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# Mixed monolayers of alkane thiols with polar terminal group on gold: investigation of structure dependent surface properties

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## Abstract

Adsorption of thiols with cationic or anionic terminal group on gold has been studied from mixed solutions of 11-Amino-1-undecanethiol (AUT) and 3-Mercaptopropionic acid (MPA) using quartz crystal microbalance with dissipation (QCM-D), X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM) and contact angles. The goal is to probe the nature of such layers, and the additivity or otherwise of the pH responsiveness, with a view to evaluate their suitability as smart materials. For each of the two pure (unmixed) cases, ordered molecular monolayers are formed with sulfur binding to gold and the alkane chain pointing out from the surface as expected. Adsorption from the thiol mixtures, however, leads to a more complex behavior. The surface concentration of thiols from the mixtures, as determined by QCM-D, is considerably lower than for the pure cases and it reaches a minimum at a 3:1 MPA/AUT relative concentration in the solution. The XPS results confirm a reduction in adsorbed amount in mixtures with the lowest overall intensity for the 3:1 ratio. Monolayers formed from mixtures display a wettability which is much lower and less pH sensitive. Collectively these results confirm that for adsorption from mixed systems, the configuration is completely different. Complex formation in the mixed solutions leads to the adsorption of molecules parallel to the surface in an axially in-plane configuration. This parallel layer of thiols is mechanically relatively robust to nano-shaving based on AFM measurements. These results will have a significant impact on the design of biomimetic surface coatings particularly when mixtures of oppositely charged molecules are present on the surface, as is commonly the case in biological, proteinaceous surfaces (eg. hair and skin).

**Key words:** Self-Assembled monolayer (SAM), thiols, Quartz Crystal Microbalance with Dissipation (QCM-D), Atomic Force Microscopy (AFM) and X-ray Photoelectron Spectroscopy (XPS)

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