Interfacial Electron Transfer through Self-Assembled Monolayers with Lateral Hydrogen Bonds.

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The influence of the hydrogen bonds on mediated electron transfer between the surface-confined redox probe (i.e. ferrocene) and the metal of the electrode was studied. The self-assembled monolayers formed by molecules containing one, two or three amide moieties were used as model systems in these investigations. Electrochemical methods and scanning tunneling microscopy were used to determine the kinetics of electron transfer and the structure of monolayers, respectively. The kinetic parameters (i.e. rate constants and reorganization energies) for mediated electron transfer were determined using Marcus treatment.[1] Amide-containing assemblies were chosen because of their ability to form extended internal hydrogen-bonded network.[2] However, this ability is strongly dependent on the location of amide groups in the monolayer. Namely, it was found that diamide bolaamphiphiles with terminal -SH group are able to form two planes of hydrogen bonds within the monolayer on condition that the amide groups in a single molecule are separated by even number of methylene units.[3] We previously reported the enhanced electronic coupling between the redox probe and the metal of the electrode in the presence of hydrogen bonded network within the monolayer assembly.[4]

At present, we focus on the amide location effects on kinetics of mediated electron transfer. We found that the ability to form the hydrogen-bonded network within the monolayer is not the only factor controlling the rate of electron tunneling. Our results indicate that the distance between the hydrogen bond plane and the electrode surface is of crucial importance. The enhancement of electronic coupling is found only in the presence of deeply "buried" hydrogen bonded network – located close to the electrode surface. On the other hand, hydrogen bonding between the terminal amide groups (close to the monolayer outer plane) does not affect the efficiency of electron transfer across the monolayer. This is probably connected with the interactions of amide moieties and molecules of water (e.g. water - mediated hydrogen bonding). Thus we conclude that the environment surrounding the amides should be taken into account if we consider the influence of hydrogen bonds on electron transfer through the monolayer. Based on these observations, we suggest that the electron delocalization due to the presence of hydrogen bonds is important for the extent of coupling between the electronic states of the redox probe and the metal of the electrode, providing that hydrogen bonding takes place in the neighborhood of the electrode surface. However, the conclusion above could be valid for aqueous solutions or other protic solvents. Therefore, for comparison, the kinetics of mediated electron transfer was investigated also in aprotic solvent, i.e. acetonitrile. Under these conditions, the formation of hydrogen-bonded network by the amide moieties located in the outer plane of the monolayer is not perturbed in such extent as it takes place in aqueous medium. The results of the experiments performed in acetonitrile will be also discussed.

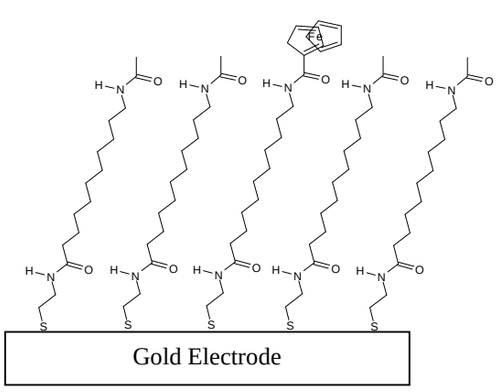

Figure 1. The scheme of monolayer assembly containing two planes of hydrogen-bonded amides.

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