# GREENER SURFACE ACTIVE AGENTS
## Structure/Property/Performance Relationships

**Research Team**: Jun Wu, Prof. Somasundaran

**Overview**: Greener surfactants for desired viscosity and foamability

**Technical Information**:

- Micelles evolve from spheres to worm-like micelle networks
- Networks lead to viscosity enhancement
- Synergism leads to desired foaming properties

**Industrial Relevance**: Personal Care & Household Care

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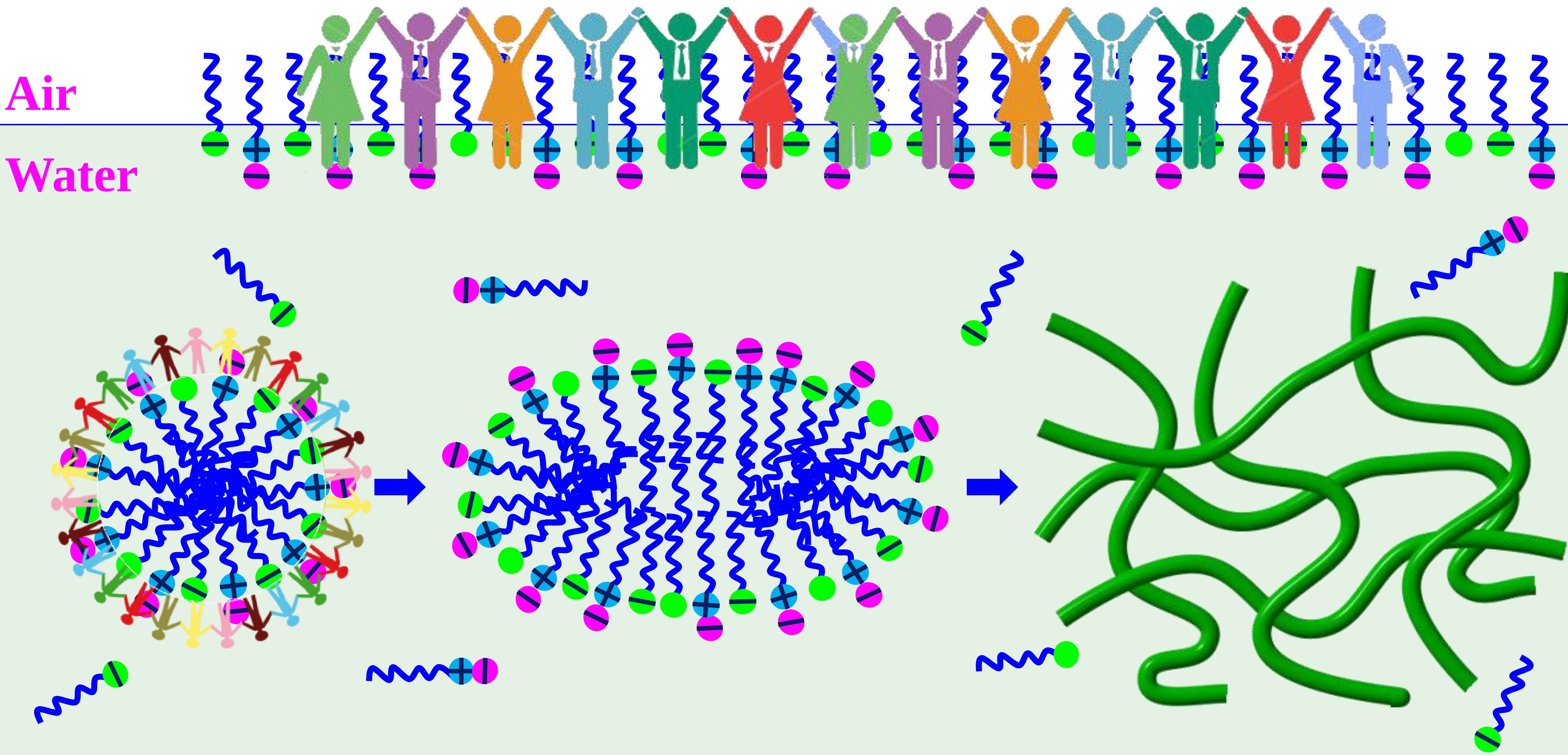
# Packing of Surfactants in Solutions and at Interfaces




