatic amine electrooxidation on gold is indicated by the fractional reaction order with respect to the substrate concentration, z_A. Figure 6 displays the plots of the logarithm of current density versus the logarithm of substrate concentration at a constant electrode potential of 150 mV vs SCE. The slope of the straight lines of the appropriate $\log j - \log c_A$ relationships gives the reaction order, z_A equal to 0.30 ± 0.01 for $c_A \leq 1$ mM being the same for all the amines studied. An increase in the surface coverage by adsorbed species leads to $z_A \approx 0$ for amine concentrations higher than 1×10^{2} mM (Fig. 6).

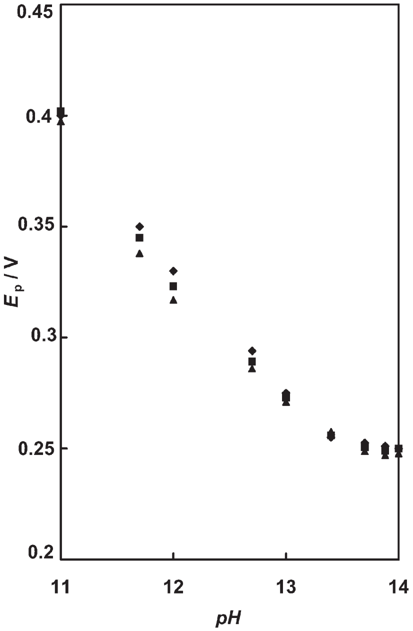


FIG. 3
The dependence of the peak potential on the pH of the supporting electrolyte solution for 1 mM amine: ethylamine (◆), propylamine (■), butylamine (▲)

Further support of the adsorption of the amines preceding their oxidation can be gained from tensammetric measurements. A representative set of *C*–*E* curves illustrating changes in the differential capacitance of the double layer as a function of the gold electrode potential, obtained in the supporting electrolyte solution (1 × 10^2 mM NaOH) and in this solution with various butylamine concentrations (c_A), is presented in Fig. 7. The shape of the *C*–*E* curves for all other amines under investigation is similar.

A gradual suppression of the *C*–*E* curves with increasing bulk amine concentration in the electrolyte solution takes place in the potential range of the characteristic minimum in the vicinity of the potential of zero charge (E^{pzc}) of the gold electrode and of the adsorption/desorption maximum on the negative charged surface. This observation gives a clear evidence of the substitution of water with amine molecules at the gold surface. The amine molecules are able to form surface complexes by the coordinative interaction between the electrode surface and the electron lone pair at the N atom. A relatively strong adsorption of aliphatic amines on gold manifests itself

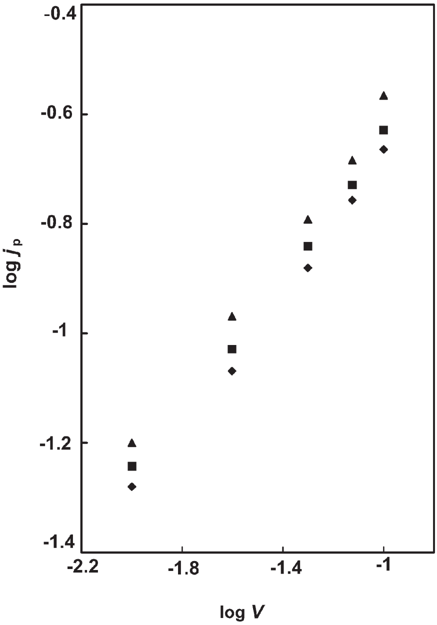


FIG. 4
The dependence of logarithm of the peak current density on logarithm of the potential sweep rate for 1 mM amine on the gold electrode in 1 × 10^2 mM NaOH: ethylamine (◆), propylamine (■), butylamine (▲)

by the fact that the C–E curves for the highest solute concentration, at $E <$ –1000 mV vs SCE do not coincide with the corresponding tensammetric curve of the supporting electrolyte solution. This implies that some adsorbate molecules still remain at the electrode surface.

It should be emphasised that the potential range in which amine molecules adsorb on gold/alkaline solution interface coincides with that in which adsorption of hydroxide ions occurs[24,27–29]. Thus a quantitative evaluation of the C–E curves is not possible because of the competing adsorption of amine and hydroxide ions at the electrode surface. The tensammetric measurements with a non-adsorbing supporting electrolyte solution, 2×10^1 mM $NaClO_4$, have been discussed elsewhere[26]. Stronger interaction between the amine molecule and the electrode surface, reflected by the standard Gibbs energy of adsorption (ΔG^0_{ad}) increasing for each consecutive member of the amine homologous series[27], may account for the observed increase in the oxidation rate with increasing number of carbon atoms in the amine molecule (see Fig. 1). A comparison of the data in Fig. 6 with those presented previously in a neutral medium (see Figs 1 and 2 in ref.[26])

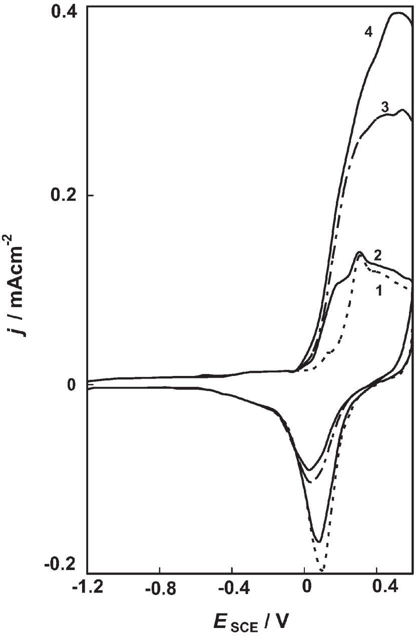


FIG. 5
Cyclic voltammograms of the gold electrode in 1×10^2 mM NaOH (1) and with increasing concentration of propylamine: 0.1 (2), 5 (3), 10 (4) mM; dE/dt = 100 mV s^{-1}

reveals that the potential range of amine adsorption as measured with respect to E^{pzc} does not change with pH of the electrolyte solution. However, when transferring the results obtained in a neutral medium to the alkaline system, one has to keep in mind different properties of the electrolyte solutions.

