

# Oil emulsification using responsive carbon black particles

Amitesh Saha,<sup>†</sup> Ani Nikova,<sup>‡</sup> Pradeep Venkataraman,<sup>§</sup> Vijay John,<sup>§</sup> Arijit Bose<sup>†</sup>

<sup>†</sup>University of Rhode Island, <sup>‡</sup>Cabot Corporation, <sup>§</sup>Tulane University

## Provide an alternative dispersant that

- Keeps emulsions stable at high dilutions over months
- Reduces PAH partitioning into aqueous phase
- Potentially has low toxicity to bacteria and marine life

Pickering emulsions from high specific surface area (200m<sup>2</sup>/gm) carbon black potentially satisfies these criteria

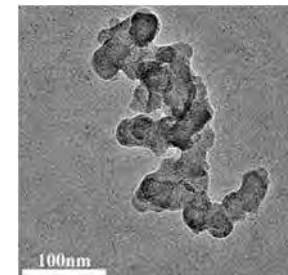
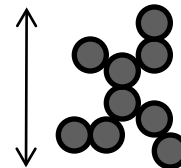
## Carbon black

Primary particle size 20nm ●

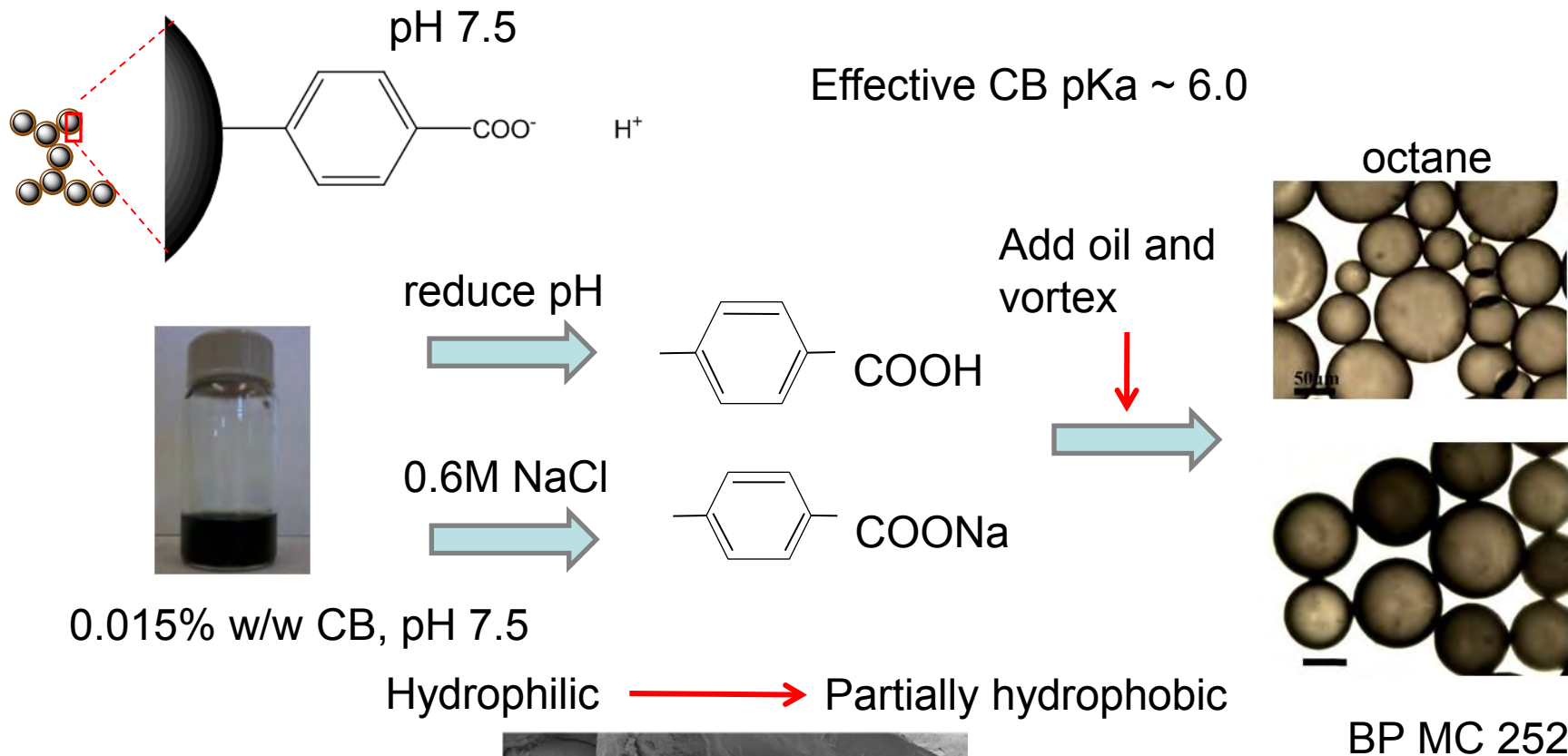
Specific surface area ~200 m<sup>2</sup>/g

Aggregate size 100 - 150nm

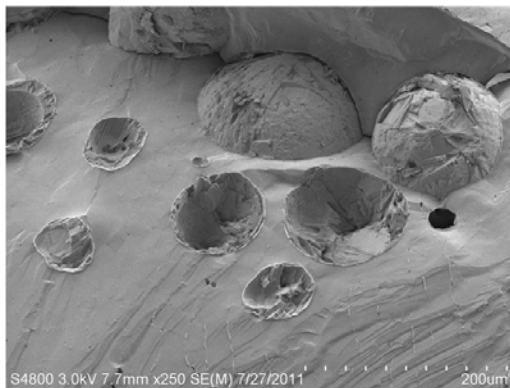
**Not spheres!**



# Strategy

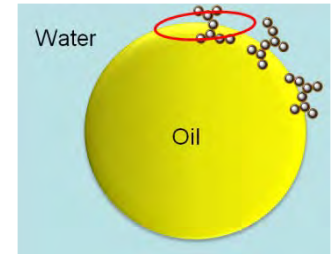


Cryo-SEM  
(O-in-W emulsion)

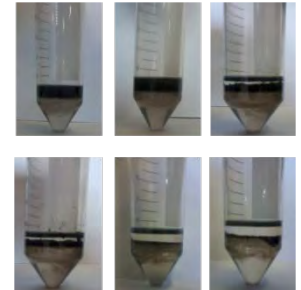


# Future work

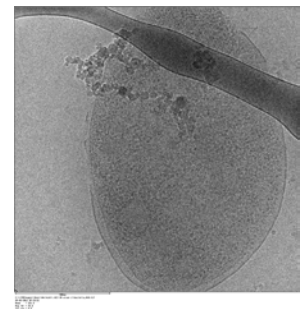
- Fractal particles at oil-water interfaces – physics



- Stability of emulsions – centrifuging



- Biodegradation- Bacteria interactions with CB and CB stabilized emulsions (droplet size)

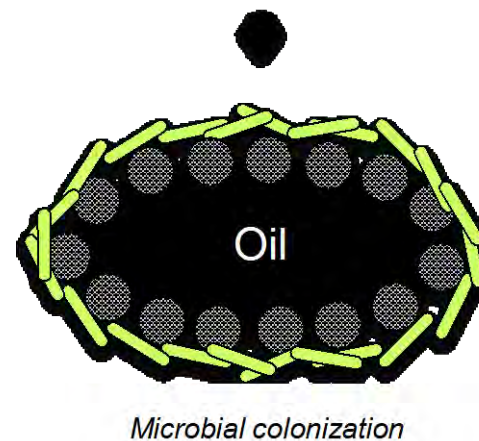
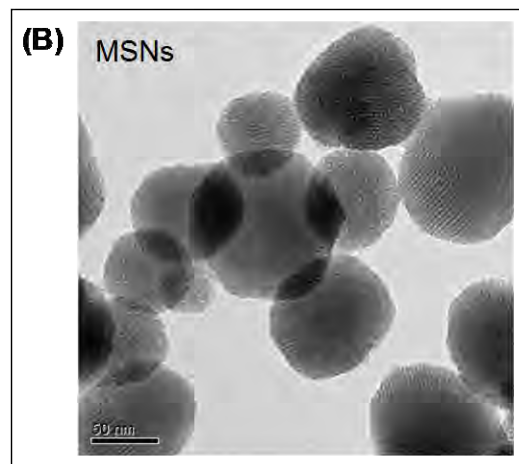
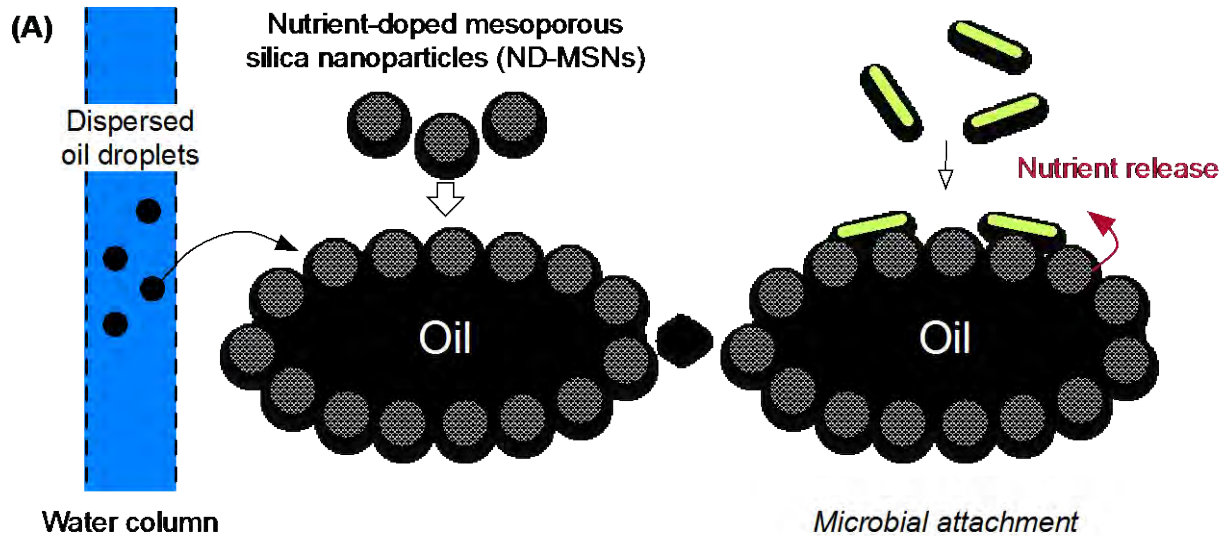


- PAH partitioning into aqueous phase

- Anything else?