Structure ⇒ Packing ⇒ Properties

Synergism ⇒ Packing ⇒ Performance

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# Development of the Greenness Index

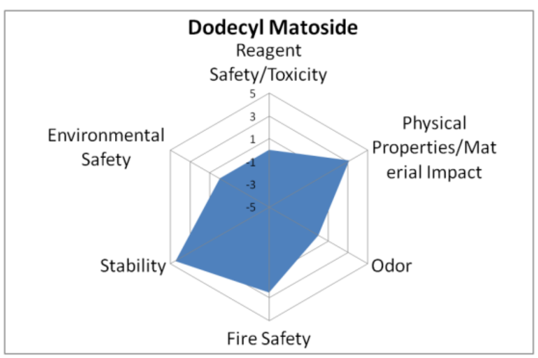
**Research Team**: P. Somasundaran(ps24@columbia.edu, 212-854-2926),
Yang Shen, Partha Patra, D. R. Nagaraj, Raymond Farinato and Amy Essenfeld

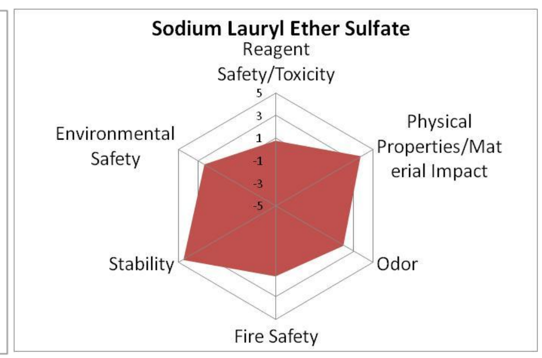
**Goal**:
To develop a holistic tool which can evaluate the reagents and processes in an industry comprehensively

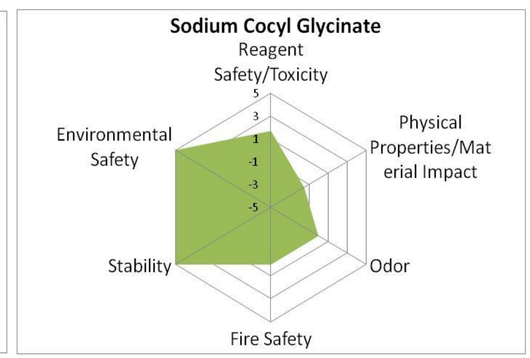
**Previous Findings**:
- Strategy/Methodology for evaluation from cradle to grave *(all life stages)* has been determined
- A prototype Greenness Index program has developed in Excel
- Three-Tier-Spider-Diagram has been designed as the final format to visualize the greenness
- The 1st tier called Materials Greenness *(corresponding to the manufacturing/storage/transportation stages of the reagent's life)* can be used for preliminary comparison of reagents based on the MSDS information

**Current Findings**:
- Prototype program is under further enhancement *(especially for 2nd and 3rd tiers)*
- Strategies to deal with various challenges *(e.g., taking into consideration of chemical interactions)*
- Industrial input in terms of weighting factors to be collected via survey we have prepared

**Ex:**
**Material Greenness**
Spider-Diagrams




**Future Directions**:
- Further develop and enhance the program
- Collect feedbacks from various industrial members
- Transform the current program into a web-based software and allow wider application

**Principal IAB Sponsor(s)**: Vale, Barrick, Newmont, FMI and Cytec Industries

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# Fundamental study of surfactant behavior at the solid/liquid interface in corrosion inhibition

**Research Team**: Kevin W. Powers, PI, kpowers@perc.ufl.edu; Akshay Rajopadhye, Esteban Peralta, Melissa Andrews, Valentina Otero, Edward Kelly, Yakov Rabinovich, and Brij Moudgil

**Goal**: **To examine the fundamental surfactant structure at the solid/liquid interface leading to improved performance cost effectiveness of surfactants and other additives used to inhibit corrosion in aggressive environments.**

**Previous Findings**:

- Corrosion rates were obtained from the electrochemical investigation using potentiometry.
- Compared the results obtained from gravimetric analysis with those obtained from electrochemical investigation to validate methodology.
- Measured force distance curves and yield strength of surfactant structure on glass surface using Atomic Force Microscopy (AFM).
- Established the electrochemical-atomic force microscopy (EC_AFM) technique for micro-electrochemical measurements.