In the light of the above-presented results and taking into account that acetonitrile was determined as a product of ethylamine oxidation, possible reaction pathways (Scheme 1) involve the first electron transfer connected with the oxidation of the hydrogen atom abstracted from the NH_2 group of adsorbed amine molecule as the reaction rate determining step.

The presence of acetonitrile as a product of ethylamine oxidation has been confirmed by ^{1}H and ^{13}C NMR analysis of solution after ethylamine electrolysis. The following peaks were detected in ^{1}H NMR (CD_3Cl) spectrum: δ 1.92 (3 H, s, CH_3) and in ^{13}C NMR (CD_3Cl) spectrum: δ 1.3 (CH_3); 117.9 (CN), where δ is the shift in ppm of the NMR signal. Nitrile is known to be strongly adsorbed on gold[30] and thus it may block the electrode sur-

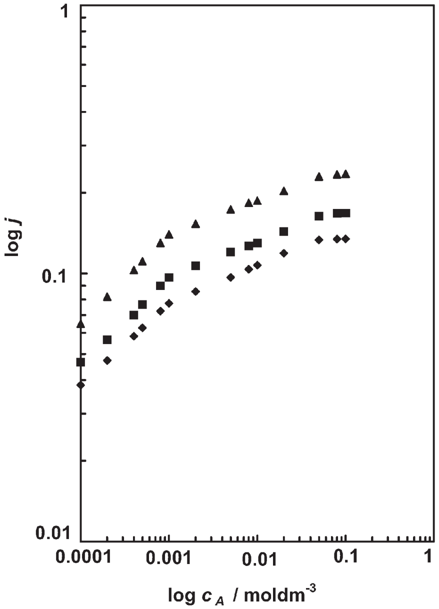
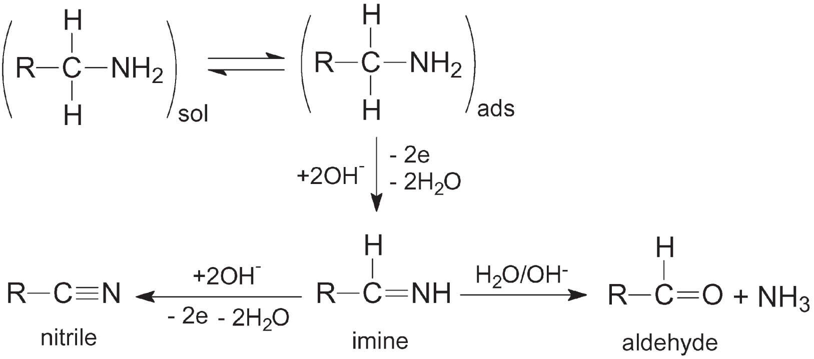


FIG. 6
The dependence of the current density at E = 150 mV vs SCE on the amine concentration in 1×10^{2} mM NaOH: ethylamine (◆), propylamine (■), butylamine (▲); dE/dt = 100 mV s^{-1}



SCHEME 1

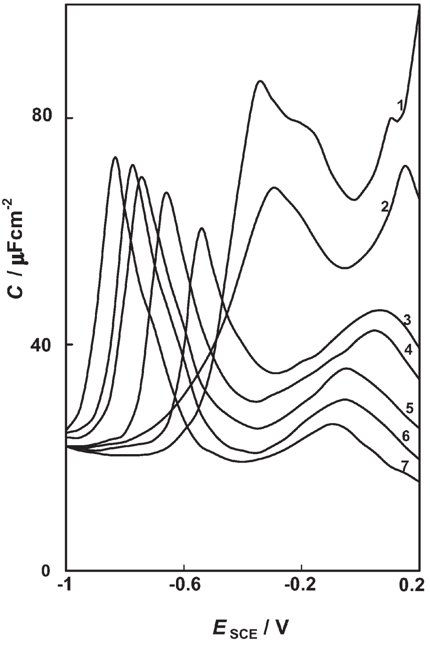


FIG. 7

Differential capacitance–potential curves recorded on the gold electrode in 1×10^2 mM NaOH (1) and with increasing concentration of butylamine: 5×10^{-2} (2), 5×10^{-1} (3), 1 (4), 1×10^1 (5), 2×10^1 (6), 1×10^2 (7) mM; $dE/dt = 5$ mV s^{-1}

face for further substrate adsorption and oxidation. This may be, among others, the reason for the approximately unaltered current density observed at higher amine concentrations (Fig. 6). On the other hand, the hydrolysis of imine may also take place giving appropriate aldehydes and ammonium salts as products. However, aldehydes have not been detected in the reaction products after electrolysis. Some further details about the proposed mechanism, especially the existence of the intermediate species should be elucidated by using in situ spectroelectrochemical techniques.

CONCLUSIONS

From the kinetic and tensammetric results it is evident that amine molecules are adsorbed on the gold electrode surface in the range of potentials preceding the electrooxidation process. The process considered occurs via a mechanism catalysed by the gold oxide layer and leads to imine and further to nitrile. Differences in the adsorption properties of amines may account for the observed increase in the oxidation rate with increasing number of the carbon atoms in the amine molecule.

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