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Adsorption of adipic acid conjugates at the Au(1 1 1) electrode|aqueous solution interface ☆

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ABSTRACT

The adsorption of adipic acid, an aliphatic dicarboxylic acid, has been studied at the Au(1 1 1) electrode|aqueous solution interface by cyclic voltammetry, chronocoulometry and *in situ* infrared spectroscopy. The voltammograms recorded at different pH values in adipic acid, biadipate and adipate solutions point to the adsorption of anionic species. A potential dependent order–disorder phase transition is apparent from the voltammetric curves, the transition potential being directly influenced by the solution pH. From infrared spectra it is concluded that as the electrode potential is made more positive, the amount of carboxylic groups in the adsorbed layer increases. The maximum surface excess concentration, $\Gamma = (4.4 \pm 0.6) \times 10^{-10}$ mol cm^{-2}, and the adsorption free energy, $-\Delta_{\mathrm{ads}}G = 125–190$ kJ mol^{-1}, have been determined by a thermodynamic analysis of the chronocoulometric data.

1. Introduction

Self-assembly provides a versatile method of obtaining highly organised two-dimensional films with specific interfacial properties. Although self-assembled monolayers (SAMs) formed from sulphur containing compounds are amongst the most studied systems [1,2], other species such as nucleic acid components or heterocyclic molecules can also form monolayers with long-range order [3,4]. In the recent years, there has been a growing interest in using carboxylic acids as building blocks for SAMs [5] or for metal–organic frameworks [6]. Most of these studies have been conducted without explicitly examining the influence of the electric field, which may play a determining role and affect the nature and structure of the film. For instance, carboxylic and polycarboxylic acids can be adsorbed on metal surfaces and form different adlayer structures depending on the electrode potential [7–12]. The affinity of carboxylate group for gold surfaces has also been used to measure the conductance of individual dicarboxylic molecules tethered between a gold surface and the gold tip of a scanning tunnelling microscope [13]; these experiments are typically performed in high electric fields. Studying the adsorption, under polarisation conditions, of dicarboxylic acids on model surfaces allows a better understanding of the influence of the electrode potential on the nature, interfacial structure and thermodynamic properties of the adsorbed monolayers. We present herein an electrochemical and spectroscopic study on a model system, consisting of adipic acid, a small α,ω-dicarboxylic acid ($HOOC–(CH_2)_4–COOH$), adsorbed on Au(1 1 1).

2. Experimental

2.1. Reagents

All the solutions were prepared with ultrapure water (Milli-Q®, Millipore). Adipic acid (Fluka, puriss. p.a. > 99.5%), KOH (Sigma–Aldrich, FIXANAL® standard solution) and perchloric acid (70%, Fluka, puriss. p.a.) were used without further purification. Potassium perchlorate (Fluka, puriss. p.a. > 99.0%) was recrystallised from ultrapure water. Potassium biadipate and potassium adipate were prepared by addition of, respectively, one or two equivalents of potassium hydroxide to a stock solution of adipic acid.

2.2. Electrochemical experiments

The electrochemical experiments were conducted in an all-glass three electrode cell, using a platinum grid as counter electrode, a

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☆ This work is dedicated to Prof. Jacek Lipkowski on the occasion of his 65th birthday, in recognition of his outstanding contribution to electrochemistry and his role in the fruitful long-standing collaboration between the authors.

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saturated calomel electrode (SCE) as reference electrode, and a gold single-crystal with the (1 1 1) crystallographic orientation as working electrode. The Au(1 1 1) electrode was grown, oriented and polished in the lab following the procedure developed by Hamelin and co-workers [14]. A flame-annealing procedure was applied before each experiment, which involved carefully heating the single-crystal electrode to a gentle orange glow in the flame of a Bunsen burner, and then allowing it to cool down just above the surface of ultrapure water. This procedure results in a thermal reconstruction of the electrode surface. The electrochemical cell was controlled by an Autolab PGSTAT20 (Metrohm-Autolab) potentiostat equipped with a Scangen module. Dissolved oxygen was removed by purging the solution with nitrogen for at least 20 min before starting the experiments, and a flow of nitrogen was maintained over the solution surface throughout the measurements. The hanging meniscus methodology ensured that only the (1 1 1) face of the single-crystal was in contact with the solution.

Chronocoulometry was employed to obtain the charge density curves [15]. The potential was held at −0.4 V for 5 s, then stepped to the potential of interest for 15 s, to ensure that equilibrium was reached. The electrode potential was then switched to −0.65 V, and the current transient recorded. The procedure was then repeated for all the electrode potential values of interest. The current–time curves were converted to charge transients by integration, and extrapolation to $t = 0$ led to the relative charge densities. The absolute charge densities were obtained by determining independently the potential of zero charge of the Au(1 1 1) electrode in the absence of surfactant.