**Current Findings**:

- Transitioned to polished 1010 carbon steel samples as standard substrate for continued investigations
- Analyzed the effect of surface roughness on corrosion inhibition for selected surfactants.
- Introduced Electrical Impedance Spectroscopy (EIS) as an additional tool for evaluating surface structures. EIS can be conducted both for bulk measurements or through the EC-AFM.

**Future Directions.**

- Identify structure-property-performance factors for designing more effective corrosion inhibition formulations.
- Integrate findings to apply to different solvent systems and surfaces.

**Principal IAB Sponsor(s)**: BP, Shell, Exxon Mobil, Ecolab, Nalco, Cytec….

# Protein and Surfactant Interactions

**Research Team**: P. Somasundaran (PS24@Columbia.edu, 212-854-2926), M. Chin

**Goal**: **Understanding the mechanism by which surfactants positively or negatively affect protein function and vice versa**

**Previous Findings**: **Emerging importance of micelle structure on protein function**

- APG affects enzyme activity of subtilisin AND HRP similarly
- Mechanism is driven by interactions with micelles
- Micelle shape and/or packing density may play critical role

**Current Findings**: **Role of surfactant mixture on enzyme activity**

• Enzyme activity increases are more affected by surfactant mixture (APG) than homogeneous compound (Dodecyl maltoside)

• Flexibility of peroxidase increased by APG but not by DM. Further connection between surfactant influencing enzyme activity through increasing enzyme flexibility

**Future Directions**:

- Systematic study of surfactant mixture and enzyme activity to find optimal surfactant conditions for protein formulations

# AIR – Visible Light Activated Antimicrobial Coatings

**Research Team: Vignesh Nandakumar, Zachary Fritz, Vijay Krishna, Ben Koopman and Brij Moudgil**

**Overview:** Healthcare acquired infections have increased the time of stay and the costs incurred for treatment of diseases. Using visible light activated transparent antimicrobial coatings to inactivate microbes on surfaces is an economic solution and can help reduce the number of hospital acquired infections.

**Previous Findings**:

- PhotoProtect ™ is effective against MRSA surrogate (*S.aureus*) and performs better than P25
- Site simulated experiments showed effective results for 9-12 months of testing
- PhotoProtect™ has also been shown to be effective against *A.niger,* a commonly found fungi.
- Proof for visible light inactivation has been established with *S.aureus*

**Current Findings**:

- Inactivation efficiency of PhotoProtect ™ with surrogate bacteria (*S.aureus*) and human pathogens (MRSA)

**Future Directions**:

- Testing inactivation efficiency of PhotoProtect ™ with viruses and fungi for expanding the range of activity for the coatings
- Establishing inactivation efficiency of PhotoProtect ™ on different touch surfaces
- Number of cycles to inactivation and failure for assessing the active timespan of coatings

**Principal Sponsor(s): NSF**

# Essential Oil Formulations to Treat Citrus Greening

**Research team**: B. M. Moudgil (bmoudgil@perc.ufl.edu,352-846-1194), L. Bengani, P. Sharma, G. Mancebo, T. Ibnat , E. Alvarado, E. Triplett, L. Albrigo

**Goal:** Funded by Citrus Research and Development Foundation; the immediate objective of this project is to develop soft nanoparticle formulations with essential oils (EOs) to treat bacterial infected citrus

**Objectives:**

- Develop foliarly applicable oil-in-water (o/w) microemulsions (Mes) of EOs using GRAS and agriculturally approved surfactants
- Evaluate antibacterial efficacy against surrogate bacteria and phytotoxicity of developed MEs
- Greenhouse /field testing of formulations on infected trees
- Study the phloem uptake of non-phytotoxic formulations by foliar application and improve delivery with aid of adjuvants.

