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Structure—reactivity relationships: the oxidation of aliphatic amines on the gold electrode

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Abstract

The electrooxidation of isomeric butylamines at a gold electrode in contact with an alkaline electrolyte solution was studied by cyclic voltammetry. Differences in the electrochemical activity of the isomers were found. It was ascertained that the amine oxidation is catalysed by the gold oxide layer. Substrate molecules are adsorbed on the gold electrode surface in the potential range preceding the oxidation. The adsorptive behaviour of the substrate molecules was evaluated on the basis of changes in the differential capacitance of the double layer at the electrode/solution interface.

1. Introduction

Among the noble metals platinum and gold are the most active electrocatalysts. Platinum has the highest catalytic activity in acid solutions [1–3], whereas gold is the most active in alkaline environments [1, 3–14]. The oxidation of organic substances at platinum is accompanied by a characteristic, though very undesirable, effect of surface blocking by strongly adsorbed intermediate species [2]. Despite a relatively high heat of adsorption observed for hydrogen on platinum, enabling fast dehydrogenation of organic compounds in the range of low electrode potential, the inhibition effect is dominant. This effect does not apply to the gold electrode which is characterized by relatively weak adsorption properties [15–22]. Though these properties account for the poor catalytic activity of gold in acid solution in alkaline solutions, when hydroxide ions are adsorbed on the gold surface [6, 7, 13, 23–29], gold proves to be a more effective catalyst for dehydrogenation of organic compounds than platinum. The oxidation rate of organic compounds on gold in alkaline solutions is higher than that on platinum though often, but not always, at higher electrode potentials [1, 7, 13].

The organic compounds selected for this study were aliphatic amines, widely used as starting or intermediate agents in the production of various chemical compounds such as polymers, corrosion inhibitors, pesticides and pharmaceuticals. In spite of the unquestionable significance of aliphatic amines in industrial, clinical and environmental applications [30] their electrochemical behaviour has been scarcely examined. For platinum electrodes in acetonitrile, Mann et al. [31, 32] have established that the mechanism of oxidation of aliphatic amines depends on the electrode potential. Horányi et al. [33, 34] have postulated that the oxidation of methylamine and butylamine at a platinized platinum electrode in acidic, as well as in alkaline medium, leads to adsorbed cyanide species. This conclusion has been confirmed by spectroscopic results of Huerta et al. [35, 36] who studied the oxidation of methylamine and ethylamine on monocrystalline Pt electrodes. Studies on gold have been limited to the voltammetric response of ethylamine upon anodic oxidation in aqueous alkaline media. The simultaneous oxidation of ethylamine and gold oxide (AuO) formation has been observed both by Luo et al. [37] and Johnson et al. [38–40]. Acetonitrile has been proposed as a product of this amine oxidation.

Taking into account that little work has been devoted to aliphatic amine oxidation, more research is needed to clarify the electrooxidation mechanism of this class of organic compound. This study concerns the oxidation of 2-butylamine and iso-butylamine on gold in contact with an alkaline supporting electrolyte solution. For completeness, the results were supplemented with data on adsorption of the molecules under investigation.

2. Experimental

The solutions were prepared using water purified in a Millipore Milli-Q system, 2-butylamine, iso-butylamine of Aldrich analytical grade quality and NaOH of Merck analytical grade quality. The measurements were performed at 295 K. All solutions were purged with high purity argon.

Cyclic voltammetric (*j–E* curves) and differential capacitance of the electric double layer versus electrode potential (*C–E*) curves were measured in a conventional three-compartment cell separated by glass frits using a gold bead (99.999% purity) as working electrode and a gold sheet as counter electrode. A hydrogen electrode (RHE) in the supporting electrolyte solution, as proposed by Will et al. [41], was used as reference. For easier comparison with published data, all potentials are quoted versus the saturated calomel electrode (SCE).

