

**STUDIES ON THE ADSORPTION OF SURFACTANTS AND POLYMERS
TO SURFACES AND THEIR EFFECTS ON
COLLOIDAL FORCES**

Ayşen Tulpar

Dissertation submitted to the Faculty of Virginia Polytechnic Institute and State University in
partial fulfillment of the requirements for the degree of

Doctor of Philosophy

IN

CHEMISTRY

Professor William A. Ducker, Chairman

Professor Alan Esker

Professor Timothy E. Long

Professor Brian M. Tissue

Professor Thomas C. Ward

September 8, 2004

Blacksburg, Virginia

Keywords: Surface Charge, Self-Assembled Monolayer, Atomic Force Microscopy,
Surface Plasmon Resonance

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ABSTRACT

Surfactants, polymers, and their mixtures are widely used in commercial formulations of paints, water-based adhesives, detergents, food, and other products. This thesis describes measurements of the forces acting on colloidal particles in surfactant and polymer solutions. The change in force on addition of surfactants and polymers is usually caused by adsorption to an interface. In this thesis, I also describe the effect of surface charge density, surface crystallinity, surface heterogeneity, and preadsorbed polymer on surfactant adsorption.

A new method for the stabilization of colloidal particles is introduced via the synthesis and adsorption of unnatural proteins. Unnatural proteins can be synthesized using the natural ‘machinery’ of a bacterial cell with almost any primary sequence, and provide an environmentally friendly route to colloidal stabilization. As a model system, we study the stabilization of alumina, because alumina has a high Hamaker constant and is therefore difficult to stabilize. An unnatural protein with the sequence, thioredoxin-Pro₃₉Glu₁₀ is used. The Glu₁₀ is anionic (pH > 3) and is designed to adsorb to positively charged alumina (pH < 9). The thioredoxin-Pro₃₉ is hydrophilic so it should remain in solution, thereby providing a steric barrier to the approach of two particles in a range of salt and pH conditions. Ellipsometry experiments show that thioredoxin-Pro₃₉Glu₁₀ adsorbs to alumina. Force measurements with the Atomic Force Microscopy (AFM) colloid probe technique show that adsorption of the unnatural protein leads to repulsive forces that decay exponentially with the separation between the surfaces, and are independent of salt concentration. The loss of a salt-dependent force shows that adsorption of the unnatural protein has effectively neutralized the charge on the alumina. Thus, I have shown that an unnatural protein can be used to control the stability of a colloidal system. In general, the same hydrophilic block can probably be added to a variety of anchoring blocks to stabilize different colloidal particles.

Electrostatic forces are frequently responsible for the stabilization of colloidal particles. The decay length of these forces is dictated by the electrolyte concentration. The relationship between the decay length and the concentration is well understood for fully dissociated

electrolytes. Here, I examine the decay-length in solutions where the ions associate strongly. The forces are measured between silica surfaces in aqueous carboxylic acid and surfactant solutions. The decay lengths of the electrostatic double-layer force in both these solutions are well described by the usual expression for decay length when the concentration of ions is obtained from an activity measurement.

The effect of the surface properties of the solid substrate on surfactant adsorption is also described in this thesis. The adsorption characteristics of a charged surfactant onto fixed charged surfaces as a function of surface charge density is reported. This is the first time that a method has been introduced for making a series of known fixed charged surfaces. Investigating surfactant adsorption to these surfaces has improved our understanding of the role of charge density in surfactant adsorption and desorption. The desired surface charge density is achieved by the use of gold-thiol self-assembled monolayers (SAMs) of different ω -groups ($-\text{OH}$ and $-\text{N}^+(\text{CH}_3)_3$). The mole fraction of $-\text{N}^+(\text{CH}_3)_3$ on the mixed SAM dictates the surface charge density. The charge on $-\text{N}^+(\text{CH}_3)_3$ is fixed and does not self-regulate. The adsorption of sodium dodecyl sulfate (SDS) to the interface between these model surfaces and aqueous solutions of SDS is investigated. Atomic Force Microscopy (AFM) of the adsorbed surfactant reveals no surface micelles above the critical micelle concentration, cmc , over a wide variety of $-\text{N}^+(\text{CH}_3)_3$ densities. This shows that the lateral mobility of ions other than surfactant at the interface is important for the formation of surface micelles of ionic surfactants. Adsorption isotherms of SDS (with no added salt) measured by Surface Plasmon Resonance (SPR) show a plateau region in which the surface excess of SDS is equal to the known fixed surface charge. This demonstrates that the adsorption is electrostatically driven. There is no critical surface charge density at which adsorption rises rapidly. Thus there appears to be no ‘hemimicelle concentration’. My work suggests that the formation of hemimicelles depends on the lateral mobility of the surface ions. Desorption experiments starting above the cmc show rapid desorption of SDS into water until the surface excess is equal to the surface charge density. The rapid desorption is followed by a much slower desorption. The elucidation of this fast-slow desorption pattern based on charge density is made possible by the preparation of a set of constant charge surfaces.