**Current Findings:**

- Formulations show high bacterial inhibition ( > 90%) with Essential oils A & B (EO-A, EO-B) and with Thyme Oil
- Formulations show low phytotoxicity at relevant concentrations
- Selected formulations are being tested for their efficacy on infected plants

**Future Directions:**

- Greenhouse/ filed testing of developed formulations on citrus greening infected citrus plants
- Study uptake and transport of formulations by phloem of the citrus plant
- Characterization of citrus leaf surface / formulation physical characteristics like wettability and surface friction

**Principal Sponsor(s): CRDF**

# DISPERSION OF HIGH SOLIDS CONTENT SLURRIES

**Research Team**: Dr. Brij Moudgil (bmoudgil@perc.ufl.edu, 352-328-7292), Dr. Hassan El Shall, Prof. P. Somasundaran

**Goal**: Develop the knowledge base and predictive methodologies to control the dispersion behavior of multi-phase and poly-disperse particulate systems. Specifically to develop a relationship between the rheological behavior of particulate systems and surfactant/polymer adsorption onto the particle surface

**Previous Findings**:

•Solid like structure in high solid content slurries might be responsible for high viscosity

• Reduction of viscosity of high solid content slurries is attributed to breaking this structure by the used dispersants.

•Dispersants with higher molecular weights provide better steric stabilization due to longer chains

•Dispersants with higher charge density provide better electrostatic stabilization due to more charge neutralization

•Dispersants with higher molecular weight and higher charge density seem to be most effective in reducing the slurry viscosity

•Several models have been proposed in the literature describing the relative viscosity as a function of concentration.

•In addition, several studies have been conducted to correlate models' parameters with suspension properties such as particle size, solvent viscosities, temperature, etc.

**Current Findings:**

-PAA chemically adsorbs on alumina surface at the iep (9.8) as indicated by adsorption measurements and FTIR spectra

-AFM measurements and force calculations suggest steric stabilization of alumina in presence of PAA at the iep (pH 9.8)

**Future Directions:**

•In this phase of our study, suspensions' relative viscosities will be used to study the functional dependence of the fitting parameters in the models proposed by Mooney, Krieger-Dougherty, Batchelor, and Brady on various physical, chemical, and interfacial properties of the particulate system.

•Utilize this knowledge to device a model that can manipulate the inter-particle forces and obtain desired properties of suspensions thereby.

**Principal IAB Sponsor(s)**: Kemira, Imerys, Sumicol

# Foaming and Frothing Behavior of Green Surfactants and Fine Particulate Systems

PI: Dr. Brij Moudgil (bmoudgil@perc.ufl.edu), Dr. P. Somasundaran (ps24@columbia.edu),
Team: Jun Wu, Irina Chernyshova and Ponisseril Somasundaran
Columbia University
Alina Ayoub, Kyle Schmidt, Angelina Georgieva, H. El-Shall, and Brij Moudgil
University of Florida

**Goal**:
- Provide an enhanced understanding of antagonistic and/or synergistic effects on foaming performance of green surfactants with hydrophobically modified fine particles, fatty alcohols and silicone oil

**Previous Findings**:
- Green Tri-Blend and Plantapon have similar foamability and similar performance.
- Green Tri-Blend foamability is more pH dependent than Plantapon

**Current Findings**:
- Green Tri-Blend has a higher foamability at lower temperatures and the benchmark has a higher foamability at higher temperatures
- Octanol/silica/silicone oil mixtures have similar defoaming effects on both Green Tri-Blend and Plantapon

**Future Directions**:
- Use of statistical design for evaluation of statistically significant factors influencing the foamability of surfactants in the presence of particles

Principal IAB Sponsor(s): Kemira, Inc., Sumicol, Inc., Ecolab, Inc., Cytec Industries, Inc., Unilever, Inc., Church&Dwight, Inc.