The experimental setup used in this work to record the *j–E* and *C–E* curves was described previously [9]. The *C–E* curves were obtained by superimposing *ac* sinusoidal voltage signal (15 Hz, 5 mV) on a slow linear electrode potential scan ($dE/dt = 0.005$ V s^{-1}). It should be noted that a slower scan rate of 0.002 V s^{-1} did not affect the *C–E* curves. The equilibrium of adsorption/desorption was checked in additional experiments at different frequencies. For frequencies in the range 5–40 s^{-1} no frequency dispersion of the differential capacity was observed in the potential range between $E = -1.0$ V and $E = 0.1$ V versus SCE, in supporting electrolyte. This potential range narrows ($E = -0.4$ V to $E = 0.0$ V) in solution containing amine. It was found that stirring of the solutions had no effect on the course of the *C–E* curves, which indicated that mass transport did not limit the rate of adsorption/desorption of amine at the bulk concentrations studied. These findings suggest that the differential capacity data in the above mentioned potential range can be considered at equilibrium.

Prior to each series of measurements, the working electrode was electrochemically activated by cycling ($dE/dt = 0.1$ V s^{-1}) in the potential range between $E = -1.1$ V and $E = 0.0$ V versus SCE in supporting electrolyte (0.1 M NaOH), in which no electrochemical reactions occur on the gold surface. This procedure avoids structural changes at the gold surface. Furthermore, the roughness factor remains constant. When reproducible values of the differential capacitance of the double layer (*C*) were obtained, a roughness factor of 1.1 was calculated assuming the differential double layer capacitance of a smooth gold electrode of 22 μF cm^{-2} at *E* between -1.0 V and -0.85 V versus SCE [42, 43]. 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. The shapes of the *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.

3. Results and discussion

The cyclic voltammograms recorded at the gold electrode in the supporting electrolyte solution, 0.1 mol dm^{-3} NaOH (curve 1), and in the presence of 2-butylamine and iso-butylamine are depicted in Figs. 1 and 2, respectively. According to Newman et al. [44] the bare gold surface in an alkaline solution is covered by different species depending on the electrode potential. The well-defined anodic peak at $E = 0.3$ V versus SCE visible in the *j–E* curve of the bare electrode is assigned to gold oxide formed via the reaction: $2Au + 3H_2O \rightarrow Au_2O_3 + 6H^+ + 6\bar{e}$ and the cathodic peak at $E = 0.08$ versus SCE corresponds to its reduction. As can be seen from Figs. 1 and 2 both amines under investigation are inactive at the gold electrode at low potentials. The electrooxidation of 2-butylamine begins at potentials of about $E \approx -0.075$ V versus SCE and proceeds irreversibly in parallel with gold oxide formation, whereas iso-butylamine oxidation is shifted by about 0.05 V in the positive direction. As follows from

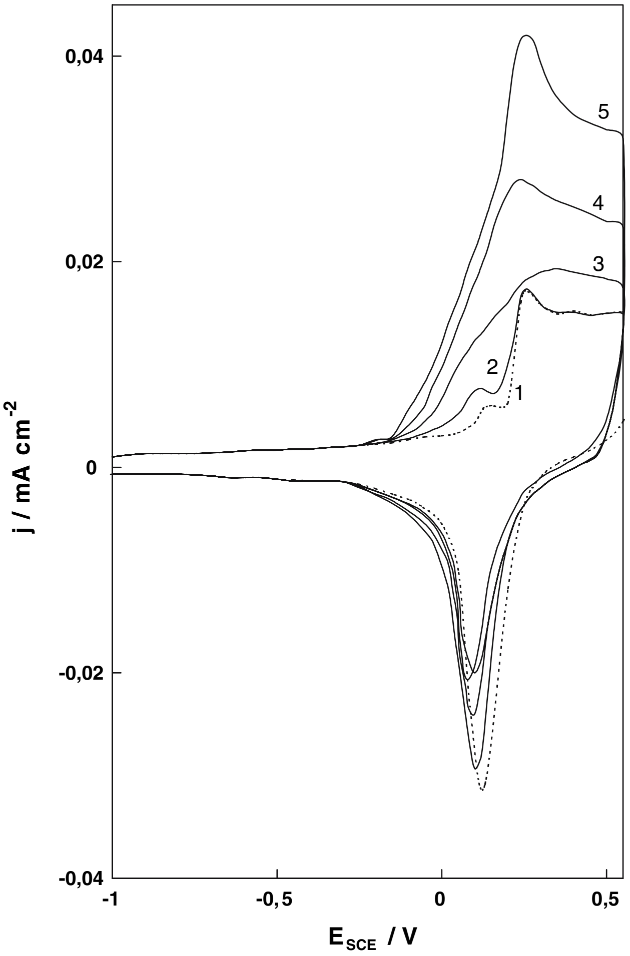


Fig. 1. Cyclic voltammograms of gold electrode in of 0.1 mol dm^{-3} NaOH (1) and with increasing concentration of 2-butylamine: (2) 0.00001 mol dm^{-3}; (3) 0.0001 mol dm^{-3}; (4) 0.001 mol dm^{-3}; (5) 0.01 mol dm^{-3}, $dE/dt = 0.01$ V s^{-1}.

