ARTICLE IN PRESS

Journal of Electroanalytical Chemistry xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Journal of Electroanalytical Chemistry

journal homepage: www.elsevier.com/locate/jelechem

Electric field induced proton transfer at α,ω-mercaptoalkanecarboxylic acids self-assembled monolayers of different chain length

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ARTICLE INFO

Keywords:
Gold
Self-assembled monolayers
Carboxylic acid terminated thiols
Electric field driven protonation/deprotonation
Electrochemical impedance spectroscopy

ABSTRACT

A comprehensive experimental investigation of the influence of the chain length on the electric field induced proton transfer at α,ω-mercaptoalkanecarboxylic acids self-assembled monolayers (SAMs) is conducted by means of voltammetric and electrochemical impedance spectroscopic measurements. The chain length has a significant impact on the total protonation/deprotonation charge and on the kinetics of the phenomenon. The results are discussed in light of existing theoretical models describing this electric field driven protonation/deprotonation process. Characteristic proton transfer frequencies were independently determined by impedance spectroscopy and by scan rate dependent voltammetric analyses. The two types of measurements are in mutual agreement and show that the protonation/deprotonation slows down as the chain length increases.

1. Introduction

Following the pioneering work of Bain and Whitesides [1] on the impact of surface immobilisation on the acidity of acid/base groups of self-assembled monolayers (SAMs), there has been a continuing interest in the last decades in understanding and controlling the parameters affecting the protonation, and hence the charge state, of surface confined molecules and biomolecules. When the SAMs are formed on conductive substrates, the electric field has been used for instance to switch reversibly interfacial properties such as the wettability of surface modified by charged monolayers [2] or to modulate the strength of ionic salt bridges at the nanoscale [3].

A more subtle effect is the direct influence of the electric field on the protonation state of acid groups, i.e. the possibility to protonate or deprotonate the SAM through the applied potential. Smith and White provided a theoretical background for such electric field induced proton transfer phenomenon [4,5], demonstrating that voltammetric responses related to the protonation/deprotonation can be measured and are related to the influence of the electric field on the ionisation of the SAM. Early experimental evidences were provided by Bryant and Crooks [6] on aromatic SAMS (4-mercaptopyridine and 4-aminothiophenol), while theoretical refinements were proposed by Fawcett and colleagues to account for finite size effects at the interface [7,8] and confronted to experimental data gathered at 2-mercaptoethanesulfonic SAMs.

White and Peterson proposed a comprehensive study on the voltammetric response of the long chain 11-mercaptoundecanoic acid (MUA) immobilised at Ag(111) electrode, focusing on the pH of the solution and on the nature of the electrolyte cation [9]. Since then, MUA SAMs have been used as a model system for further investigations on electric field driven protonation/deprotonation. Burgess et al. [10] proposed a kinetic model based on electrochemical impedance spectroscopy to explain the pH dependence on the peak height for the electric-field driven protonation/deprotonation of SAM of carboxylic terminated thiols and employed MUA as an experimental test bed for this model. In an ongoing series of contributions, the group of Andreu and Calvente [11–15] has provided a detailed physico-chemical description on the phenomenon based on the assumption of two different environments experienced by surface-immobilised acid moieties, and provided analytical expressions for the voltammetric or impedimetric responses associated with the electric field induced proton transfer. MUA was again investigated experimentally by these authors to compare the theoretical and experimental behaviours. The phenomenon is nowadays rather well documented and has been reported to occur in numerous instances [16–24].

