

MATHEMATICS, PHYSICS AND COMPUTER SCIENCE  
UCBA COLLEGE

SUMMER RESEARCH OPPORTUNITIES FOR UNDERGRADUATE WOMEN

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PROJECT TITLE: Investigation of physical and thermodynamic properties of surfactant hydration to better understand the molecular origin of skin aggressiveness

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### Project Description

Surfactant molecules are characterized by their tendency to adsorb at surfaces and interfaces such as liquid-liquid, liquid-solid and, liquid-vapor. The driving force of this adsorption is the unique amphiphilic (meaning both) nature of their molecular constituent. All surfactant molecules consist of at least two parts, one which is soluble in water (Hydrophilic head group) and one which is insoluble (Hydrophobic tail group). This amphiphilic nature drives them to surfaces and interfaces to adsorb, and, as a result, the surface tension (or amount of work required to expand the interface) is reduced. Specifically, when a surfactant adsorbs from aqueous solution at a hydrophobic surface, it normally orients its hydrophobic tail group towards the surface and exposes its polar head group to the water. This leads the surface to become hydrophilic and, as a result, the interfacial tension between the surface and water has been reduced.

Due to this intriguing ability of lowering surface and interfacial tension, surfactants are widely used as wetting agents and this phenomenon is of fundamental importance to diverse applications that include, among others, detergents, coating technologies, enhance oil recovery, drug delivery and pharmacy. Much current concern is drawn to the dermatological problems related to exposure of unprotected skin to surfactant solutions which is currently poorly understood at the molecular level. Using this proposed research we determined to better understand the correlation between skin irritation potential and hydration thermodynamic properties by simulating a series of widely used anionic surfactants, sodium dodecyl sulfate (SDS),  $C_{12}H_{25}OSO_3Na$  and the ethoxylated derivatives of SDS, sodium lauryl ether sulfates (SLES),  $C_{12}H_{25}(OCH_2CH_2)_xOSO_3Na$ , where  $x = 1$  (SLE1S),  $x = 2$  (SLE2S), and  $x = 3$  (SLE3S). Experimental studies have suggested that, higher the degree of ethoxylation, lower it gets the skin irritation potential, SLE3S being the mildest. We hypothesize that the head group ion size of these surfactant has a direct effect on the local electrostatic contribution to the hydration entropy. Specifically, larger the ion size weaker the charge

density of head groups and, as a result, the minimal perturbations of water structure in the first hydration shell. The amount of perturbation of water structure in the first hydration shell is suggested to correlate with the skin irritation potential of these molecules. Similar results have shown for singular ion hydration by Thomas L. Beck. This study showed that the local electrostatic contribution, however, varies widely as a function of ion size; the sign yields a direct indication of the kosmotropic (strongly hydrated) or chaotropic (weakly hydrated) nature of the ion hydration.

Extensive molecular dynamics simulations and free energy calculations are planned to be performed over a range of temperatures to determine the electrostatic and van der Waals contributions to the hydration entropies and enthalpies of this series of surfactants. The surfactant models will be build from the scratch using molecular modeling packages and the models will be transferred to CHARMM molecular modelling program to simulate in explicit water molecules at ten different temperature levels. The molecular dynamics Free energy perturbation (FEP/MD) method will be perform to compute the hydration free energy calculations in each temperature point and finally, the electrostatic and van der Walls hydration entropy and enthalpy contributions are computed by performing the vanĖřt Hoff analysis on hydration free energies at different temperatures.

Computational modelling of surfactant hydration and computation of hydration thermodynamic properties will certainly add new insights into the knowledge base of molecular level behavior of these molecules in solution and their effects when interacting with a surface. Overall, the expectation is to advance our fundamental perception of how surfactants perturbed the water structure in hydration shell and the resultant implications on skin aggressiveness while simultaneously guiding the design of novel surfactants with improved properties.

We will use primarily the CHARMM molecular dynamics simulation package for all our free energy computational work. CHARMM is a widely used simulation program that has been designed specifically for work with small molecules, biopolymers and solvent systems. The recently granted computational resources and time at the Ohio Supercomputing Center (OSC) will be fully used to investigate the SDS hydration entropy studies. All the necessary computational resources and computer time for the proposed research are readily available for us at OSC. Molecular mechanics, visualizations and documenting for publications will be conducted on our group personal computer. We collaborate with Dr. Thomas Beck, Professor of Chemistry & Physics, University of Cincinnati, an expert in the free energy research field and a research team at P&G.