109d Atr-Ftir Study of Adsorption Kinetics and Structural Arrangement of an Anionic Fluorinated Surfactant at Germanium/Water Interface

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Adsorption of anionic fluorinated surfactants, tetraethylammonium perfluorooctylsulfonate (TEA-FOS) onto hydroxylated germanium from aqueous solution is studied in situ using polarized attenuated total reflection FTIR spectroscopy. At pH 6.0, slow and extensive adsorption leading to multilayer formation is observed for a series of bulk solution concentrations spanning from 10% of the critical micelle concentration (1.0 mM) to well above the cmc. Three kinetic stages, with an autoaccelerating last stage, are observed by monitoring the intensity of the fluorocarbon(CF_2)sym bands at 1151 cm^{-1}. The final autoaccelerating stage can be explained either by adsorbed surfactant creating sites more attractive for further adsorption than the bare germanium surface, or by nucleation and growth of islands of dense multilayer on the germanium surface. Circular dichroism measurements of (CF_2) stretching bands indicate a slight orientation of the fluorocarbon director normal to the surface as adsorption proceeds, but not perfect close-packed layer formation. Further studies indicate that both pH and salt concentrations have significant effect on the adsorption kinetics as well as structural arrangement. With increase of pH, the final surface coverage decrease. However, at even pH ~10, far above the IEP of germanium, the three stage adsorption of anionic surfactant onto negatively-charged surface still can be observed, which indicates that the tetraethylammonium ions mediates the interactions between the surfactant headgroups and the surface. The presence of salt can greatly increase the initial adsorption rate and affect the final surface coverage when equilibrium is obtained.