
CHAPTER 7: SUMMARY

In this thesis, the adsorption and coadsorption behavior of purine (adenine and guanine) and pyrimidine (thymine, uracil and the pyrimidine derivative bromouracil), as well as the nucleosides (adenosine and thymidine) were studied on Au(111) under electrochemical conditions.

The adsorption and coadsorption kinetics of adenine and thymine on Au(111) and on polycrystalline gold as well as the coadsorption of thymine and uracil on Au(111) are presented. As the adsorption behavior of thymine on Au(111) is already quite well understood, only a brief description of the adsorption states is given. At negative potentials the thymine molecules are randomly adsorbed, when a phase transition takes place forming a well-ordered condensed film, where the molecules are oriented parallel with respect to the electrode surface. At more positive potentials, the molecules undergo a reorientation to an upright position, forming a chemisorbed film. It is interesting to point to the dissolution kinetics of the thymine chemisorbed film. In the cyclic voltammograms only two processes could be seen for the dissolution, but a careful analyses of the current-time transients showed that the dissolution occurs in at least three steps, depending on the potentials. For thymine adsorption on a polycrystalline gold electrode no phase transition was found, but we assumed the formation of the physisorbed condensed film at negative potentials supported by the capacity curves, which show a minimum indicating an adsorption followed by an increase of the capacity (transition region). At positive potentials the capacity quickly decreases, as an indication for strong adsorption of thymine (chemisorption).

Uracil adsorption on Au(111) has a similar feature that thymine, i.e., the molecules are physisorbed at negative potentials and chemisorbed at positive potentials. Regarding to the coadsorption behavior of thymine and uracil, we did not find any indication for an interaction.

At negative potentials adenine is 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). At positive potentials adenine is also strongly adsorbed on the electrode surface, however, but in an upright position, the same orientation as thymine for the same potential range. Adenine adsorption on gold polycrystalline electrode showed a small peak at negative potentials, but not well resolved on comparison with Au(111). We assume that this peak is a formation of a

π^* -complex between the π^* -orbital of adenine and d-orbital of the gold electrode. This is supported by the capacity curves.

The coadsorption of thymine and adenine the shape of the cyclic voltammogram changes completely when compared with the shape of the bases alone. Well-resolved peaks at negative potential were clearly seen. We assume that the formation of the complex between the π^* -orbital of adenine and the d-orbital of the gold electrode is influenced by a kinetic effect caused by the interaction between the bases. On gold polycrystalline, the same adenine-thymine charge transfer complex was assumed.

The adsorption dynamics of bromouracil on Au(111) is very similar to that of thymine and uracil in the pH values of 2 and 8, respectively.

For guanine adsorption the shape of the CV changes drastically from pH = 2 to pH = 6 and pH = 8. At pH = 2, guanine, a purine base, behaves as a pyrimidine base (thymine, uracil), i.e., at negative potentials the physisorbed film is formed and at positive potentials the chemisorbed film is formed. With increasing pH values, no phase-transition could be seen, but well resolved peak pairs at negative potentials were observed. As the positions of these peaks depend only slightly on the bulk concentration of guanine and on the temperature, we assume a strong adsorption of guanine at negative potentials, comparable with adenine adsorption at the same potential range.

For the coadsorption kinetics of bromouracil and adenine at pH = 2, we have no indication for really good interaction between the bases due to the lower interaction between them or due to the stable structure of bromouracil at negative potentials. In the bromouracil and guanine system (pH = 2) both molecules are physisorbed at negative potential and chemisorbed at positive potentials. This makes the differentiation between the molecules more complicated. For the coadsorption of thymine-guanine at higher pH values also no interaction was found.

The adsorption of the nucleotides adenosine and thymidine was studied. The molecules are adsorbed on the electrode surface, but no indication of an ordered condensed film was found. This is due to the presence of the sugar group, which may change the orientation of bases. For the coadsorption of adenosine and thymidine also no indication of interaction was found. The reason may be probably the same as mentioned above.