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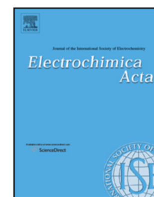

In situ Fourier transform infrared reflection absorption spectroscopy study of adenine adsorption on gold electrodes in basic media

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SUMMARY

In situ *Fourier transform infrared reflection absorption spectroscopy (FT-IRRAS)* has been used in the external (SNIFTIRS method) and the internal (ATR-SEIRAS) reflection configurations to determine the pH influence, in the neutral and basic range, on the adsorption of adenine on Au(111) and gold nanofilm electrodes from D_2O and H_2O solutions.

In D_2O solutions, the main adsorbate band around 1640 cm^{-1}, due to a ring stretching mode, shows different characteristics in the spectra collected at pH values at which the neutral and the basic adenine forms predominate in solution. The analysis of these differences, in comparison with the respective spectra of adenine in solution, permits us to conclude that both forms of adenine can adsorb chemically. The high sensitivity of the ATR-SEIRAS method has been used to analyze the contribution to the spectra of each form of adsorbed adenine as a function of the pH of the solution. The pKa_2 obtained for the adsorbed species from this analysis is almost coincident with the pKa_2 reported for adenine in solution, indicating that the coordination to the electrode and the second acid-base equilibrium involves different atoms of the adenine molecule. This result confirms the previously proposed adsorption model for adenine, implying the bonding of adenine to the electrode by the amine nitrogen (N_{10}) and either the ring nitrogens N_1 or N_7, while the second acid-base equilibrium of adenine involves the ring nitrogen N_9.

Comparison of the 3400-3600 cm^{-1} region of the ATR-SEIRAS spectra of adenine obtained in H_2O solutions at different pH values, which corresponds to the characteristic–OH stretching mode of the interfacial water molecules, permits us to discard the co-adsorption of water molecules in neutral and basic media, contrary to the case of adenine adsorption from acid media.

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1. Introduction

Most of the processes occurring at bio-interfaces involve electrochemical phenomena. Because of that, it is interesting to study the behaviour of molecules of biological relevance at the electrode interface, which offers the possibility of controlling the electric field among other environmental parameters. In the case of DNA bases, there is some extra interest in the study of their adsorption at electrodes because of plausible applications in biosensors design, the fabrication of new bio-compatible materials and the development of new supramolecular organizations to be used as vectors for the cellular delivery of drugs with nucleotide structures.

We have previously studied the adsorption of adenine on gold single crystal and gold nanostructured electrodes, in neutral and acid media by means of different electrochemical, spectroscopic and microscopic techniques, [1–5]. The characterisation of the adsorption process by cyclic voltammetry and differential capacitance in neutral media on the low index gold single crystal electrodes [1] showed that the adsorption phenomena is strongly dependent not only on the crystallographic orientation, but also on the reconstructed or unreconstructed state of the surface. In fact, the adsorption of adenine on freshly flame annealed reconstructed gold surfaces is accomplished by the lifting of the surface reconstruction. The chronoamperometric study in neutral solutions of the thermodynamics of adenine adsorption on Au(111) electrodes concluded that chemisorption takes place with adenine acting as electron donor [1]. The maximum surface excess obtained from the thermodynamic data was consistent with a tilted orientation of the molecular plane relative to the electrode surface. The

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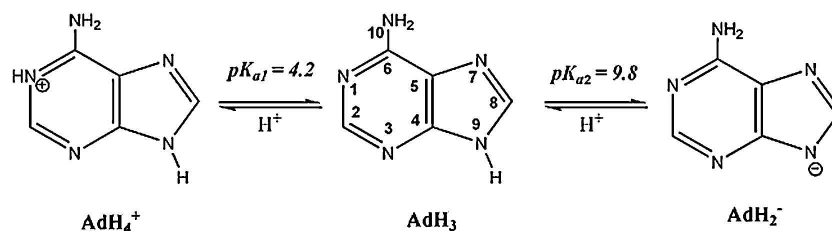

Scheme 1. Adenine structure with numeric labels and its acid base equilibria.

analysis of the frequency and electrode potential effects on the Electrochemical Impedance Spectroscopy measurements provided the kinetic parameters of adenine adsorption/desorption on Au(111) electrodes [2].

Fourier transform infrared reflection absorption spectroscopy (FT IRRAS) is a valuable tool in order to get molecular information from species adsorbed on solid electrodes interfaces, [6–10]. In situ IRRAS measurements can provide information about the nature of the adsorbates, their orientation relative to the electrode surface, the atoms involved in the interactions with the metal surface, the nature of the intermolecular interactions at the interface and the influence of the solvent. In a previous work, the adsorption of adenine on gold single crystal and gold thin-film electrodes was studied in neutral media by means of in situ FT-IRRAS measurements [3]. The spectroscopic results obtained were analysed on the basis of previously published data for the adsorption of adenine on various substrates [8,10–32]. From this analysis it was proposed that, independently of the potential and of the crystallographic orientation of the electrode, adenine is coordinated to the gold electrode surface through the nitrogen of the amine group (N_{10}) and another nitrogen atom, probably the nitrogen (N_7) of the imidazol ring, with the molecular plane tilted relative to the electrode surface. This adsorption model involves a sp^3 hybridization for amine nitrogen N_{10}, as previously suggested for the adsorption of adenine on different substrates [32].