2.3. In situ infrared spectroscopy experiments

The spectroscopic measurements were performed with a Nicolet 5700 (Thermo Scientific) FTIR spectrometer equipped with a liquid nitrogen-cooled MCT detector, and using an in-built syringe type spectroelectrochemical cell with a hemispherical ZnSe optical window. The Au(1 1 1) electrode was approached from the ZnSe window in a thin-layer configuration. The angle of incidence of the IR beam was fixed around the optimum value of 31°, as calculated by the Fresnel equations for the ZnSe|H_2O|Au interface at 1400 $\mathrm{cm^{-1}}$ [16,17]. The electrode potential was controlled by a μ-Autolab Type III (Metrohm-Autolab) potentiostat. Subtractively Normalised Interfacial Fourier Transform Infrared Spectroscopy (SNIFTIR) was employed, applying a multistep procedure. The potential was fixed at the base potential E_1 and 200 interferograms were collected with a *p*-polarisation at a 4 $\mathrm{cm^{-1}}$ resolution. The potential was then stepped to the sample potential E_2, at which 200 interferograms were also recorded. The procedure was repeated 20 times, giving a total of 4000 interferograms for each potential. The SNIFTIR spectra are displayed as a relative difference between the reflectivities recorded at the sample and base potential, $\Delta R/R = [R(E_2) - R(E_1)]/R(E_1)$.

3. Results and discussion

3.1. Voltammetric investigations

Voltammetric curves recorded in the absence and presence of adipic acid in a 0.1 M solution of potassium perchlorate are presented in Fig. 1. The cyclic voltammogram (CV) obtained with the pure electrolyte in the so-called "double-layer" region has the characteristic appearance expected for a solution containing only non-adsorbing ions, and is limited in the positive direction by the onset of gold oxidation. Upon addition of adipic acid into the solution, adsorption of organic species markedly changes the voltammetric response. The adsorption takes place only at potentials above −0.2 V, as inferred from the superposition of the base electrolyte voltammogram below this value. Additionally, adsorption of the surfactant shifts the electrode oxidation to higher potentials. The adsorption of hydroxide anions is known to be the first step of gold oxidation. The shift arises from two effects, namely the decrease of pH (and, accordingly, of hydroxide concentration) due to the addition of adipic acid and the blocking effect of the adsorbed species which prevents the hydroxide adsorption. Fig. 1 shows that the first and second scans (solid and dashed line, respectively) recorded immediately after the flame-annealing procedure (see the Section 2) differ significantly from each other during the forward (positive direction) potential sweep, in accordance with similar observations reported for the adsorption of other carboxylic containing compounds [9]. After annealing, the Au(1 1 1) forms the ($\sqrt{3} \times 22$) reconstructed superstructure, and the pronounced peak centred around +0.32 V in the first scan is attributed to lifting of the reconstruction accompanied by a significant adsorption of the surfactant. Although a potential-induced reconstruction takes place when the electrode potential is swept back to sufficiently negative values, the resulting surface structure is slightly different from the initial, thermally-induced reconstructed surface [18], leading in the second and subsequent voltammetric scans to a distinct current–potential response.

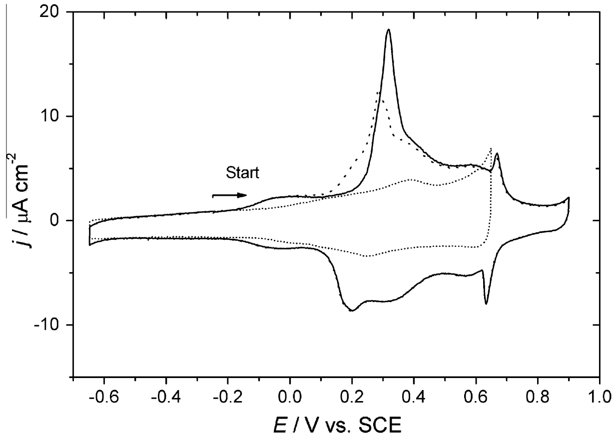

Fig. 1. Cyclic voltammograms recorded in 0.1 M $KClO_4$ in the absence (dotted line) and presence (solid and dashed lines) of 8.0×10^{-5} M adipic acid. The solid and dashed lines represent the first and second cycle, respectively. $\upsilon = 50\ \mathrm{mV\ s^{-1}}$.

The morphology of this steady-state voltammogram is reminiscent of that obtained in the presence of potassium biadipate. In this latter case, it was shown [10] that the sharp peaks (or "spikes") at +0.67 V and +0.63 V are associated with a first-order transition between a disordered layer, at potentials lower than the spikes, and a compact ordered film existing at potentials more positive than the peaks. The compact character of the ordered adlayer is supported by its low, almost potential-independent differential capacitance, and by the difference noted between the anodic and cathodic peak potential values. This hysteresis, often encountered with two-dimensional (2D) condensed layers, is due to different kinetics for the dissolution and formation of the compact film, which usually requires a nucleation step [3]. However, at higher scan rates and/or lower surfactant concentrations, the kinetics of ordering might become controlled by mass-transport, as shown in Fig. 2. This figure presents the steady-state voltammograms recorded at various scan rates in the presence of lower adipic acid concentrations. The voltammograms were normalised by the scan rate to fit in a common ordinate. The scan rate strongly influences the positive-going part of the voltammogram, which is associated with the adsorption of the surfactant and compact layer formation, while the dissolution and desorption are barely affected during the