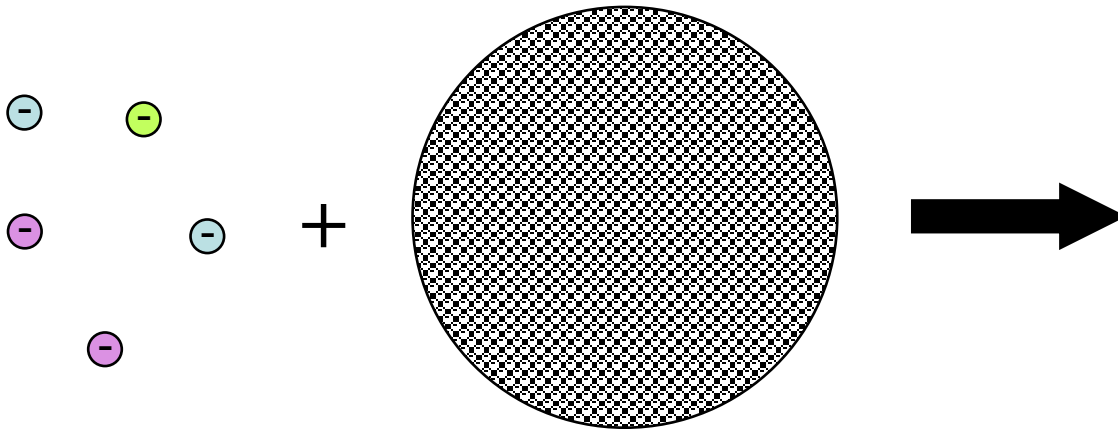
# Nutrient-doped mesoporous silica nanoparticle oil dispersants to enhance microbial degradation

Geoffrey D. Bothun, Chemical Engineering, University of Rhode Island



# Nutrient-doped mesoporous silica nanoparticle oil dispersants to enhance microbial degradation

Adequate nutrient supply ( $\text{NO}_3^-$ ,  $\text{PO}_4^{3-}$ , Fe) critical for biodegradation



$$\Delta E = \pi r_p^2 \gamma_{o/w} (1 - |\cos \theta|)^2$$

- Capillarity and SiOH density
- Ion adsorption and leaching kinetics
- Ion effects on PE stability
- Toxicity analysis
- Biodegradation enhancement

Atlas & Hazen, *Environ. Sci. Technol.* 45 (2011) 6709

Rogers & Bennett, *Chem. Geol.* 203 (2004) 91

Reisfeld et al., *Appl. Microbiol.* 24 (1972) 363

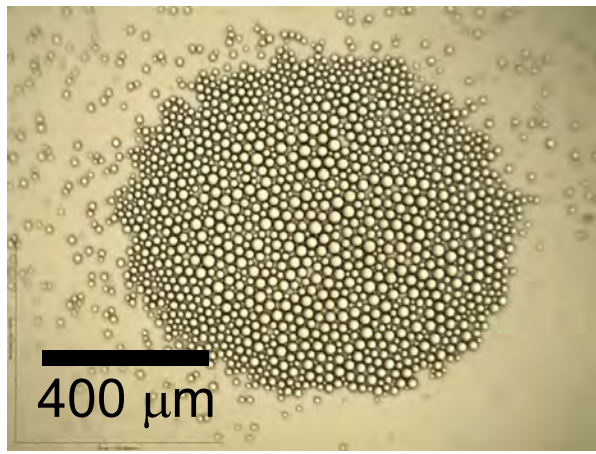
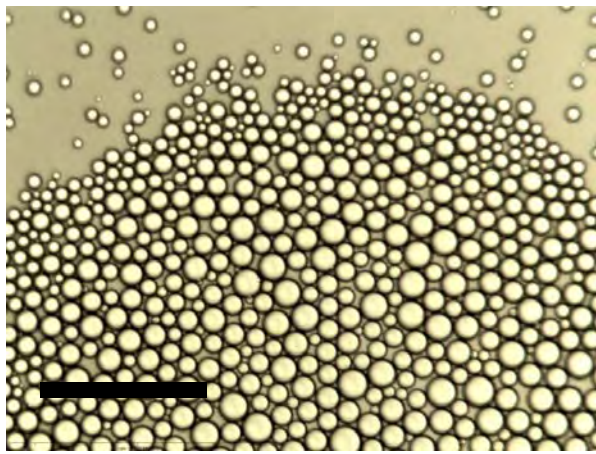
# Porous silica nanoparticles (20X)

0.1 wt%

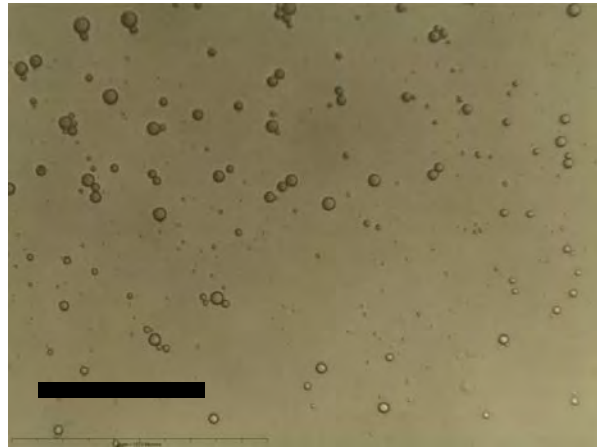
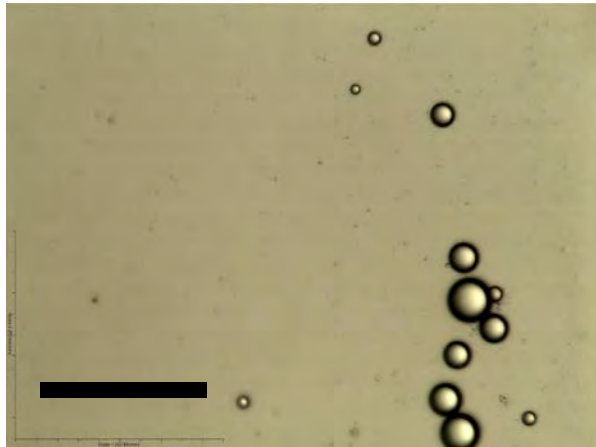
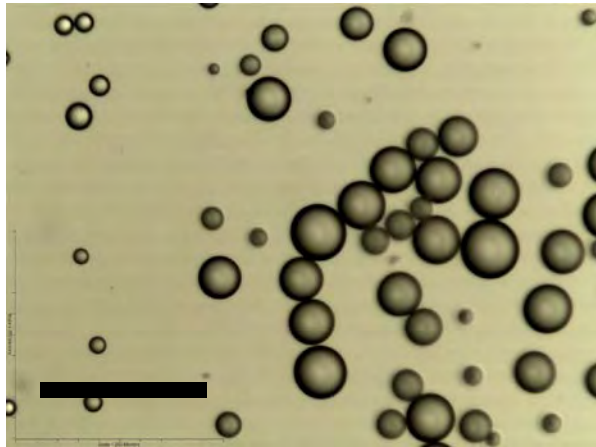
0.5 wt%

1 wt%

Octane



Toluene



Droplet size 

# ***Interfacial Engineering through Particles***

*Lenore L. Dai*

*Chemical Engineering, Arizona State University*

- ◆ **Project Objective #1:**  
**Developing environmentally responsive solid dispersants**
  
- ◆ **Project Objective #2:**  
**Understanding oil-water interfacial rheology through particle tracking**

**Funding Acknowledgement**

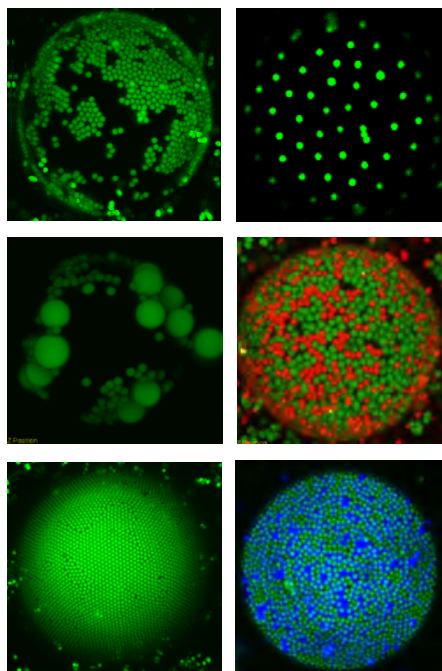
**National Science Foundation**

**C-MEDS/ Gulf of Mexico Research Initiative**



# Developing Environmentally Responsive Solid Dispersants

## Rich Morphology of Pickering Emulsions

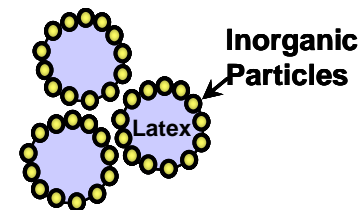


S. Tarimala and L. L. Dai, *Langmuir* 2004;  
S. Tarimala, C. Y. Wu, and L. L. Dai, *Langmuir* 2006;  
H. Ma and L. L. Dai, *Langmuir* 2011.