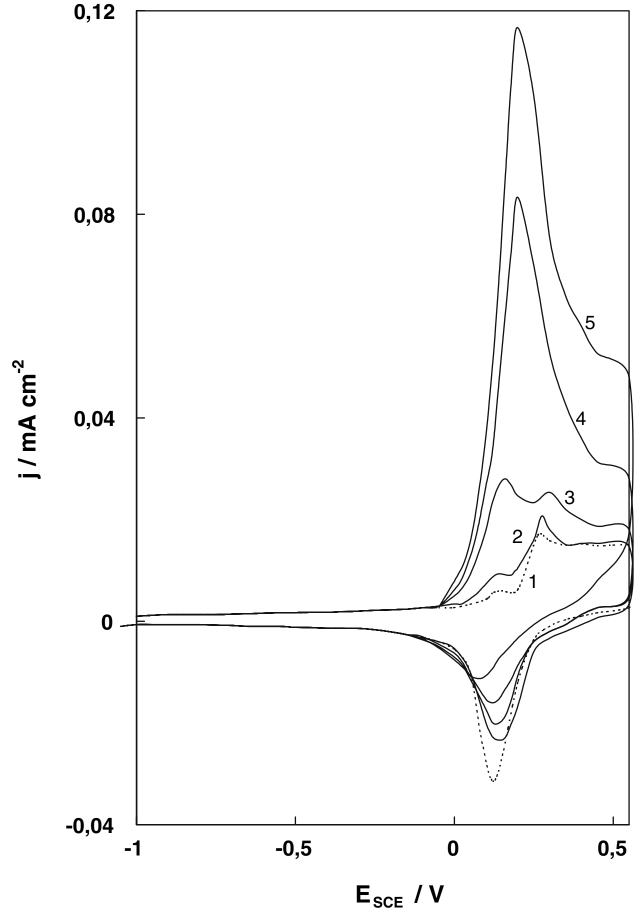


Fig. 2. Cyclic voltammograms of gold electrode in of 0.1 mol dm^{-3} NaOH (1) and with increasing concentration of iso-butylamine: (2) 0.00001 mol dm^{-3}; (3) 0.0001 mol dm^{-3}; (4) 0.001 mol dm^{-3}; (5) 0.01 mol dm^{-3}, dE/dt = 0.01 V s^{-1}.

the cyclic voltammograms the charge used for reduction of gold oxide in the presence of amines is smaller relative to that consumed in a solution without a solute. This observation points to participation of the gold oxide in the oxidation of amines. A similar conclusion was drawn for methanol oxidation on polycrystalline gold [45, 46].

For both amines studied a characteristic feature is an increase in anodic current with increased substrate concentration (c_A) in the electrolyte. The j–E curves are shifted negatively when the bulk amine concentration increases and at the same time the maximum in the anodic peaks shift positively, Figs. 1 and 2. The latter observation is typical of reactions involving adsorbed molecules. An increase in amine coverage may generate a decrease in 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.

It should be noted that the oxidation of the isomer with the –NH$_2$ group attached to the first ordered carbon atom (iso-butylamine) yields current densities about three times higher than those obtained for the isomer with the –NH$_2$ group linked to the secondary ordered carbon atom (2-butylamine). The striking difference between the two isomers, caused by the molecular structure, is obvious.

Adsorption of the amines preceding their oxidation is supported by the results of differential capacitance of the electric double layer versus potential measurements. This technique provides a simple way to achieve reproducibility of the electrode surface, in particular in the case of metals which undergo structural rearrangement or anodic oxidation, such as gold [22]. The representative sets of C–E curves illustrating changes in the differential capacitance of the double layer as a function of the gold electrode potential, obtained in 0.1 mol dm^{-3} NaOH as supporting electrolyte and with various butylamines concentrations (c_A) are presented in Figs. 3 and 4.

