Nano-Organization of Molecules at Electrified Interface: Anionic Surfactant Overlayer Formation through Potential Dependent Binding on Viologen-Functionalized Self-Assembled Monolayer

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Nano-organization of molecules at electrified interface is among the most fascinating chemistry in the area of interfacial nano-dynamics [1]. It is known that a self-assembled monolayer (SAM) of viologen-functionalized alkyl thiol on a Au electrode exhibits anion dependent formal potential of one-electron reduction of viologen dication (V²⁺) [2]. This is due to the anion binding to both V²⁺ and its one-electron reduced mono-cation mono-radical form (V⁺) with different binding equilibrium constants. We found that alkylsulfates also bind to the SAM with chain length-dependent binding constants. The formal potential in the presence of dodecylsulfate (DS⁻) below cmc is much more negative than that in the presence of the same concentration of hexafluorophosphate. Using the chain length and concentration dependencies, we quantitatively discriminate two types of simultaneously acting interactions, namely electrostatic and chain-chain interactions. The latter as a function of chain length can be regarded as the “Traube's rule” of a SAM. As the results of the binding, DS⁻ forms its bilayer at higher concentrations on the SAM as revealed by quartz microbalance measurements (see model at the right). This bilayer completely blocks the direct electrochemistry of hexacyanoferrate but realizes its mediated reduction at the formal potential of V²⁺/V⁺ couple. Results of electroreflectance measurements [3] reveals that the binding never affects the orientation of longitudinal axis of V⁺ moieties in the SAM.

References