The work presented here provides a systematic investigation of the effect of the chain length, in α,ω-mercaptoalkanecarboxylic acids SAMs, on the electric field induced protonation/deprotonation phenomenon, as monitored by voltammetric and impedimetric measurements. The results are discussed within the frameworks of the models developed by Burgess et al. [10] and by Andreu and colleagues [12,13,15] (an Appendix is provided to highlight some selected aspects of each model). These models are extended regarding the kinetic aspects by implementing the Laviron's methodology for the study of kinetics of electron transfer [25], and it is shown that the chain length

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https://doi.org/10.1016/j.jelechem.2018.03.010
Received 28 November 2017; Received in revised form 5 March 2018; Accepted 6 March 2018

Please cite this article as: Smiljanic, M., Journal of Electroanalytical Chemistry (2018), https://doi.org/10.1016/j.jelechem.2018.03.010

strongly affects the kinetics of the electric field induced proton transfer.

2. Experimental

A polycrystalline gold bead electrode was used as the substrate for the immobilisation of the SAMs. Prior to each experiment, the gold bead was annealed in the butane flame. For the preparation of the SAMs, the following carboxylic acid terminated thiols were used as received: 3-mercaptopropanoic acid (Sigma, 99 + %), 6-mercaptohexanoic acid (Sigma, 90%), 8-mercaptooctanoic acid (Sigma, 95%), 11-mercaptoundecanoic acid (Sigma, 95%), 12-mercaptododecanoic acid (Sigma, 96%) and 16-mercaptohexadecanoic acids (Sigma, 90%), which will further be denoted as MPA, MHA, MOA, MUA, MDA and MHDA, respectively. The modifications of the gold surfaces were performed by overnight (unless otherwise stated) immersion in 5 mM ethanolic solutions of carboxylic-terminated thiols. Before subjecting it to further electrochemical measurements, the coated gold bead electrode was rinsed carefully with absolute ethanol (VWR Chemicals, NormaPure) and ultrapure water (Milli-Q from Millipore).

Electrochemical experiments were performed in conventional three electrode setup, with gold bead, large surface area gold wire and double junction Ag|AgCl, 3 M KCl as the working, counter and reference electrodes, respectively. The supporting electrolyte used in cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) experiments was 50 mM NaF (Merck, Suprapur) whose pH was adjusted to the desired value with 0.1 M NaOH (Chem-Lab). Deaeration of the electrolyte was performed prior to each experiment using high purity nitrogen (Air Liquide, 99.999%). For the EIS measurements, frequencies between 100 kHz and 0.05 Hz with rms amplitude of 5 mV were used depending on the chain length of the SAMs. In the cases of MPA, MHA and MOA SAMs, frequencies up to 100 kHz were applied and a 4th electrode consisting of a Pt wire coupled capacitively with the reference electrode was used in order to prevent artefacts that occur in the high frequency range [26]. In the case of MHDA, low frequencies down to 0.05 Hz were applied. Acquisition of all the experimental data was performed with a PGSTAT30 (Autolab-Metrohm) potentiostat equipped with a Scangen and a Frequency Response Analyser modules, and controlled by the Nova software, which was also used for the fitting/simulation of the EIS.

3. Results and discussion

3.1. Cyclic voltammetry

The potential induced protonation/deprotonation has been investigated for different α,ω-mercaptoalkanecarboxylic acids SAMs. Fig. 1 depicts a representative example of the dependence of the voltammetric response of a MPA SAM, formed by a 20 min immersion, on the electrolyte pH.

Within the explored range of pH, a clear reversible pair of peaks is observed, which shifts toward more negative potentials with the increase of the electrolyte pH and whose intensities pass through a maximum. The shift of the peak potential with the pH is around 57 mV/pH. This overall behaviour is qualitatively similar to that reported for MUA SAMs formed on gold [10,12] or on silver [9], though the actual values of the peak potentials, intensities and of the maximum pH slightly vary from one study to the other, as these are very sensitive to various parameters such as the immersion time [13], the composition of the electrolyte (nature of the cation [18], ionic strength [12,18]) or the time elapsed in the electrochemical cell before the voltammetric measurement [12,13,18]. Although the electric field induced proton transfer is pseudo-capacitive in essence, the voltammetric peaks have characteristics very similar to those displayed by surface-immobilised redox-species. This was already noticed in early work [10], and substantiated by analytical expressions derived by Calvente and colleagues [12,13]. Protonation/deprotonation peaks were obtained for all of other carboxylic acids investigated in the present study, as well as the same trend in the dependence of the peak potential on the pH value. For identical immersion times, a slight tendency was observed regarding the pH of maximum intensity, which was higher for shorter alkane chains: around 9.4 for MPA and MHA and close to 8.8 for MHDA. Between these extremities, α,ω-mercaptoalkanecarboxylic acids with intermediate chain lengths (MOA, MUA and MDA) exhibited the maximum near pH 9.0, which is in agreement with previous studies of MUA SAMs [10]. Since all SAMs exhibited a voltammetric peak of significant intensity at the pH of 9.0, this value was deemed convenient for further comparison between the different SAMs.