# EFFECTS OF FATTY ACIDS ON POLYELETROLYTE-SURFACTANT INTERACTIONS

**Research Team:** Jose Martinez-Santiago and Prof. P. Somasundaran (Columbia Univ.)
Dr. Ananthapadmanabhan KP and Liang Tsaur (Unilever R&D, C. Totland (University of Bergen, Norway)

**Goal**: To study the effects of fatty acids on the interaction mechanisms of an oppositely charged polyelectrolyte-surfactant pair using various characterization techniques including $^1$H Nuclear Magnetic Resonance (NMR). Evaluate the impact on emulsion systems and it effects on polymer-induced flocculation.

**Current Findings (Effects of LA on oppositely charged P-S phase behavior revealed by NMR)**

- NMR was successfully used to demonstrate that before the precipitation onset some of the polymer is progressively neutralized by the oppositely charged surfactant, which gradually forms lamellar aggregates at the polymer side chain, while some polymer is adsorbed to the insoluble LA nano-aggregates present in the system.
- With increased amounts of SDES, when micelles form, LA transitions from solid-state aggregate to solubilized state at the palisade region of SDES micelles. Finally, it was observed that, in the presence of LA the complexation efficiency of the polymer-surfactant pair increased.
- These results were used to explain the flocculation disruption of fatty acids in polyelectrolyte-SDES systems in the presence of oil (emulsions).

**Future Directions**:

- Next, we plan to model the effect of fatty acids on polyelectrolyte-surfactant interaction using the thermodynamic parameters of all species involved in the system.

**Principal IAB Sponsor**: Unilever

# Modeling and Simulation for Effective Solids Handling of Wet Fibers

**Research Team**: Jennifer Sinclair Curtis (jcurtis@che.ufl.edu; 352-392-0946) and
Yu Guo, Department of Chemical Engineering, University of Florida

**Goal**: **Extend Discrete Element Method (DEM) particle simulation models to describe wet, flexible fibers**

**Previous Findings**: For flexible, wet elongated particles

- Increases in the biomass concentration from 5% to 10% showed an order of magnitude increase in the viscosity
- As the shear rate increases, the viscosity of the biomass decreases (shear thinning) and becomes relatively independent of particle size
- Implementation of liquid bridge model into the flexible fiber simulations
- Increasing particle flexibility increases particle deformation, and the size and packing density of agglomerates
- Increasing Bond number produces fewer, but larger, agglomerates

**Current Findings**: For flexible, wet, elongated particles

- DEM simulations were validated using angle of repose and shear cell testing
- Stress results obtained from stressed-controlled shear flows are similar to those from concentration-fixed shear flows, under the condition that the same normal stress in the concentration-fixed flow is applied to the stress controlled flow.
- Simulated stress fluctuations are reduced by increasing the cell size and/or reducing the shear strain rate
- Although the wet particles show strong cohesive behavior when filling the shear cell, no significant difference in shear stress is observed between dry and wet particles in shear

**Future Directions**: For the next IAB meeting, the following will be studied for fibrous particles:

- Increase blade length from 2mm to 4mm in simulations and more testing under different applied normal stresses
- Shear tests with a clear cell to visualize shear zone and allow for more detailed comparison with simulations
- Biomass testing and simulations

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**Principal IAB Sponsor(s)**: Shell and other industries that deal with fibrous materials

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# *Interactions of surfactants with stratum corneum (SC): Monitoring, Mechanisms and Mitigation*

**Research Team**: P. Somasundaran (ps24@columbia.edu, 212-854-2925), Parag Purohit

**Goal**: To study the damage processes in SC by common surfactant and solvent systems and devise strategies for mitigation

**Current Findings**:

- Damage to SC lipids by surfactant and solvent treatment was measured by drying stress and Raman studies
- Greener surfactant candidates evaluated for effects on SC
- Lipid content mapping with Raman spectroscopy
- Water content effects studied using spectroscopic methods
- Effect of pH and contact time evaluated on the SC properties
- Surfactant penetration in SC studied using depth profiling

**Future Directions:**

- Green surfactant mixed studies: stress and lipid modification (Glycinate, sarcosinate in combination with conventional systems)
- Modelling surfactant-SC interactions

**Principal IAB Sponsor: Unilever**