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Adsorption of methylamine at a polycrystalline gold/solution interface

Teresa Łuczak*

Department of Chemistry, A. Mickiewicz University, Grunwaldzka 6, PL-60-780 Poznań, Poland

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Abstract

Adsorptive behaviour of the methylamine molecules has been investigated by measuring changes in the differential capacitance of the double layer at the gold/solution interface by the tensammetric method. The differences in adsorption parameters at $\Theta < 0.8$ and >0.8 have been explained by changes in arrangement of the adsorbate.

Keywords: Adsorption; Gold electrode surface; Amines; Tensammetry; Voltammetry

1. Introduction

The modelling of electrochemical systems and their practical applications requires the knowledge of adsorption properties of electrode materials towards substrates and reactions intermediates. Valuable information on the adsorption behaviour of organic molecules is provided by measurements of a double layer capacitance of the electrode/electrolyte solution interface as a function of electrode potential [1–7]. In combination with the results of kinetic measurements, these data enable explanation of the electrosorption and subsequent electrooxidation or reduction processes.

An important part of the electrocatalytic processes is the oxidation of aliphatic organic compounds because of their practical applications. Although great significance of aliphatic amines from the industrial, clinical and environmental points of view is unquestionable, there is not much information on their electrochemical properties. On the gold electrode the relevant studies have been limited only to voltammetric response of ethylamine [8–10] upon anodic oxidation in an aqueous alkaline media. Similar data have been presented for mercury [11,12], silver [13–16] and platinum [17–22] electrodes. Adsorption studies of C_8, C_{10}, C_{16} and C_{18} amines have been carried out on gold in $LiClO_4$ methanolic solutions [23].

This paper reports, the adsorption behaviour of methylamine on a polycrystalline gold electrode as characterized by tensammetry. To our knowledge, this is the first report in literature on this subject. This study is a part of broader comparative electrochemical investigation of aliphatic amines at the electrode/solution interface undertaken in our laboratory.

2. Experimental

Cyclic voltammetric and tensammetric studies were performed in a conventional three-compartment cell separated by glass frits using a polycrystalline 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 and his co-worker [24,25] was used as a reference electrode. For easier comparison with published data, all the potentials are quoted versus the saturated calomel electrode (SCE). The surface area of the working electrode was determined as $0.3\ cm^2$. A roughness factor of 1.1 was calculated assuming the differential double layer capacitance of a smooth gold electrode of $22\ \mu F\ cm^{-2}$ at E between -0.95 and -0.75 V versus SCE [26,27].

The solutions were prepared using Millipore water, methylamine (Aldrich) and $NaClO_4$ (Fluka) twice-recrystallized from water. 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 [28]. The C–E curves were obtained by superimposing *ac* sinusoidal voltage signal (15 Hz, $5\ mV_{pp}$) on a slow

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* Tel.: +48 61 865 8008; fax: +48 61 865 8008.
E-mail address: telucz@amu.edu.pl.

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linear electrode potential scan ($dE/dt = 0.005\ \mathrm{V\,s^{-1}}$). It should be noted that a slower scan rate of $0.002\ \mathrm{V\,s^{-1}}$ did not affect the observed tensammetric curves. The equilibrium of the adsorption/desorption was checked in additional experiments at different frequencies. For the frequencies in the range from 5 to $40\ \mathrm{s^{-1}}$ no frequency dispersion of the differential capacity has been observed in the potential range between $E = -1.1$ and 0.1 V versus SCE, in the supporting electrolyte solution. This potential range narrows ($E = -0.25$ to 0.1 V) in the solution containing methylamine of concentrations between $5 \times 10^{-6}\ \mathrm{mol\,dm^{-3}}$ and $1 \times 10^{-1}\ \mathrm{mol\,dm^{-3}}$. It was found that the 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 methylamine at the bulk concentrations studied. The above experimental findings allow concluding that the differential capacity data in the above mentioned potential range can be considered at equilibrium.

As a preliminary step to each experiment, the working electrode was electrochemically activated in the supporting electrolyte solution by cycling the electrode potential ($dE/dt = 0.1\ \mathrm{V\,s^{-1}}$) between the onset of hydrogen and oxygen evolution, until a stable voltammogram and reproducible values of the double layer capacitance were obtained.

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.

3. Results and discussions

Fig. 1 presents a set of curves of the differential capacitance of the double layer as a function of the polycrystalline gold electrode potential (*C*–*E* curves) recorded in a supporting electrolyte solution ($2 \times 10^{-2}\ \mathrm{mol\,dm^{-3}}$ $NaClO_4$) and in the same solution with increased concentration of methylamine (c_A), illustrating its adsorption behaviour (for clarity of the picture not all *C*–*E* curves for studied solute concentrations are presented). The *C*–*E* curve measured with the gold electrode in the base solution at $E = -0.04$ V versus SCE reveals a characteristic diffusion minimum (curve 1 in Fig. 1). The potential of this minimum can be assumed as that of zero charge (E^{pzc}), since at the low $NaClO_4$ concentration used in this work the specific adsorption of its anions can be neglected [26]. The evaluated value of E^{pzc} is in good agreement with literature data [26,29] for a polycrystalline Au electrode, and for a monocrystalline Au(1 1 0) electrode [30,31]. The inset in Fig. 1 corresponds to the cyclic votammogram of the gold electrode in the base electrolyte solution. As follows from the figure, in a wide range of potential ($E = -1.04$ to 0.76 V versus SCE) no electrochemical reactions occur on the electrode surface.