A gradual suppression of the C–E curves with increasing bulk amine amount in the electrolyte takes place both in the potential range of the characteristic minimum in the vicinity of the potential of zero charge (E_{pzc}) of the gold electrode [47, 48] and in the adsorp-

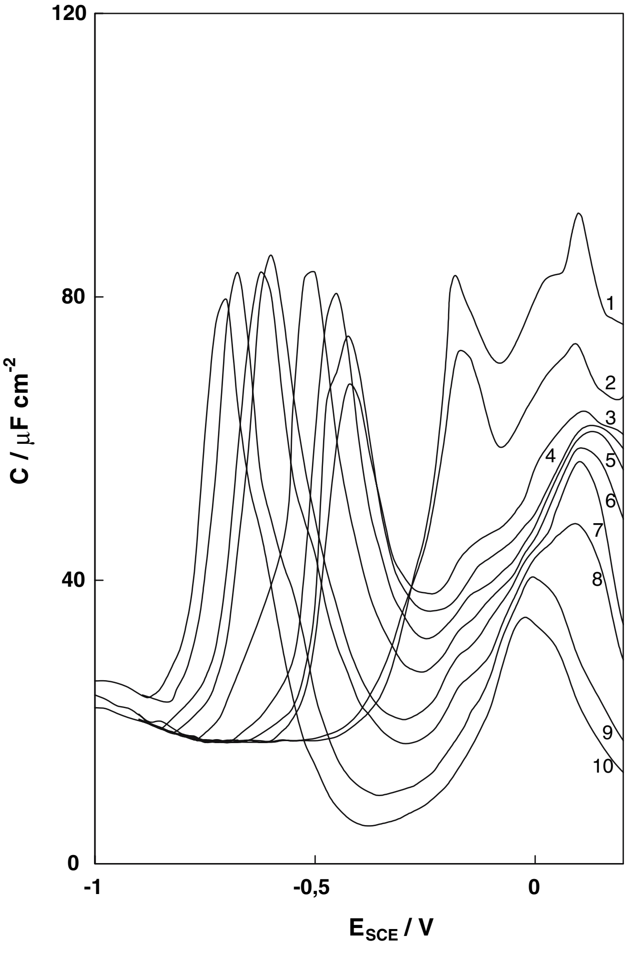


Fig. 3. Differential capacitance - potential curves for gold electrode in 0.1 mol dm^{-3} NaOH (curve 1) and with increasing iso-butylamine concentration: (2) 0.00001 mol dm^{-3}; (3) 0.0001 mol dm^{-3}; (4) 0.001 mol dm^{-3}; (5) 0.002 mol dm^{-3}; (6) 0.005 mol dm^{-3}; (7) 0.01 mol dm^{-3}; (8) 0.05 mol dm^{-3}; (9) 0.1 mol dm^{-3}; (10) 0.5 mol dm^{-3}, dE/dt = 0.005 V s^{-1}.