It is well established that the functions of biological compounds can be closely related to the acid dissociation equilibrium. In the case of DNA bases, the Watson-Crick interactions between complementary bases are more likely to occur when both bases are in their canonical form, and the presence of "unstable" tautomeric forms can yield to unpaired bases interactions [33–39]. On the other hand, the pKa values of biological molecules can change when located in organized environment, affecting their function [40–43].

Adenine has two pKa values in aqueous media [44,45] as is shown in Scheme 1. The first one, $pKa_1 = 4.2$, is related to the protonation of the pyrimidine nitrogen N_1. The second, $pKa_2 = 9.8$ accounts for the loss of the proton in the imidazol nitrogen N_9. Our previous in situ FT-IRRAS studies of adenine adsorption on gold electrodes in neutral and in acid media [3,4] showed that only the neutral form of adenine (AdH_3) is chemisorbed on the electrode under these conditions, even at pH values as low as pH 1. Therefore, pKa_1 value of chemisorbed adenine is much lower than pKa_1 value of adenine in solution. However, the presence of protonated adenine (AdH_4^+) on the electrode surface is detected at low pH values and at potentials more negative that the onset of the chemisorption of adenine, because it yields surface active IR signals at the same frequencies than adenine in solution.The signals corresponding to AdH_4^+ on the surface disappear as the chemisorption of AdH_3 is favoured, by increasing either the potential or the adenine bulk concentration or the pH value. A physisorption state was proposed for AdH_4^+. Recent in situ electrochemical STM experiments also suggest the weak adsorption of the protonated adenine [5].

On the other hand, the comparison of adenine adsorption in acid and in neutral media also reveals differences in the spectral signals corresponding to the solvent and to the anion of the supporting electrolyte [3,4], that indicate that the co-adsorption of these species with adenine takes place only in acid media.

The aim of this paper is to extend the spectroelectrochemical study of the adsorption of adenine on gold electrodes to pH values covering the pKa_2, in order to search for the adsorption characteristics of the anionic form of adenine (AdH_2^-) and to determine the pKa_2 value at the interface. The possible coadsorption of the solvent is also investigated.

2. Experimental

Solutions were prepared either in ultra pure water from a Millipore Direct-Q purifier or in deuterium oxide (Sigma 99.99%). Sodium hydroxide, perchloric acid and potassium perchlorate were from Merck Suprapur®. Adenine, from Sigma, was used without further purification. Stock solutions of adenine 10 mM were prepared in the same supporting electrolyte and spikes were added to the cell solution in order to get the desired working adenine concentration (0.01 mM, 0.1 mM or 1 mM). All the solutions were deareated by bubbling argon (Air Liquide N50) during 30 min. prior to use.

Voltammetric experiments were performed with an Autolab PGSTAT 30 multipurpose electrochemical system, controlled by NOVA 1.7 software. The working electrode was a freshly flame annealed Au(111) single crystal electrode prepared following the procedure described by Clavillier [46]. A gold wire and a saturated mercury/mercurous sulphate electrode connected to the cell via a salt bridge were used as auxiliary and reference electrodes respectively. Solution's pH was measured with a PHM 64 pH meter from Radiometer and a Hamilton borosilicate membrane combined electrode. The pH readings on deuterium oxide solutions were corrected according to [47]. All the potentials are given vs. SCE.

FT-IRRAS spectra were obtained at a resolution of 4 cm^{-1} with a NICOLET 6700 spectrophotometer equipped with a narrow-band MCT-A detector cooled with liquid nitrogen, and a V-max II accessory for reflectance measurements. The spectra were collected either with p or s polarized radiation, selected with a ZnSe motorized polarizer, and are presented as the ratio $-\log(R/R_0)$ with R and R_0 being the reflectance spectra at the sample and reference conditions, respectively. Electrochemical control of the cell was made with a CHI 1100 A potentiostat from CH Instruments.

For external reflection experiments a thin layer configuration was used, with a CaF_2 prismatic IR window bevelled at 60°. The working electrode was an Au(111) single crystal. The same auxiliary and reference electrodes were used as in the cell described above for voltammetric experiments. The external reflection spectra obtained were referenced to a desorption potential. In order to increase the signal to noise ratio, spectra calculated from sets of 50 interferograms were measured alternatively at the sample and at the reference potentials at least during 40 cycles, and the results were averaged, in the so called *Substractively Normalized Interfacial Fourier Transform Infrared Spectroscopy* (SNIFTIRS) procedure.

Internal refection spectra were obtained using the Kretchsmann configuration of spectroelectrochemical cell: the cell window consisted in a silicon prism bevelled at 60°. The working electrode

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