The Influence of pH on the Adsorption of Adenine on Gold Electrodes: An In Situ Infrared Spectroscopy Study

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In situ infrared spectroscopy can provide structural information about the changes of the acid-base properties of organic molecules upon adsorption on metal electrodes [1, 2]. This information is especially interesting in the case of biological relevant molecules, because it is well known that the biological environment of some macromolecules can modify its pK\textsubscript{a} values and the changes can be determinant for their biological activity. For instance, in the case of nucleobases the shift of the pK\textsubscript{a} values into the physiological pH range is relevant in order to allow some catalytic functions, [3, 4].

Adenine adsorption on gold single crystal and thin-film electrodes in basic medium has been studied by in-situ FT-IR spectroscopy [5]. It was concluded that the molecule coordinates to the gold surface via the amine group and the N7 ring atom. In aqueous media adenine has two pK\textsubscript{a} values, i.e. 4.2 and 9.8. The lower pK\textsubscript{a} value is related to the loss of the proton on the N1 atom in adenine molecule. Only the two adenine forms associated with this pK\textsubscript{a} value are considered in this communication. Therefore, adenine adsorption has been studied in different HClO\textsubscript{4} - KClO\textsubscript{4} mixtures with pH values ranging from 1 to 5 by external and internal reflection IR spectroscopy experiments carried out with bulk Au(111) and Au(111)-25 nm thin-film electrodes, respectively. Transmission experiments have also been performed for comparison. Both H\textsubscript{2}O and D\textsubscript{2}O have been used as solvents for the sake of interpretation as the scissoring mode of the amino group overlaps with the bending mode of H\textsubscript{2}O. It is observed that the effect of pH on the two main bands for adsorbed adenine, which depends on the electrode potential, is different to that for the dissolved species. Moreover, the evolution of the spectra with the time of adsorption can be followed. The study of the frequency shifts of the surface active signals with pH, potential and time allows us to conclude the existence of more than one adsorption states. The nature and the bonding geometries of the adsorbed adenine forms are suggested.