## Pickering Emulsion Polymerization

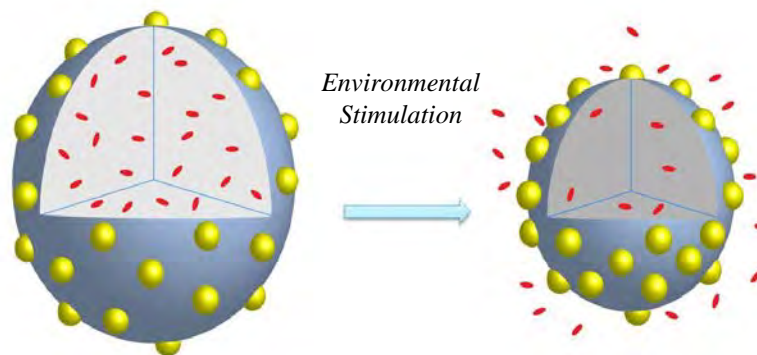
Pickering Emulsions  
(using solid particles  
as stabilizer)

Pickering emulsion  
polymerization



H. Ma & L. L. Dai, *JCIS* 2009; H. Ma et al., *Materials* 2010.

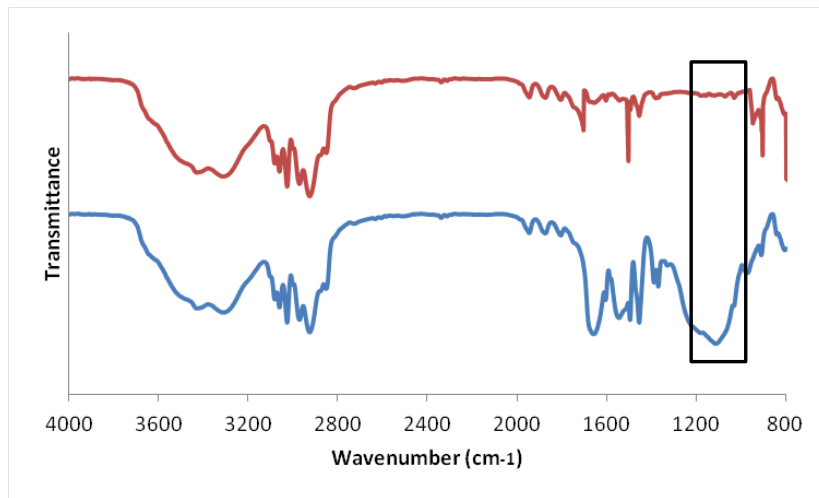
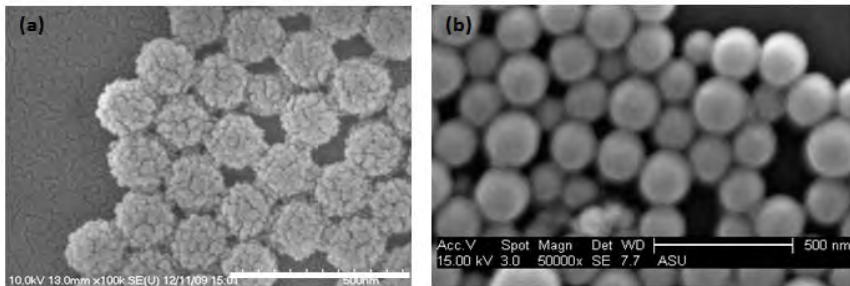
## Environmentally Responsive Solid Dispersants



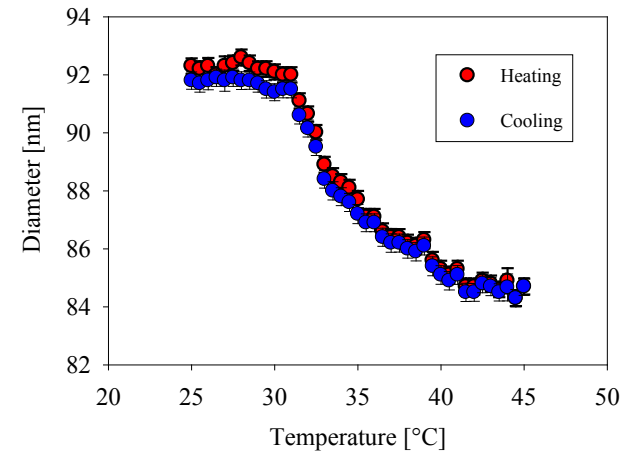


# Developing Environmentally Responsive Solid Dispersants (Continued)

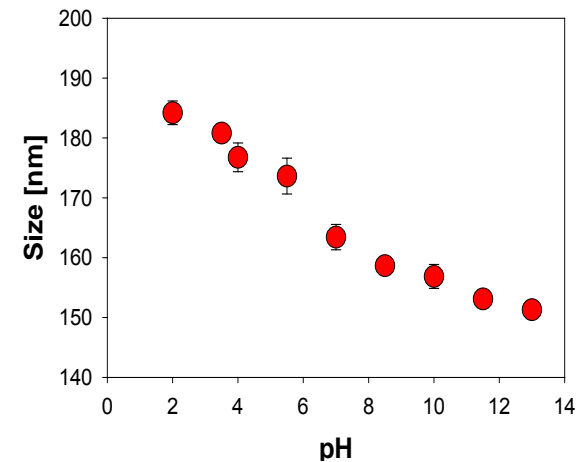
## Particle Morphology



## Temperature Sensitivity

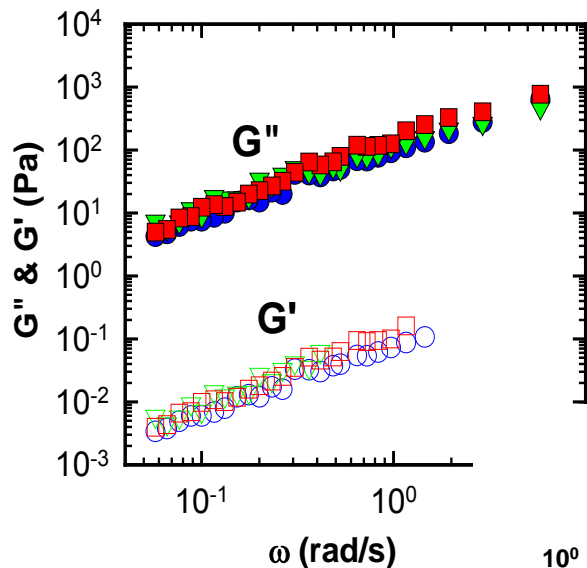


## pH Sensitivity

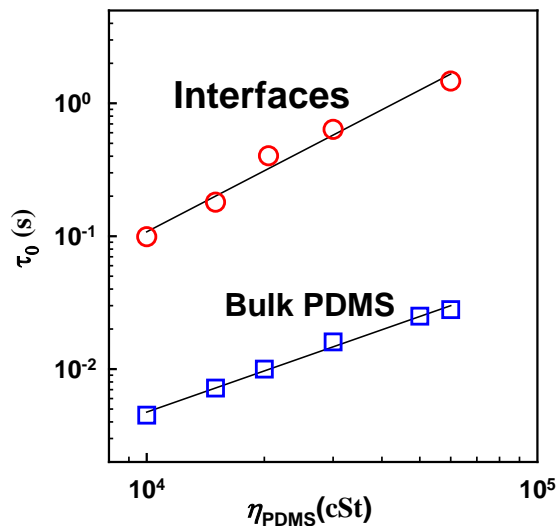


# Understanding Oil-Water Interfacial Rheology through Particle Tracking

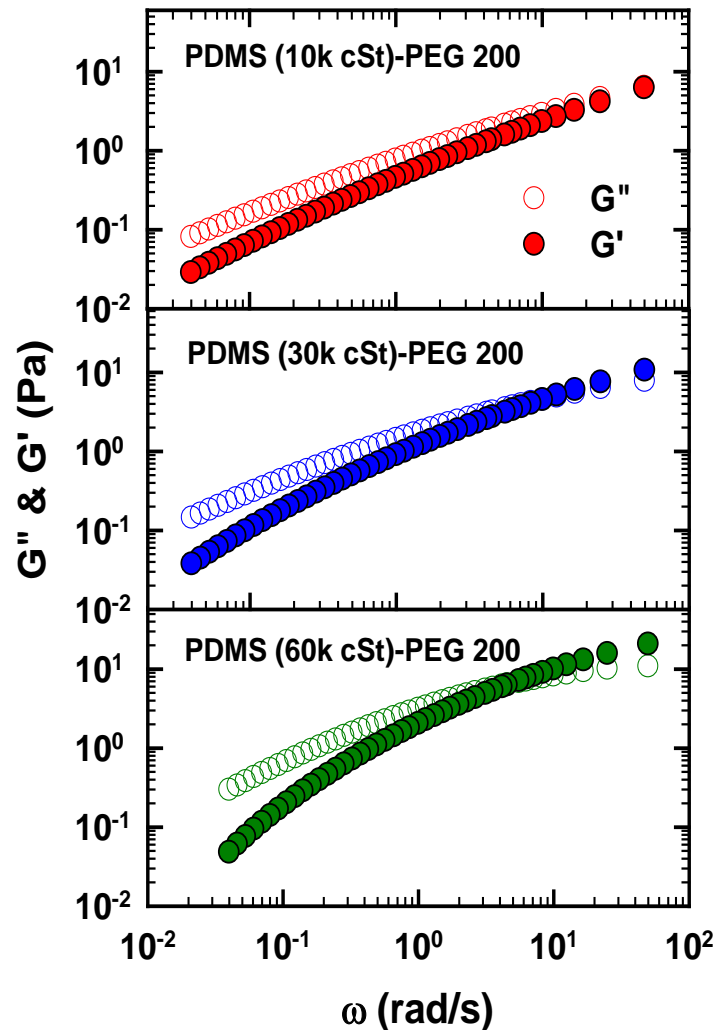
## Oil PDMS(50k cSt) - Water



## Relaxation Time



Y. M. Song and L. L. Dai,  
*Langmuir* 2010.





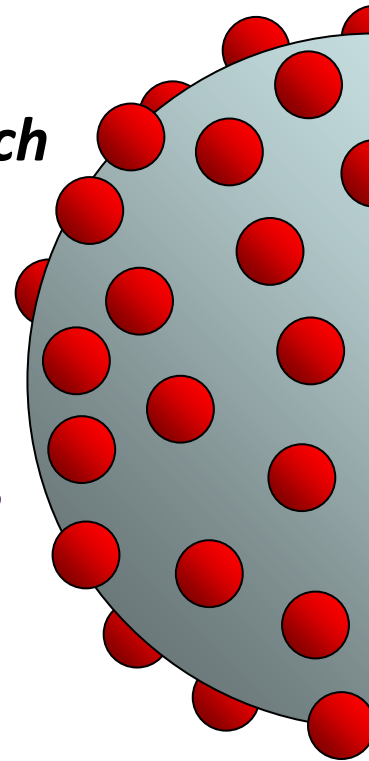
# Particle-stabilized droplets

*A. D. Dinsmore*

*Univ. of Massachusetts Amherst, Physics Dept.*

*Collaborators: T. Emrick, T. Russell, B. Davidovitch*

(Synergistic efforts supported by UMass MRSEC on  
Polymers (DMR-0820506) and NSF CBET-0967620.)