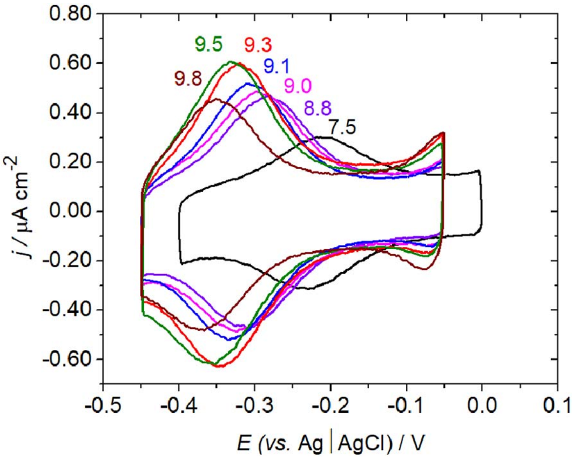

Fig. 1. Influence of the pH on the voltammetric response for the electric field driven protonation/deprotonation of MPA SAMs prepared by 20 min of immobilisation. Cyclic voltammograms were recorded in 50 mM NaF at a scan rate of 20 mV s^{-1}.

Besides the pH of the electrolyte, another factor having a tremendous influence on the voltammetric response associated with the protonation/deprotonation is the immersion time employed for the preparation of the SAM, as illustrated in Fig. 2 for MHDA. As the assembling time increases from 20 min to overnight immersion, it is clearly observed that the peaks become more pronounced and hence that the charge involved in the protonation/deprotonation process increases. A similar effect of the immersion time was reported earlier by Calvente et al. for a MUA SAM on gold [13]. In the interpretation of these authors, only a fraction of the immobilised carboxylic acids undergoes the electric field induced proton transfer, and the charge of the voltammetric peaks is a measure of this amount. According to the

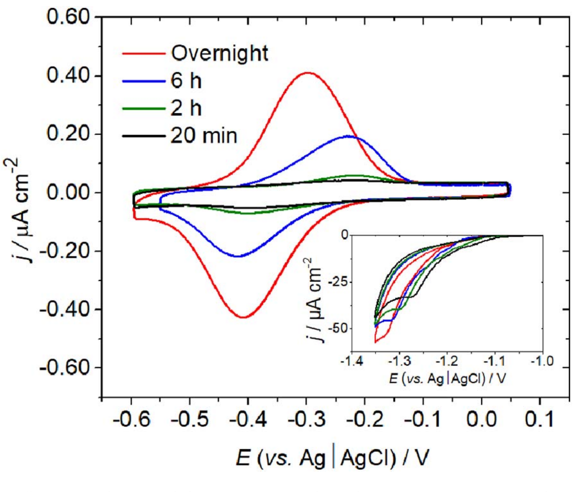

Fig. 2. Influence of the immobilisation time on the voltammetric response for the electric field driven protonation/deprotonation of MHDA SAMs. Voltammograms were recorded in 50 mM NaF, pH 9, at a scan rate of 20 mV s^{-1}. Inset: reductive desorption of the corresponding MHDA SAMs recorded in the same electrolyte at a scan rate of 50 mV s^{-1}.