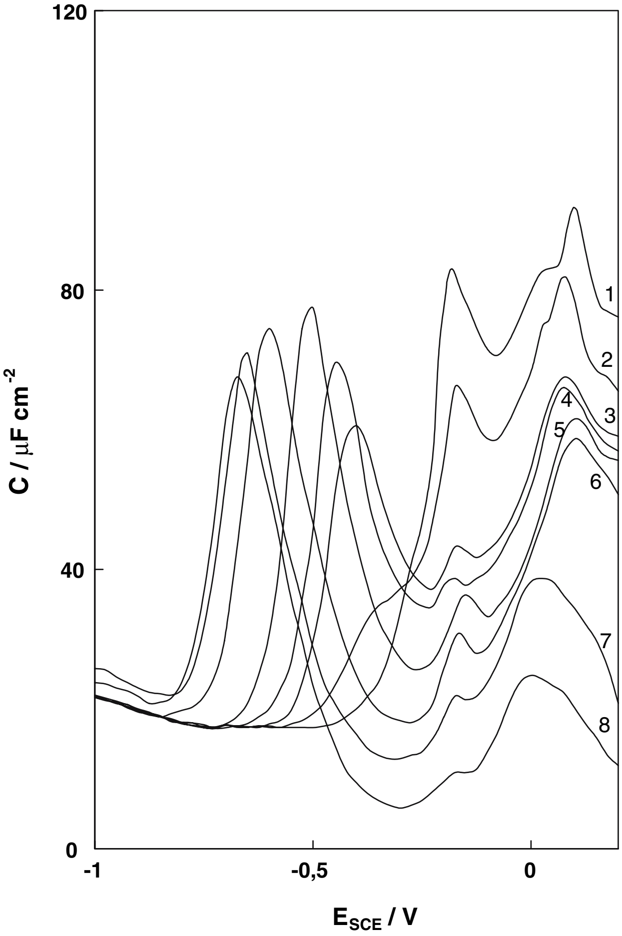


Fig. 4. Differential capacitance - potential curves for gold electrode in 0.1 mol dm^{-3} NaOH (curve 1) and with increasing 2-butylamine concentration: (2) 0.00005 mol dm^{-3}; (3) 0.0005 mol dm^{-3}; (4) 0.001 mol dm^{-3}; (5) 0.05 mol dm^{-3}; (6) 0.1 mol dm^{-3}; (7) 0.5 mol dm^{-3}; (8) 1 mol dm^{-3}, d*E*/d*t* = 0.005 V s^{-1}.

tion/desorption maximum on the negatively charged surface. This observation gives clear evidence for the substitution of water with amine molecules at the gold surface. The amine molecules are able to form surface complexes by coordinative interaction between the electrode surface and the electron lone pair localized at the nitrogen atom. Relatively strong adsorption of aliphatic amines on gold is manifested by the fact that the *C–E* curves for the highest solute concentration, at $E < -1.0$ V versus SCE do not coincide with the corresponding *C–E* curve of the supporting electrolyte solution. This implies that some adsorbate molecules still remain at the electrode surface. An inspection of the plots $\Theta = (C_{\Theta=0} - C_{\Theta})/(C_{\Theta=0} - C_{\Theta=1})$ versus c_A provides evidence for a stronger interaction of iso-butylamine than 2-butylamine with the gold electrode. A decrease in the differential capacitance is faster and a maximum value of the surface coverage (Θ) is achieved at a lower amine concentration in the case of iso-butylamine, the concentration of this isomer responsible for $\Theta = 1$ is twofold smaller than that of 2-butylamine. It should be noted that the potential range in which amine molecules are adsorbed on the gold/alkaline solution interface overlaps with that in which the adsorption of hydroxyl ions occurs [13, 21, 24–29]. Thus, a quantitative evaluation of the *C–E* curves is not possible because of the competing adsorption of amine and hydroxyl ions at the electrode surface.

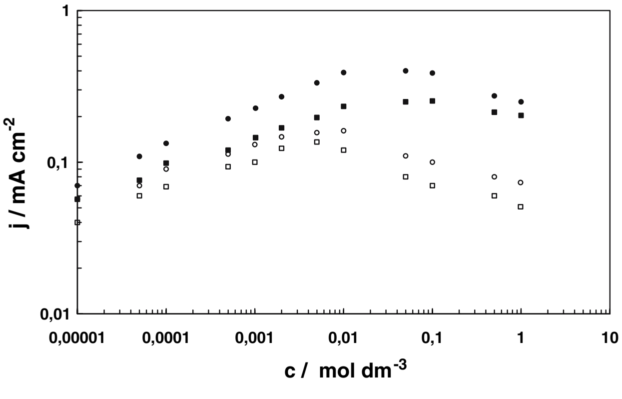


Fig. 5. Dependence of current density on amine concentrations in 0.1 mol dm^{-3} NaOH at E = 0.15 V versus SCE for (□) 2-butylamine; (■) iso-butylamine and at E = 0.2 V versus SCE for (○) 2-butylamine; (●) iso-butylamine, d*E*/d*t* = 0.1 V s^{-1}.