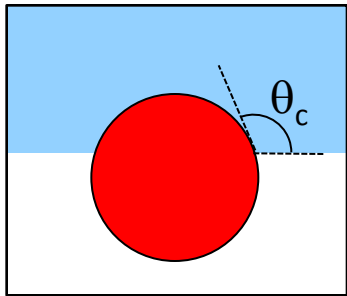


- 
- **Intentional use of particulates in dispersants offers new opportunities to control droplet fate.**
  - **Unintentional binding of particles (*e.g.*, marine snow) may occur, altering the droplet fate.**

# Current studies

## I. How particle shape affects lateral capillary forces at an interface.

(w/ Benny Davidovitch, UMass)



- If particle has fixed  $\theta_c$ :  
*anisotropic* interface  $\rightarrow$  deformation.
- ↓
- Spheres are forced toward saddles.
  - Discs *might* be forced the other way (toward large, positive curvature).

## II. How electrostatics affects particle adsorption at an interface.

- Cationic micro-particles bind spontaneously to oil-water. Anionic do not.
- Prelim. results: adsorption on metallic surfaces is reversed by applied voltage.
- Goal: Tune interfacial potential using two immiscible electrolytes, monitor adsorption & interfacial structure.

# New Studies

## I. Measure $\Delta E$ and ad- or desorption timescales for model oils & particles.

[K. Du *et al*, *Langmuir* **26**, 12518 ('10).]

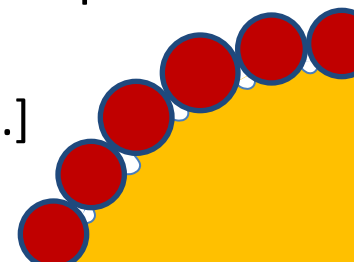
- Optical microscopy of particles & drops
- Interfacial tension measurements.
- Focus on roles of...
  - particle charge (zeta potential).
  - particle shape (i.e., roughness, sphericity).
  - ligand species.

## II. Stability of droplets with mixed particle species (charge, size, roughness).

## III. Particle adsorption on volatile-fluid droplets.

- Rigid particulate layer can stabilize zero or negative Laplace pressure.  
Will this retard dissolution of soluble compounds?

[gas bubbles: Abkarian *et al*, *Phys. Rev. Lett.* **99**, 188301 ('07).]



# Implications

- **Predict what properties of naturally existing particles determine whether they bind and how they affect droplet density and stability.**
- **Design particulates for rapid stabilization of droplets.**  
(Stable over long term? Controllably reversible? Tunable mass density?)
- **Control what happens when particles adsorb on liquid droplets that have water-soluble components.**  
(Prevent or retard dissolution?)

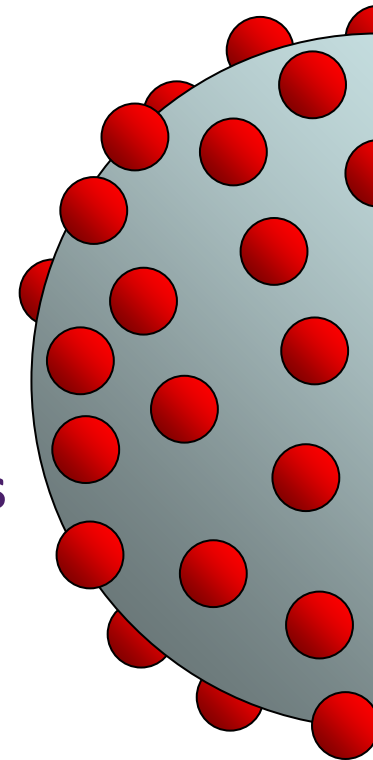


# Particle-stabilized droplets

*A. D. Dinsmore*

*Univ. of Massachusetts Amherst, Physics Dept.*

(Synergistic efforts supported by UMass MRSEC on  
Polymers (DMR-0820506) and NSF CBET-0967620.)

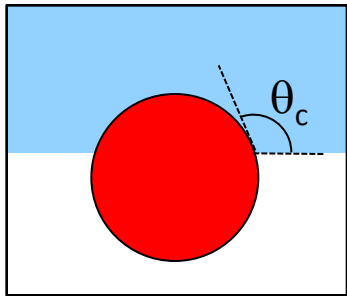


- 
- Intentional use of particulates in dispersants offers new opportunities to control droplet fate.
  - Unintentional binding of particles (*e.g.*, marine snow) may occur, altering the droplet fate.

# Current studies

## I. How particle shape affects lateral capillary forces at an interface.

(w/ Benny Davidovitch, UMass)



- If particle has fixed  $\theta_c$ :  
*anisotropic* interface  $\rightarrow$  deformation.
- ↓**
- Spheres are forced toward saddles.
  - Discs *might* be forced the other way (toward large, positive curvature).

## II. How electrostatics affects particle adsorption at an interface.

- Cationic micro-particles bind spontaneously to oil-water. Anionic do not.
- Prelim. results: adsorption on metallic surfaces is reversed by applied voltage.
- Goal: Tune interfacial potential using two immiscible electrolytes, monitor adsorption & interfacial structure.



# New Studies

## I. Measure $\Delta E$ and ad- or desorption timescales for model oils & particles.

[K. Du *et al*, *Langmuir* **26**, 12518 ('10).]

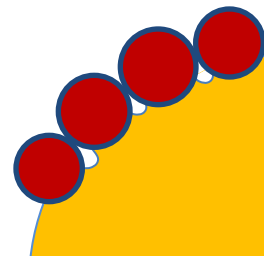
- Optical microscopy of particles & drops
- Interfacial tension measurements.
- Focus on roles of...
  - particle charge (zeta potential).
  - particle shape (i.e., roughness, sphericity).
  - ligand species.

## II. Stability of droplets with mixed particle species (charge, size, roughness).

## III. Particle adsorption on volatile-fluid droplets.

- Rigid particulate layer can stabilize zero or negative Laplace pressure.  
Will this retard dissolution of soluble compounds?

[gas bubbles: Abkarian *et al*, *Phys. Rev. Lett.* **99**, 188301 ('07).]



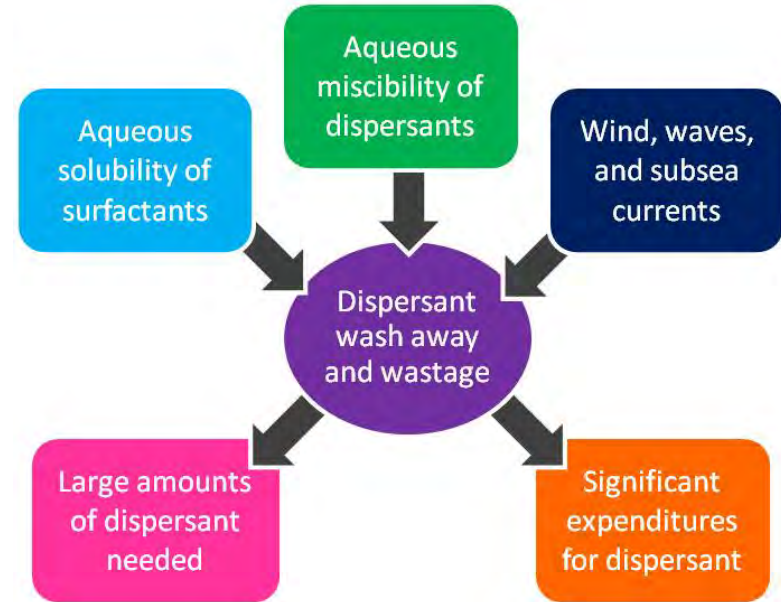
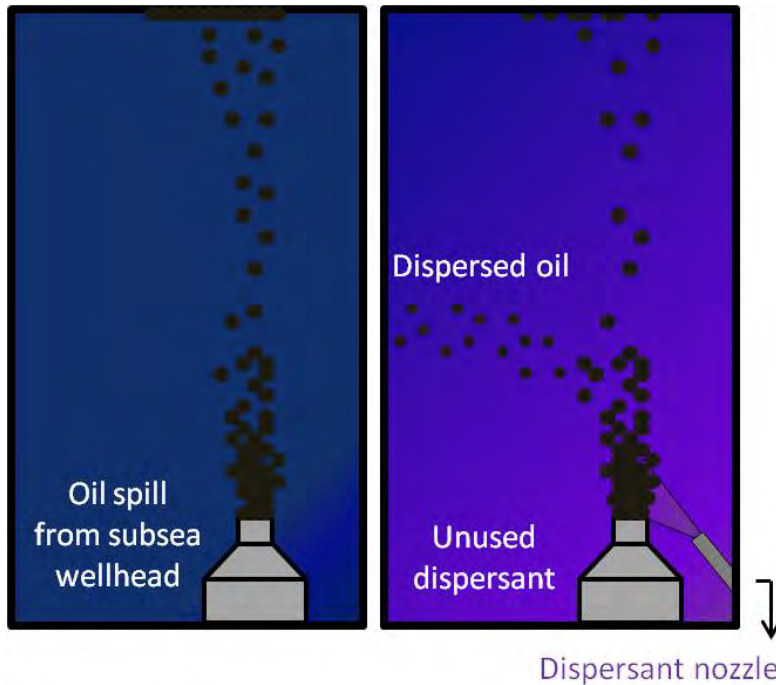
# Implications

- **Predict what properties of naturally existing particles determine whether they bind and how they affect droplet density and stability.**
- **Design particulates for rapid stabilization of droplets.**  
(Stable over long term? Controllably reversible? Tunable mass density?)
- **Control what happens when particles adsorb on liquid droplets that have water-soluble components.**  
(Prevent or retard dissolution?)

