

355f Dynamic Behavior of Interfacial Properties in Photoresponsive Surfactant Systems

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We report on the surface properties of a photoresponsive surfactant that incorporates the light-sensitive azobenzene group into its tail. Cis-trans photo-isomerization of this group alters the ability of the surfactant to pack into adsorbed monolayers at an air-water interface or into aggregates in solution, causing a significant variation in bulk and surface properties upon changes in the illumination conditions. NMR studies indicate that a solution left in the dark for an extended period of time contains trans isomer almost exclusively, while samples exposed to light of fixed wavelength eventually reach a photostationary equilibrium with significant amounts of both isomers present. Dynamic surface tension studies performed on this system under different illumination conditions (dark, UV light, visible light) show profoundly different approaches to equilibrium. At concentrations well above the CMC, the same equilibrium tension is reached in all three cases, presumably corresponding to a surface saturated with the trans (more surface active) isomer. The dark sample shows a simple, single-step relaxation in surface tension after creation of a fresh interface, while the UV and visible samples exhibit a more rapid initial decrease in tension, followed by a plateau of nearly constant tension, and finally ending with a second relaxation to equilibrium. The fact that the intermediate plateau occurs at approximately the same tension under both UV and visible light, and that the duration of this plateau and the rapidity of the initial surface tension relaxation both correlate strongly with the amount of cis isomer present in solution suggests the presence of competitive adsorption between the cis and trans isomers present in these solutions. It seems that the cis surfactant reaches the interface more quickly, leading to a cis-saturated interface having a tension value corresponding to the intermediate plateau, but is ultimately displaced by the more surface active trans isomer. Surface pressure-area isotherm measurements performed on this system give support to this hypothesis. Other dynamic experiments performed include the measurement of the response of an interface at equilibrium and saturated with a given isomer to a rapid change in either the wavelength of illumination or the interfacial area. The results of all these experiments are rationalized based on surfactant architecture and relevant transport models.