482a A Transport Theory and Validating Experiments for the Adsorption of Surfactant from Micellar Solutions to an Initially Clean Air/Water Interface Including the Direct Adsorption of Aggregates

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This presentation will focus on the development of a transport model, and validating experiments, for the adsorption of surfactant from aqueous micellar solutions onto an initially clean air/water interface, and the reduction in interfacial tension as a result of the surfactant adsorption. The adsorption of surfactant from sub-micellar solutions onto a clean interface involves the straightforward processes of diffusion of monomer from the bulk to the surface, followed by the kinetic adsorption of monomer from the sublayer underneath the surface onto the surface. Micellar aggregates in the bulk phase can augment the adsorption process by one of two routes. First, the adsorption of monomer onto the surface disturbs the monomer/micelle equilibrium and micelles can kinetically break-up releasing monomer which can then diffuse and kinetically adsorb onto the surface. Second, aggregates can directly adsorb onto the surface. Current micellar transport models, using a step wise kinetic association model, exclude direct adsorption, and account for micellar break-up by formulating kinetic-diffusive equations which become tractable only when they are simplified so as to be valid only for small disturbances from equilibrium. To formulate equations valid far from equilibrium which do not rely on the exact measurement of kinetic constants, we have previously developed asymptotic equations to describe regimes in which the time scale for disassembly of aggregates is much faster than the timescale for monomer diffusion. In this kinetic regime, monomer and micelle are in equilibrium, with the nature of this equilibrium such that micelles maintain a monomer concentration equal to the critical aggregate concentration (CAC). For total bulk concentrations just above the (CAC), adsorption of monomer onto the surface in this fast kinetic regime outscales diffusion of micelles, and creates a micelle-free zone surrounding the surface. Micelles outside of the zone diffuse towards the zone and break-up at its boundary, releasing monomers which then diffuse through the zone and kinetically adsorb onto the surface. Simulations based on this model agree well with dynamic tension experiments without adjustable parameters. At high enough total bulk concentrations of surfactant, the concentration of micellar aggregates is large and their diffusion rate exceeds the kinetic adsorption rate. The micelle free zone does not form and micelles diffuse up to the interface and either adsorb directly, or release monomer which kinetically adsorbs onto the surface. If aggregates do not directly adsorb onto the surface, the adsorption rate is only controlled by the kinetic adsorption of monomer, and this process is independent of the total surfactant concentration since the monomer concentration in the sublayer is equal to the CAC by virtue of the micelle/monomer equilibrium. Experimnental evidence, however indicates that the rate of reduction in dynamic tension continues to increase with total concentration of surfactant, suggesting the direct adsorption of micelles. We develop a model to include direct adsorption of the micelles onto the surface, in which we take into account the polydispersity of the micelle distribution and the large kinetic barrier for aggregates to adsorb and release monomer directly on the surface. This model correctly predicts the increase in the rate of dynamic tension reduction as the total bulk concentration of surfactant increases, and compares well with dynamic tension measurements for a range of high bulk concentrations.