

ABSTRACT

We report on the adsorption and the coadsorption behavior of purine (adenine and guanine) and pyrimidine bases (uracil and thymine), as well as on the pyrimidine derivative bromouracil on Au(111). The influence of the sugar group on the adsorption behavior was also investigated by using adenosine and thymidine nucleosides instead of adenine and thymine.

The adsorption behavior of thymine, uracil and bromouracil is quite similar. They shows four characteristic interfacial regions forming a condensed physisorbed film at negative potentials, where the molecules are oriented planar with respect to the electrode surface and a chemisorbed film at positive potentials with the molecules adsorbed in an upright position.

In case of purine bases at negative potentials, adenine is strongly adsorbed parallel to the electrode surface forming a charge-transfer complex between the π^* -orbital of adenine and the d-orbital of the Au(111) electrode. Guanine presented the most surprising behavior, depending on the pH value. At low pH values, it behaves like a pyrimidine, i. e., it forms a physisorbed film at negative potentials and a chemisorbed film at positive potentials. With increasing the pH value, the adsorption behavior is more similar to the purine base adenine, which means that it is strongest adsorbed at negative potentials.

For coadsorption of adenine-thymine base pairs, a mutual interaction between adenine-thymine was found at negative potentials, where the charge-transfer complex between the π^* -orbital of adenine and the d-orbital of the gold surface is strongly influenced by the interaction between adenine-thymine. For the thymine-uracil system (non-complementary base pairs), it was concluded that thymine prevents the uracil adsorption and no signal for interaction was found. In the case of bromouracil-adenine, we have no real indication for interaction between the bases. This can be due either to the lower interaction between them or to the surface structure of bromouracil at negative potentials. In contrast to the bromouracil-adenine system, bromouracil-guanine (pH = 2) are physisorbed at negative potentials and chemisorbed at positive potentials. It makes the differentiation between them more complicated. For the nucleosides adenosine and thymidine and for the adenosine-thymidine system, both molecules showed different adsorption and coadsorption characteristics when compared with the bases adenine and thymine. For the adsorption of the nucleosides, no discernible current peak at negative potentials was obtained. For the adenosine-thymidine system no interaction was found. The reason is the presence of the sugar

group, which may change the orientation of the molecules on the electrode surface preventing also an interaction between them.