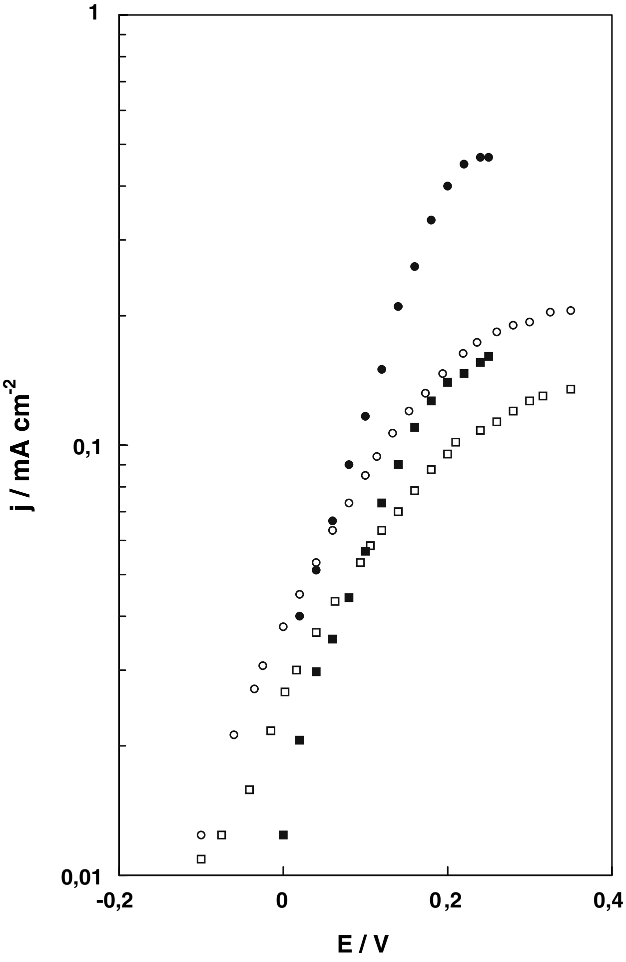


Fig. 6. Dependence of current density on gold electrode potential in of 0.1 mol dm^{-3} NaOH for: 0.0001 mol dm^{-3} 2-butylamine (□) and iso-butylamine (■); 0.01 mol dm^{-3} 2-butylamine (○) and iso-butylamine (●), d*E*/d*t* = 0.1 V s^{-1}.

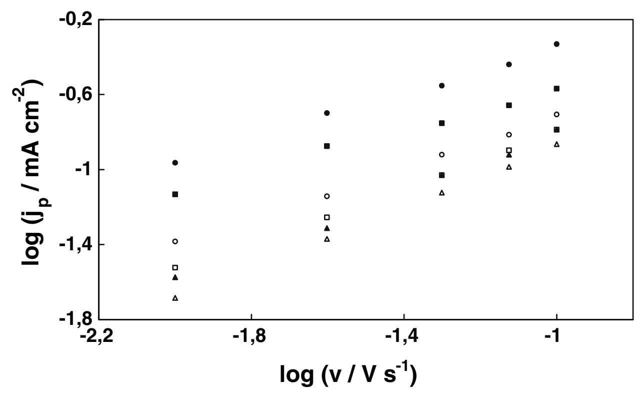
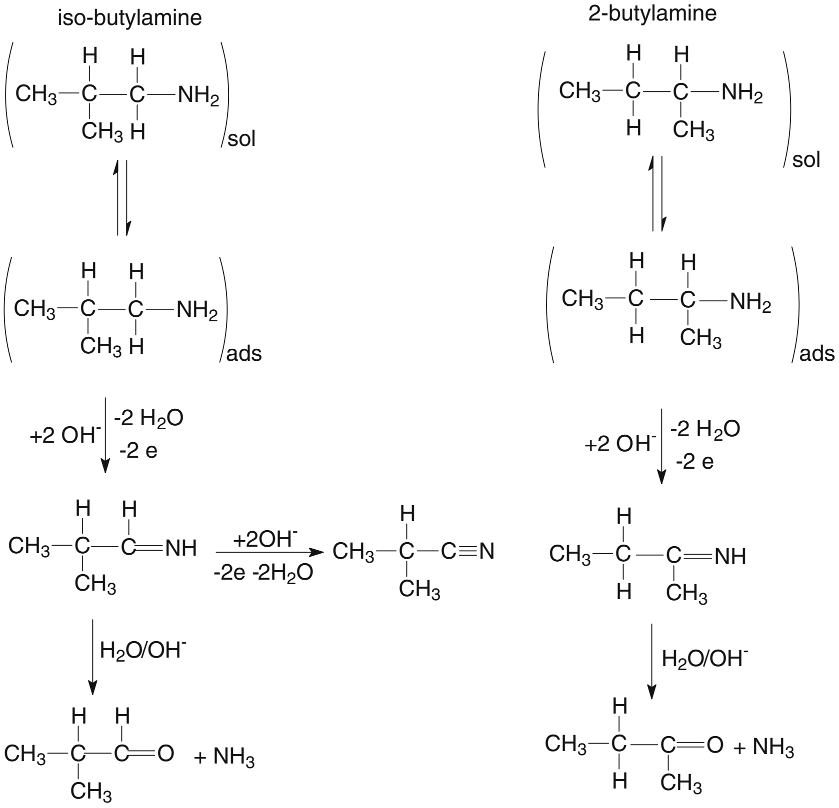