The *C*–*E* curves recorded for the solution with methylamine exhibit a typical feature of neutral organic compounds with adsorption occurring in the region of the potential of zero charge. Upon addition of increasing concentration of the solute in the bulk, the capacitance significantly decreases and the *C*–*E* curves are flattened. For the highest amine concentration studied a characteristic hump (the doted curve 9 in Fig. 1) appears on the tensammetric curve. Such an irregular change in the course of *C*–*E* curves may testify to a change in the arrangement of the adsorbate molecules at the gold/electrolyte solution with increasing solute concentration. The differential capacitance of the double layer for the majority of the methylamine concentrations studied reaches the same value at $E \approx -0.94$ V versus SCE. Only for the highest solute concentration the *C*–*E* curves do not merge with the one of the supporting electrolyte solution. This indicates that the adsorbate molecules remain at the electrode surface and confirms a strong adsorption of methylamine on the gold electrode. A similar behaviour has been observed for adsorption of other neutral organic compounds [32–35].

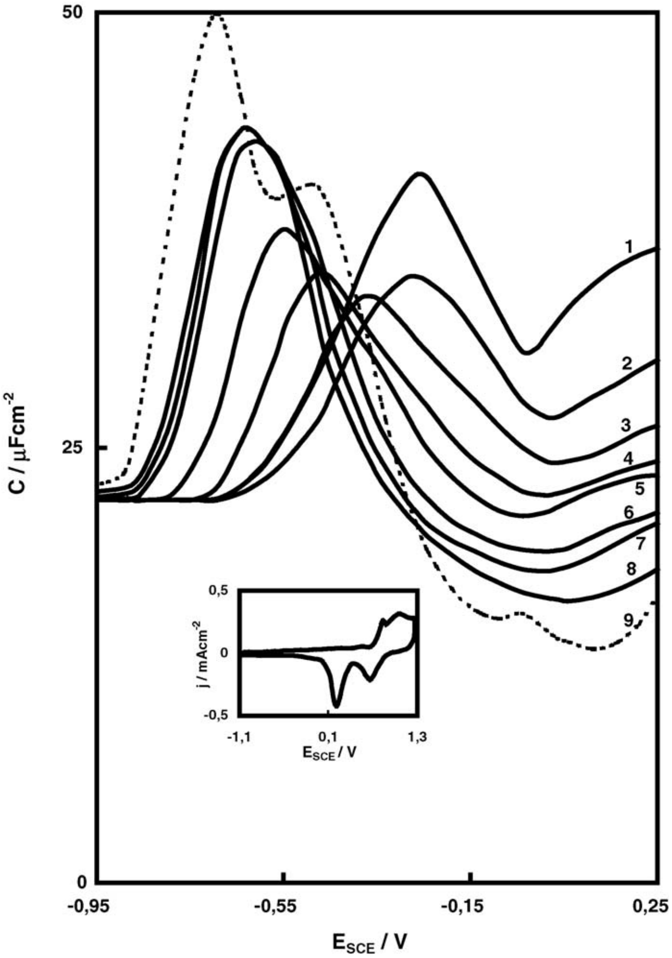

Fig. 1. Differential capacitance–potential curves recorded on the polycrystalline gold electrode in $2 \times 10^{-2}\ \mathrm{mol\,dm^{-3}}$ $NaClO_4$ (curve 1) and with increased methylamine concentration: (2) $7.65 \times 10^{-6}\ \mathrm{mol\,dm^{-3}}$; (3) $1.93 \times 10^{-4}\ \mathrm{mol\,dm^{-3}}$; (4) $4.80 \times 10^{-4}\ \mathrm{mol\,dm^{-3}}$; (5) $9.38 \times 10^{-4}\ \mathrm{mol\,dm^{-3}}$; (6) $4.75 \times 10^{-3}\ \mathrm{mol\,dm^{-3}}$; (7) $7.38 \times 10^{-3}\ \mathrm{mol\,dm^{-3}}$; (8) $9.21 \times 10^{-3}\ \mathrm{mol\,dm^{-3}}$; (9) $9.40 \times 10^{-2}\ \mathrm{mol\,dm^{-3}}$. $dE/dt = 0.005\ \mathrm{V\,s^{-1}}$. Inset: cyclic voltammogram of the polycrystalline gold electrode in $2 \times 10^{-2}\ \mathrm{mol\,dm^{-3}}$ $NaClO_4$. $dE/dt = 0.1\ \mathrm{V\,s^{-1}}$.

At potentials negative to E^{pzc} a characteristic adsorption/desorption peaks appear on the *C*–*E* curves which shift