# A Smart Dispersant Formulation for Reduced Environmental Impact and Consumption

Courtney A. Ober, Ram B. Gupta  
Department of Chemical Engineering  
Auburn University, Auburn, AL 36849

## Current Dispersant Application:



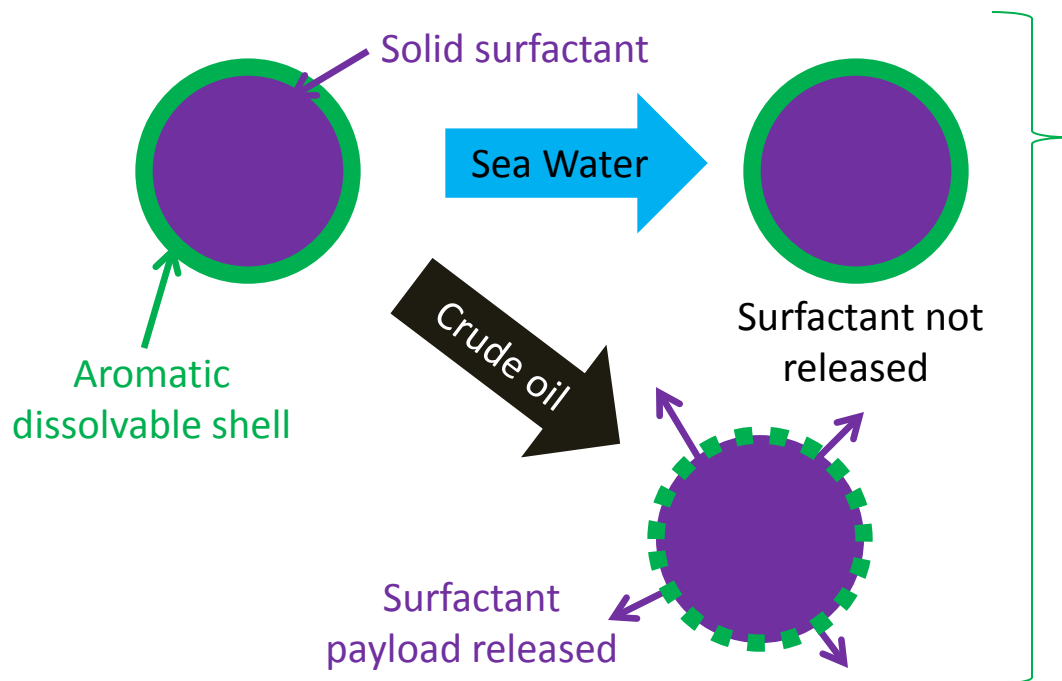
2.2 million gallons of dispersant were used in the Deepwater Horizon spill resulting in an estimated cost of \$80 million

**Objective:** To develop a smart dispersant formulation that can be targeted directly to an oil spill, therefore reducing the environmental impact and consumption of the dispersant

# Smart Dispersant Formulation: Surfactant Microcapsules

The microencapsulation of solid surfactant in a water-insoluble, aromatic dissolvable shell allows selective release of surfactant within an oil spill.

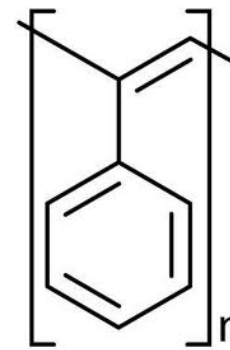
## Schematic of Surfactant Release from Microcapsules



Solubility properties of the polymer shell are critical for targeted release



## Potential Coating Polymer: Polystyrene



Solvent	Polystyrene Solubility
Benzene	0.68 g/mL
Toluene	0.60 g/mL
Xylene	0.40 g/mL
Water	0.00 g/mL

Crude oil contains ~ 15 wt. % aromatics in which the polystyrene shell will dissolve.

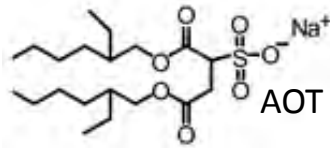
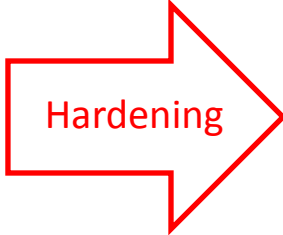
# Development of Surfactant Microcapsules



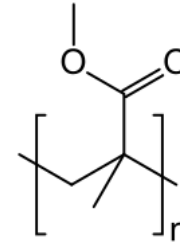
AUBURN  
UNIVERSITY



Soft, white,  
waxy material



AOT was mixed  
with ~20 wt. %  
PMMA in DCM and  
DCM evaporated

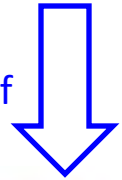


$M_w \sim 15,000$



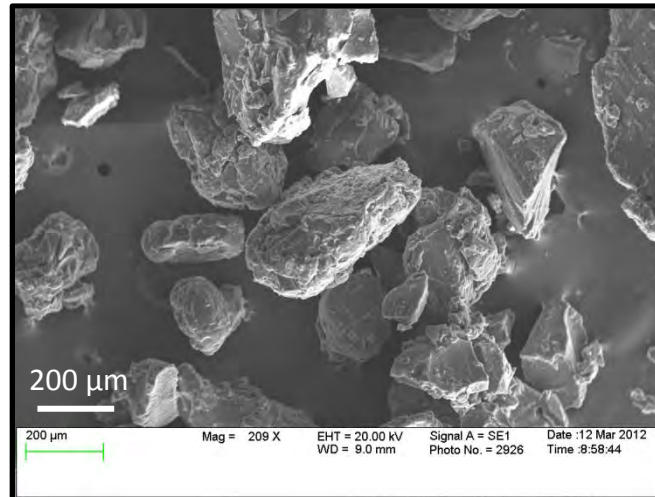
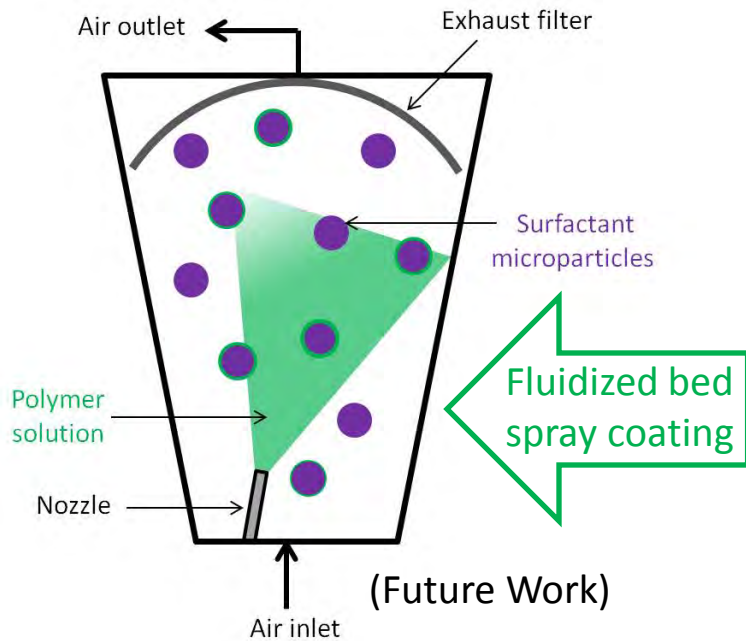
Hardened AOT

1 minute of  
grinding



IKA® M20 Universal Mill  
(Germany)

Surfactant in Corexit Dispersants: Dioctyl  
Sodium Sulfosuccinate (Aerosol OT, AOT)

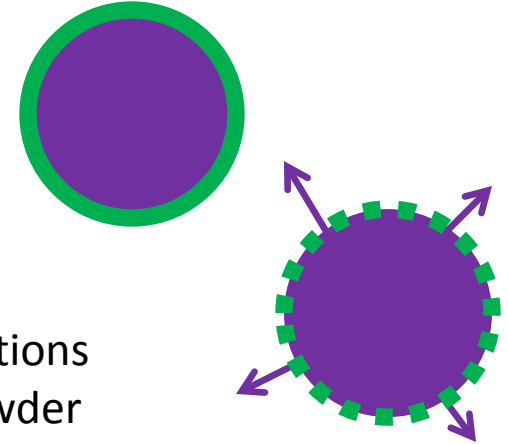


SEM image of AOT microparticles

# Advantages and Implications of Surfactant Microcapsules

## Advantages of surfactant microcapsules for oil dispersion:

- Complete utilization of surfactant
- Solid surfactant allows for maximum potency
- Reduced amount of surfactant needed
- No need for hydrocarbon-based solvents
- Decreased toxicity concerns for marine species
- Microcapsules amenable to both surface and subsea applications
- Microcapsules can be delivered as a water slurry or solid powder



## Broader implications of proposed work:

- Solid formulation may increase stability and shelf-life
- Encapsulation may prevent adverse health effects in clean up workers
- Formulation techniques can be applied to a wide variety of surfactants
- Preparation of microcapsules will be inexpensive and use standard equipment
- Preparation techniques will be easily scalable



Bench-top  
spray coater



Commercial  
spray coater

# CryoImaging Emulsification Processes

Alon McCormick, Minnesota

with Grad Students David Riehm and Han Seung Lee

- Complementary techniques
  - cryoTEM
  - cryoSEM
  - Cryofracture Replicate TEM
- Collaborations with other consortium members (Bose, John)
- Interest in kinetic transitions, mechanisms via imaging

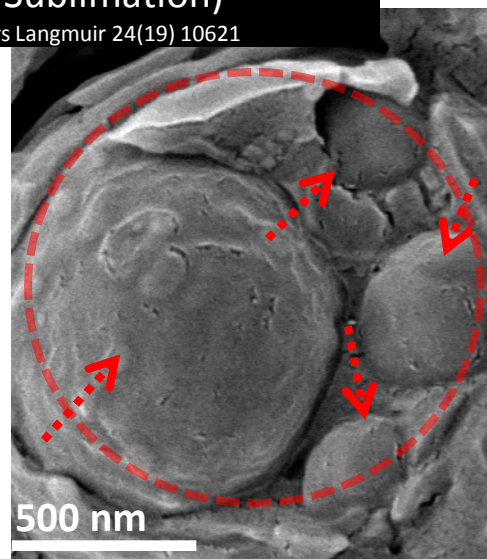
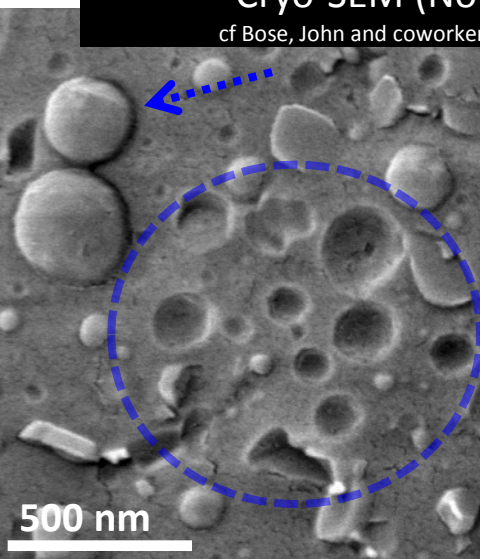
# Effect of surfactant mix on ultrafine emulsification (Han-Seung Lee, in Preparation)

