

**POLARIZATION MODULATED  
INFRARED REFLECTION ABSORPTION  
(PM-IRRAS) SPECTROSCOPIC AND  
SURFACE PLASMON RESONANCE (SPR)  
MEASUREMENTS OF  $\omega$ -  
MERCAPTOALKANOIC ACID SELF-  
ASSEMBLED MONOLAYER (SAM)  
PROTONATION EQUILIBRIA**

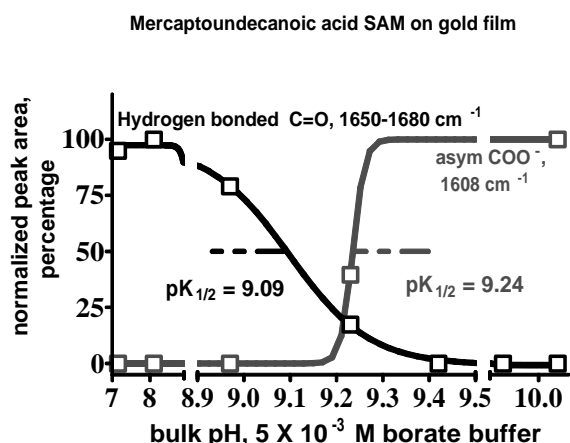
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Protonation equilibria of monolayers, self-assembled onto gold (or silver) substrates, (ie., of SAMs) are of fundamental importance and practical relevance for the successful construction of nanostructured ultrathin films by electrostatic interactions. It is generally recognized that the dissociation constant, the pKa, of SAMs is substantially different than that of the corresponding carboxylic acids in bulk aqueous solutions. This difference is believed to originate in the reorientation of the monolayers upon protonation as well as in altered micro-environment (polarity, polarizability, H-bonding and solvent reorganization among other properties) of the carboxyl groups in the SAM.

We have self-assembled 3-mercaptopropionic acid (3MPA) and 11-mercaptoundecanoic acid (11MUA) monolayers on gold and silver substrates. The thickness of SAMs were determined by the two-solvents (methanol and in ethanol) and two color (He-Ne laser excitation at 632.8 nm and diode laser excitation at 850 nm) angle-scan SPR measurements. The obtained thickness values,  $0.50 \pm 0.02$  nm for 3MPA and  $1.13 \pm 0.03$  nm for 11MUA, indicate the formation of upright  $\omega$ -mercaptopropionic acid monolayers. Employing a high resolution bicell photodetector for time resolved SPR we have determined the rate constant for the SAM formation to be in the  $10^{-2} \text{ min}^{-1}$  range. Cyclic voltammetry of a Fe(III)/Fe(II) redox couple in aqueous solution (using the SAM coated substrate as a working electrode) indicated defect free coverages of the substrate by the 3MPA and 11MUA SAMs.

Values previously determined for the pKa's of 3MPA and 11MUA SAMs by

electrochemical quartz crystal microbalance determination, impedance titration, cyclic voltammetry, laser induced temperature jump, and surface force titration by atomic force microscopy ranged from 4.4 to 8.5. To resolve this discrepancy and to establish the mechanism(s) responsible for the pKa values of  $\omega$ -mercaptopropionic acid SAMs we have undertaken a systematic investigation of the protonation equilibria of 3MPA and 11MUA SAMs in aqueous solution by combined PM-IRRAS, and spectroelectrochemical



measurements and report here our findings. The apparent pK<sub>1/2</sub> (ie., the bulk pH- value at which 50% of the mercaptoundecanoic acid is ionized) is seen in Figure to be  $9.1 \pm 0.1$ . Applying potential at pH = 0.1 (in the absence of water) has also changed the extent of the ionization of the SAM. Significance of these results are discussed.

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