Adsorption and co-adsorption of adenine and thymine on gold electrodes as a function of pH

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The importance of the complementary DNA bases adenine and thymine in genetic expression and replication and in biotechnological applications has impelled the study of their adsorption on solid electrodes. The orientations and interactions of adsorbed molecules on electrode surfaces can be revealed by combination of electrochemical methods with modern in-situ Fourier infrared methods. The pH can affect the molecular organisations and interactions of the DNA bases on the surface because it can modify the preponderance of the different tautomeric forms. It is known that the existence of some unstable tautomeric forms induces unpaired bases interactions, which seems to be related with some illness.

Adenine adsorption on gold electrodes has been studied by in situ FT-IR spectroscopy at several pH values [1-3] and it has been found that in acid media deprotonation of the molecule is involved in the chemical adsorption process but in neutral and basic media the two forms involved in the second pKₐ of adenine can be simultaneously adsorbed. On the other hand, thymine adsorption on gold electrodes has been studied in acid and neutral media [4] and it was proposed that the chemical adsorption implies deprotonation of the molecule. The co-adsorption of adenine and thymine in very acid media seems to be a cooperative process in which both molecules rearrange in order to facilitate the Watson-Crick or the Hoogsteen interactions [5].

In this communication the adsorption and the co-adsorption of both bases are presented as studied by voltammetry and by external and internal reflection absorption FT-IR spectro-electrochemical experiments in a wide pH range. Gold thin-film electrodes and Au(111) electrodes have been used. Experiments have been performed in H₂O and in D₂O as solvents and they have been suitably designed in order to compare the spectra of co-adsorbed bases to those of the individual adsorbed bases. It is found that the behaviours depend on the tautomeric forms that can be adsorbed. Plausible interactions between the two molecules when co-adsorbed are discussed.