Optimum (NP 3.25g)

Overdose (NP 6.00g)

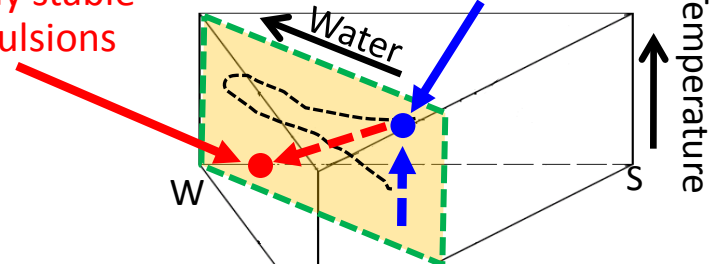
Cryo-SEM (No Sublimation)

cf Bose, John and coworkers Langmuir 24(19) 10621



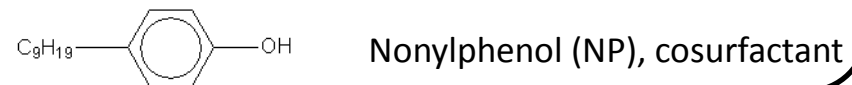
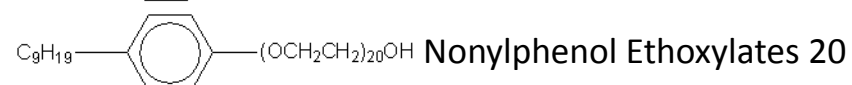
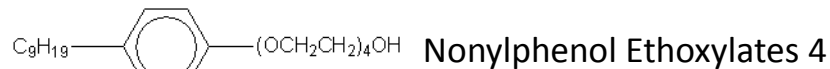
Kinetically stable fine emulsions

Microemulsions



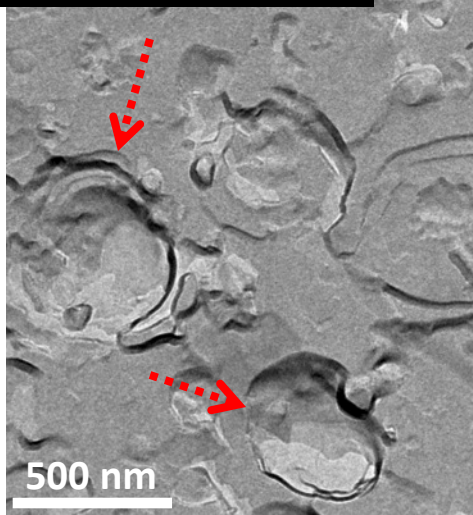
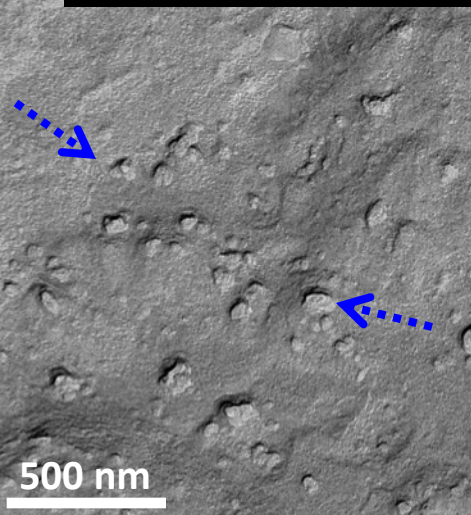
⊗ Composition

- 85.0 wt. % DI-Water (W) O
- 9.63 wt. % n-Hexadecane (O)
- 5.37 wt. % Nonionic Surfactants (S) (4:5:1)



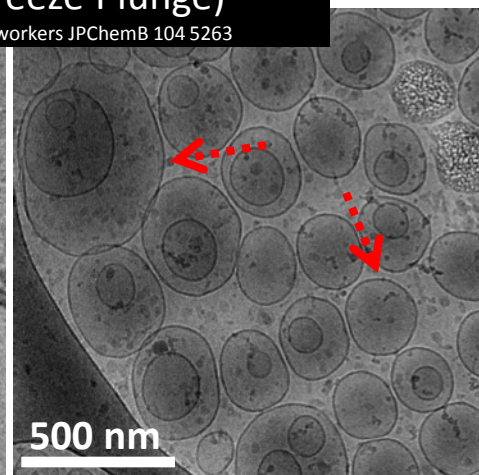
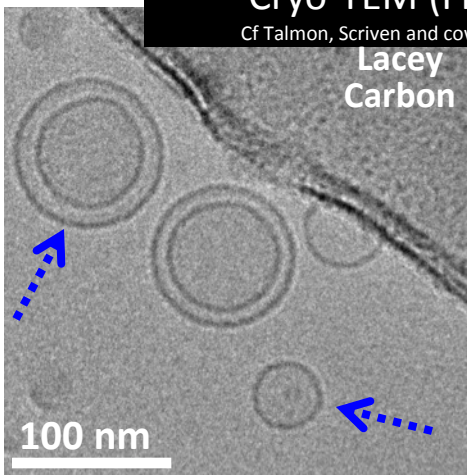
Cryo-fracture-replicate TEM

(w/ Zasadzinski) cf Strey and coworkers, Coll Surf A 228, 159



Cryo-TEM (Freeze Plunge)

Cf Talmon, Scriven and coworkers JPChemB 104 5263





# Physical Chemistry of Typical Corexit 9500 Surfactants

## Surfactant Classes:

### Anionic

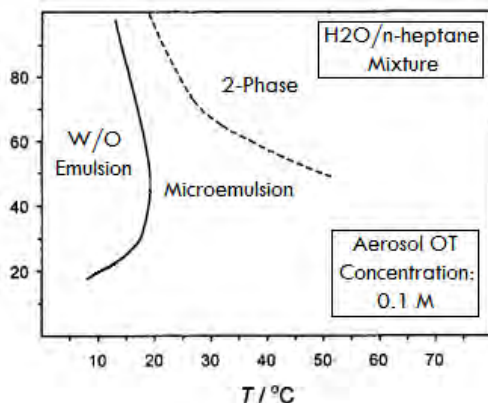
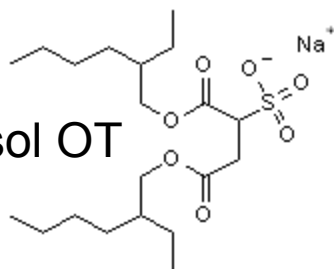
#### Hydrophobic Attributes:

- Large Adsorption Area (Allows Rapid Saturation of Oil-Water Interface)
- Microemulsion at Room Temperature
- Cosurfactant Unnecessary

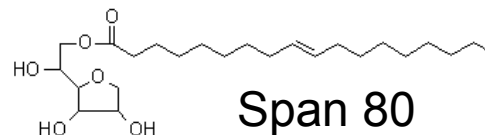
#### General Attributes:

- Soluble in both Water and Paraffins
- High Diffusion Coefficient
- Sulfonate Group is:
  1. More Stable than Sulfates
  2. Less Prone to Precipitation in Presence of Salt than Carboxylic Acids

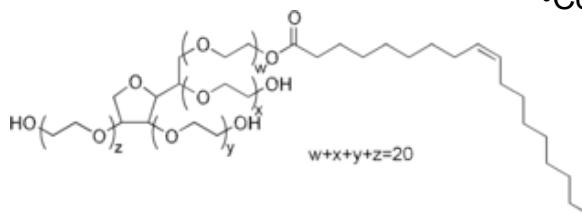
Aerosol OT



### Nonionic



Tween 80



Adapted from Nave et al. "What Is So Special About Aerosol-OT?" Langmuir 2000, 16, 8741

### Cationic Zwitterionic

#### Sorbitan Ester Attributes:

- Made of Fats and Sugars
- Widely Varying HLBs (Span 80 = 4.1, Tween 80 = 15)
- Completely Miscible

## Directions of Inquiry:

- How robust to (temperature, salinity, etc.) is emulsification with mixtures of surfactants of complementary temperature (etc.) sensitivity?
- How robust with (or even enhanced with) solids?



# **A New Class of Food-Grade Dispersants for Treatment and Remediation of Marine Oil Spills**

**Srinivasa R. Raghavan**

University of Maryland, College Park

**Objective:** We propose to develop an alternative dispersant formulation based on food-grade phospholipids such as lecithin (from soybean or egg). Lecithin-based dispersants will be **safe, nontoxic, inexpensive**, and will be **comparable in effectiveness** to the Corexits.

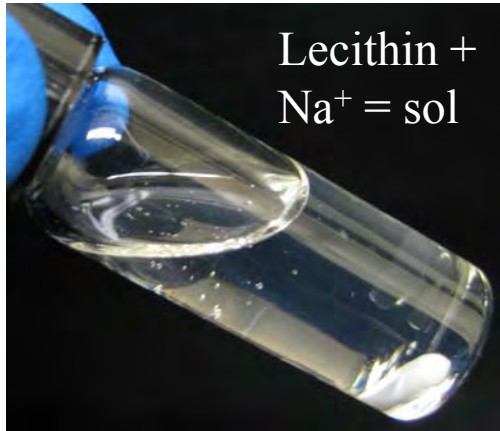
**Key Concept:** While lecithin alone is not an efficient dispersant of oil in water, we propose that it can be “activated” by **complexing with multivalent cations** like calcium ( $\text{Ca}^{2+}$ ).