Fig. 7. Dependence of logarithm of peak current density on logarithm of potential sweep rate for iso-butylamine of 0.0001 mol dm^{-3} (▲); 0.001 mol dm^{-3} (■); and 0.01 mol dm^{-3} (●) and for 2-butylamine of 0.0001 mol dm^{-3} (Δ); 0.001 mol dm^{-3} (□); 0.01 mol dm^{-3} (○) on the gold electrode in 0.1 mol dm^{-3} NaOH.

The decisive role of the 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. The plots of logarithm of the current density versus the logarithm of amine concentration at constant electrode potentials, $E = 0.05$ V versus SCE, are shown in Fig. 5. The slope of the straight lines of the appropriate log j–log c_A relationships gives the reaction order z_A equal 0.20 ± 0.01 for $c_A \leq 0.01$ mol dm^{-3}, being the same for both amines. An increase in the surface coverage by absorbed substrate molecules seems to be the reason for a decrease in the reaction order for amine concentrations over 0.01 mol dm^{-3} (see Fig. 5).

Moreover, adsorption of the organics affecting the reaction kinetics is evident from the Tafel analysis. The j–E relationships plotted in log j–E coordinates give straight lines in the potential range 0.05 V–0.2 V versus SCE, (Fig. 6) giving the value of Tafel slope, $\mathrm{d}E/\log j = 2.303RT/\alpha nF$, equal 0.20 ± 0.01 V and 0.25 ± 0.02 V per decade for iso-butylamine and 2-butylamine, respectively. The electron transfer coefficients, αn, consistently lower than 0.5 and decreasing with increasing amine concentration support the assumption of an adsorption step preceding the first electron transfer step determining the overall reaction rate (rds). In the case of the simple rds with no contribution of adsorption, a slope of only 0.12 V decade^{-1} should be found [49]. As expected, on oxidation of the adsorbed substrate molecules the current densities do not decrease as a result of solution stirring by bubbling inert gas.

Further insight into the mechanism of amine oxidation was obtained by examination of the process studied at various potential sweep rates. log j_p versus log v plots were constructed, (Fig. 7). The average values of the dlog j_p/dlog v slope for the appropriate straight lines are 0.64 and 0.73 for iso-butylamine and 2-butylamine, respectively. The fact that the slopes never attain the limiting values of 1 or 0.5 means that the mechanism of oxidation is not pure from the kinetic point of view,



Scheme 1.

since for a pure adsorption controlled process the slope should be 1 and for a pure diffusion controlled process it should be 0.5.

By taking into account the kinetic and differential capacitance results, the possible reaction pathways for electrooxidation of the aliphatic amines under investigation on gold in alkaline medium can be described as follows: Scheme 1.

The oxidation of the amine molecules, adsorbed at the metal surface covered with a gold oxide layer, takes place at the nitrogen atom and results in the formation of a radical cation, followed by its deprotonation. The first product of amine oxidation is imine, which for isobutylamine can then be oxidized to nitrile. On the other hand, the hydrolysis of imine may also take place giving ammonium and the appropriate aldehyde or ketone as a final product, depending on the order of the carbon atom to which the amino group in the substrate molecule was attached.

The small differences in the values of the kinetic parameters obtained for both amines suggest that their electrooxidation proceeds in the same way. The observed differences in current density obtained for isobutylamine and 2-butylamine may be a consequence of their different molecular structure and, thus, different adsorbability at the gold/solution interface.

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