# Motivation

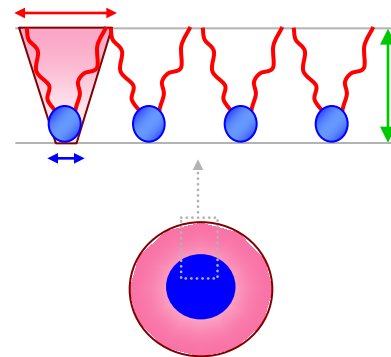
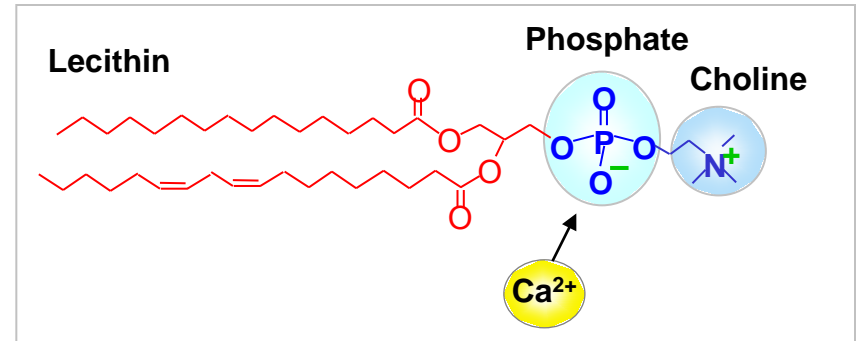
- Current dispersants used to treat oil spills such as the Corexits are all based on synthetic surfactants.
- Questions about the toxicity of these dispersants, especially to aquatic life.
- Can we develop a new generation of dispersants using non-toxic, food-grade amphiphiles?
- Lecithin from soy or egg-yolk is a food-grade phospholipid. Can we make it a good dispersant?



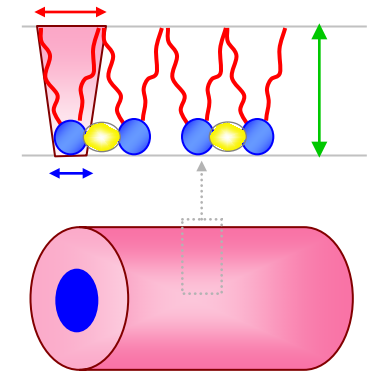
# Hypothesis and Previous Work



We recently found that lecithin can be activated to **gel oils** (n-alkanes) by adding salts of **multivalent cations** ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{La}^{3+}$ )



Spherical reverse micelles in oil;  
**weak** dispersant of oil in water.



Cylindrical reverse micelles in oil;  
**strong** dispersant of oil in water.

Lee, H. Y.; Raghavan, S. R. et al. "Can Simple Salts Influence Self-Assembly in Oil? Multivalent Cations as Efficient Gelators of Lecithin Organosols." *Langmuir* **2010**, 26, 13831-13838

We hypothesize that the **dispersing power** of lecithin can be similarly activated by combining with  $\text{Ca}^{2+}$

# Next Steps

Over the next year, we will systematically test our hypothesis and determine whether lecithin + cations can successfully disperse oils of different kinds in water.

1. Dispersion tests will be conducted with model oils + water + dispersant.

2. Current “gold standard”, i.e., various Corexits, will be tested for comparison.

3. Effect of cation type, cation:lipid molar ratio, and the nature of the carrier fluid will be key variables.

## **Thanks to:**

C-MEDS / BP for funding

Prof. Vijay John

Prof. Dick Weiss

Prof. George John

Prof. Shih-Huang Tung

# Understanding the Effects of Nanoparticle Size and Ligand Chemistry on Pickering Emulsions

Christopher B. Roberts and Pranav Vengsarkar

*Nanoparticle-stabilized Pickering emulsion offer opportunities to create oil-in-water emulsions applicable to oil-spill cleanup*

**Objective:** Improve our fundamental understanding of the influence that nanoparticle characteristics and stabilizing agent chemistry have on the stability of Pickering emulsions



AUBURN UNIVERSITY

DEPARTMENT OF  
CHEMICAL ENGINEERING

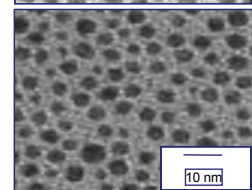
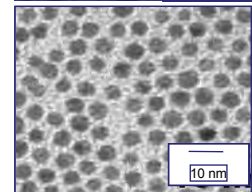
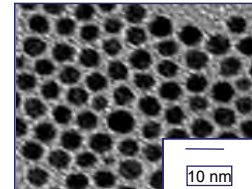
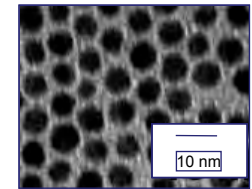
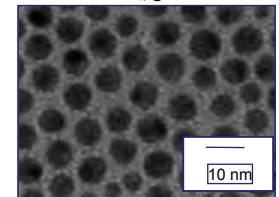
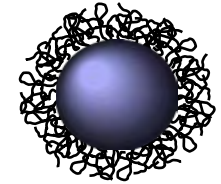
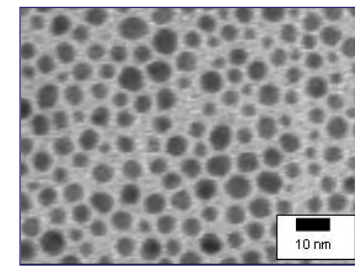
# Concept and Specific Aims

## *Core Concept:*

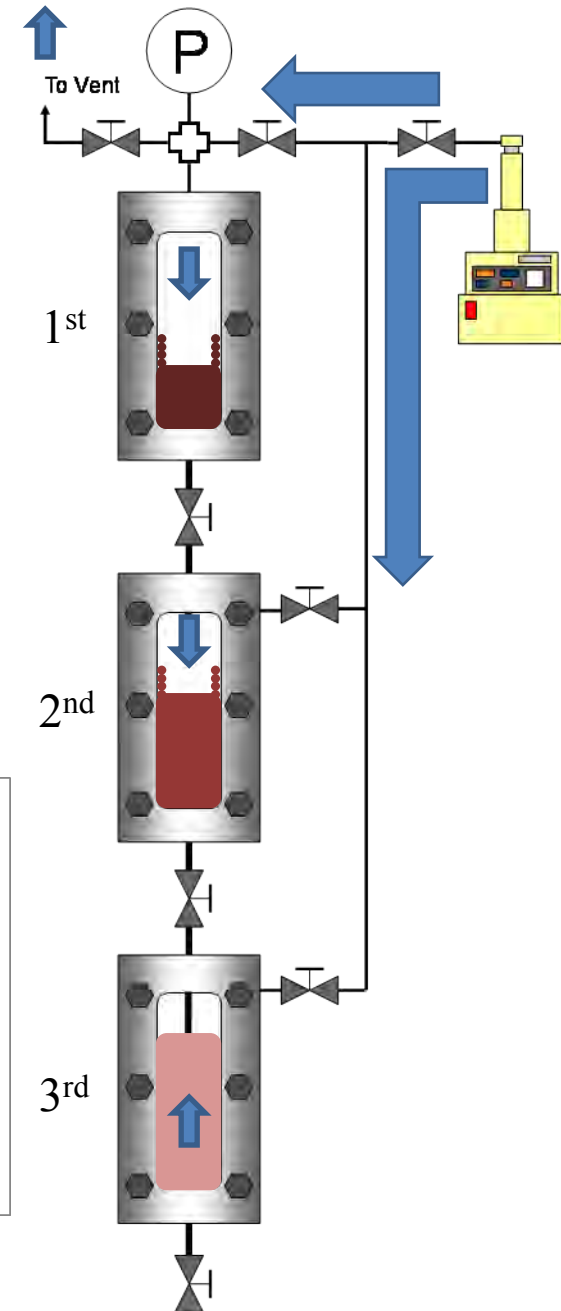
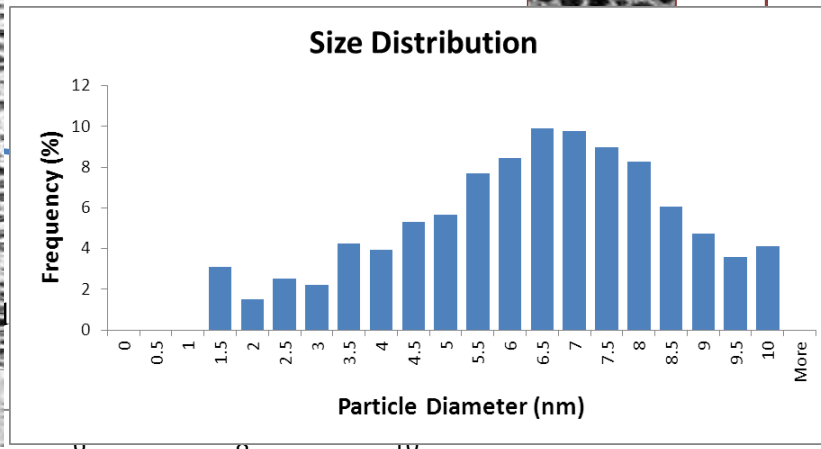
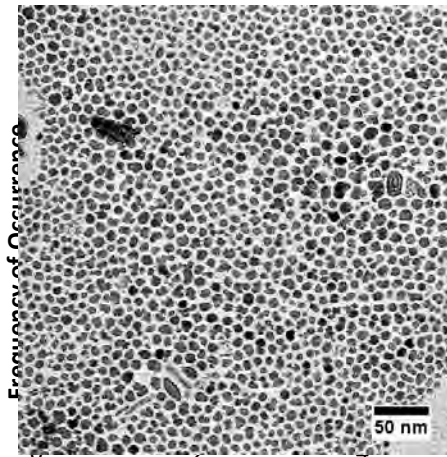
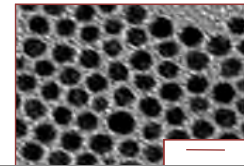
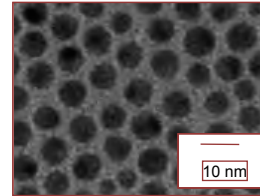
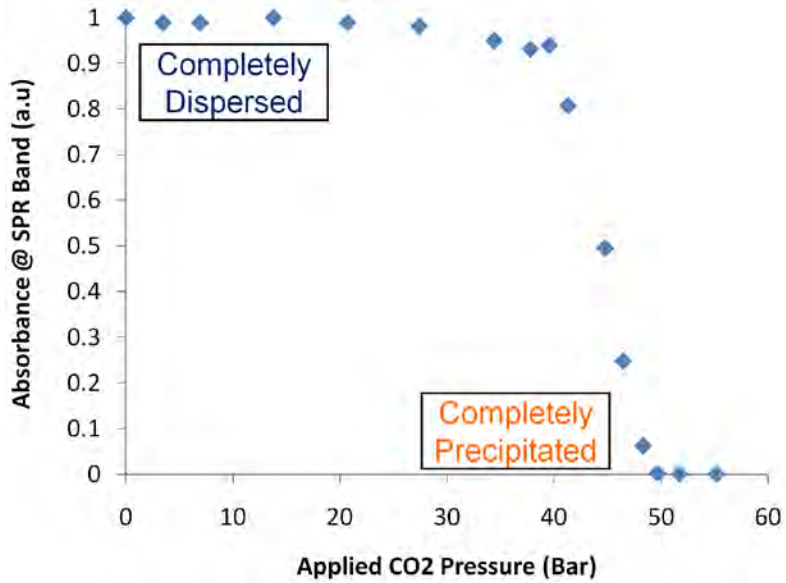
This project utilizes a novel CO<sub>2</sub>-expanded liquid nanoparticle size fractionation technique to establish the impact that precise size adjustment of Fe<sub>3</sub>O<sub>4</sub> nanoparticles has on principal emulsion properties

## *Our specific aims are to:*

- Study the effects of precise size adjustments of iron oxide nanoparticles on emulsion stability
- Determine ligand properties necessary for stable Pickering emulsion formation using benign stabilizing agents including oleic acid, CMC, etc.
- Use molecular design principles as a guide to determine optimal stabilizing agent characteristics



# Ongoing Work



Oleic Acid Capped Iron Oxide Nanoparticles



# Implications and Broader Impacts

A thorough understanding of the influence of nanoparticle size and clusters of the adsorbed particles, and their size distribution, is of paramount importance for creating stable Pickering emulsions relevant to oil recovery applications

## *Broader Impacts:*

- Improving our understanding of Pickering emulsions is important to fields beyond oil cleanup, including: materials synthesis, bioseparations, and pharmaceutical/biomedical applications
- Scientific publications and presentations
- Display about consortium at the Annual Alabama Water Resources Conference (in 25<sup>th</sup> year) to share merits of projects within Gulf Region
- Hands-on oil cleanup demonstration based on nanoparticle technology at AU Engineering E-day event and TIGERS Camps for 8th-11th graders in Gulf Region

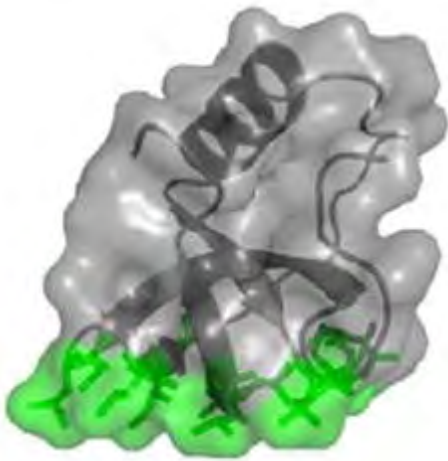
# Title: Natural dispersants and role in transport

Our objective: understand potential for natural protein surfactants.

Hydrophobins are nature's most surface-active proteins and *cerato ulmin* is one example associated with elm wilt (Dutch elm disease).

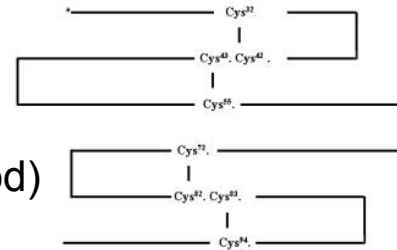
## ↓ Sequence for *Cerato ulmin*

Met. Gln. Phe.Ser. Ile. Ala. Thr. Ile. Ala. Leu. Phe. Leu. Ser.Ser. Ala. Met. Ala. Ala.  
Pro. Tyr. Ser. Gly. Asn. Ser. Asn.\* Ser. Asp. Ser. Tyr. Asp. Pro. **Cys<sup>32</sup>**. Thr. Gly.  
Leu. Leu. Gln. Lys. Ser. Pro. Gln. **Cys<sup>42</sup>**. **Cys<sup>43</sup>**. Asn. Thr. Asp. Ile. Leu. Gly. Val.  
Ala. Asn. Leu. Asp. **Cys<sup>55</sup>**. His. Gly. Pro. Pro. Ser. Val. Pro. Thr. Ser. Pro. Ser. Gln.  
Phe. Gln. Ala. Ser. **Cys<sup>72</sup>**. Val. Ala. Asp. Gly. Gly. Arg. Ser. Ala. Arg. **Cys<sup>82</sup>**. **Cys<sup>83</sup>**.  
Thr. Leu. Ser. Leu. Leu. Gly. Leu. Ala. Leu. Val. Cys<sup>94</sup>. Thr. Asp. Pro. Val. Gly. Ile.

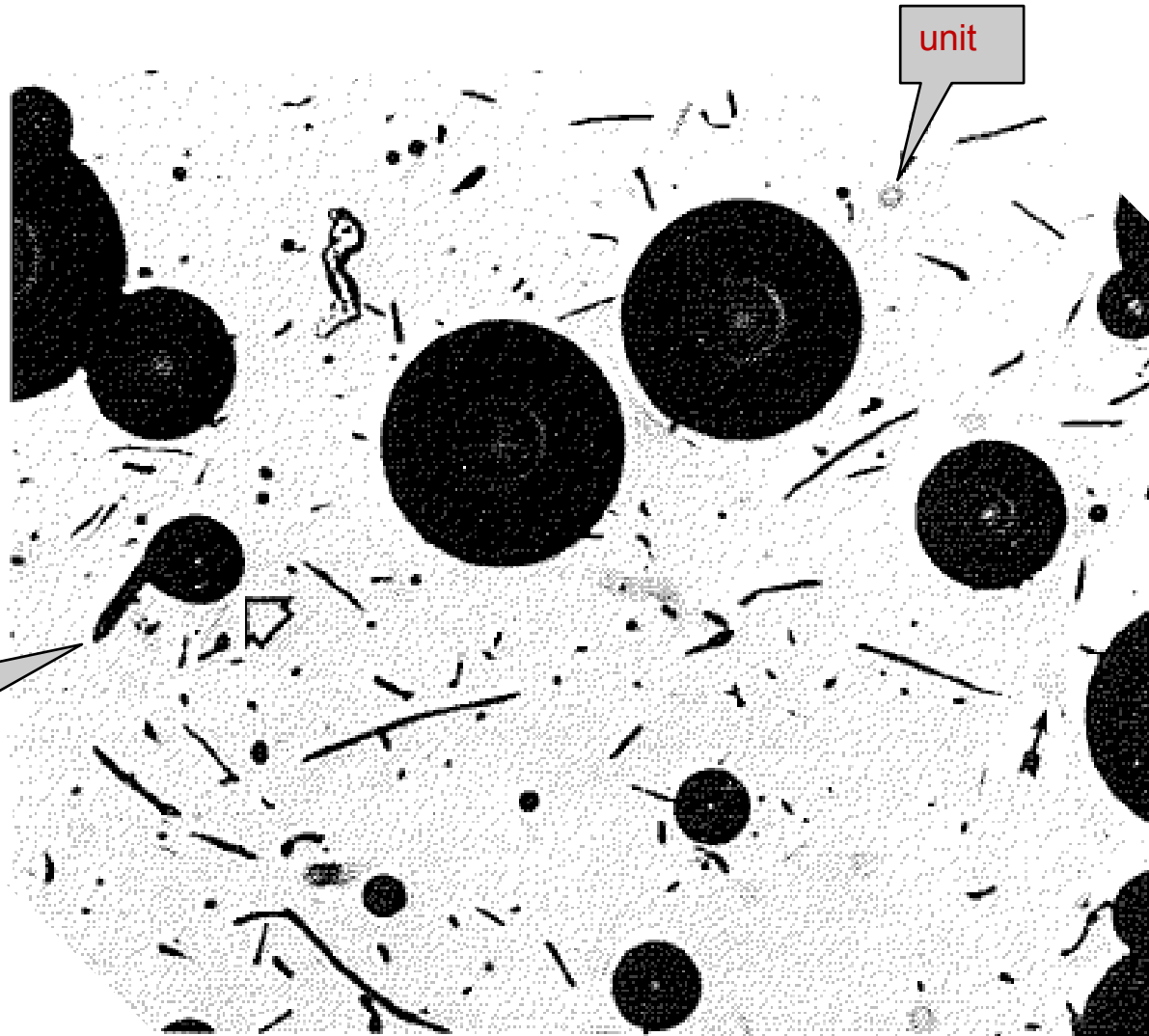


↑ Hydrophobin HFBII  
green = hydrophobic

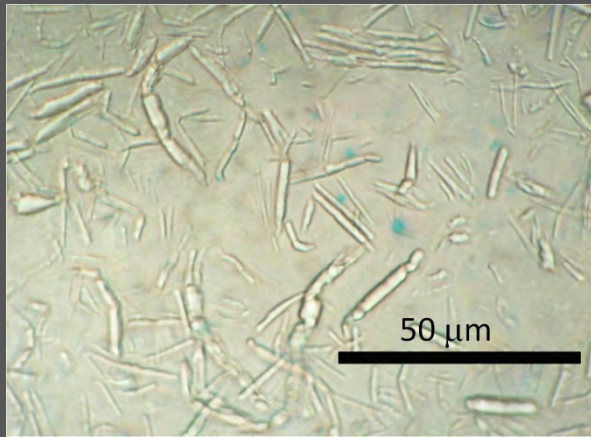
Nature's Janus particle.  
(Janus was a two-faced god)



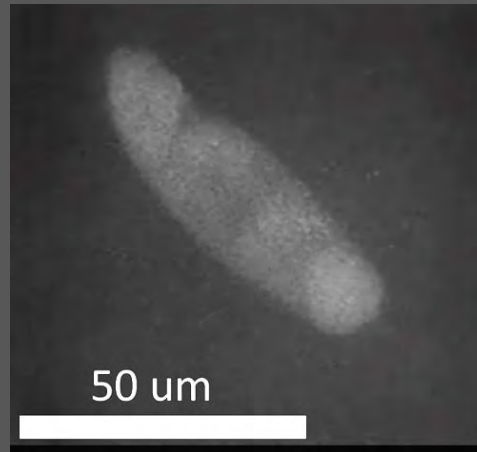
This picture, taken after application of slight vacuum, shows “fibers” of various sizes, curious little elements called “units”, fully formed spherical bubbles and one fat fibril on its way to becoming a spherical bubble.



CU also entraps oils—e.g., cyclohexane; perhaps natural dispersants can help with small or even large cleanups.



↑ Brightfield



↑ Epi-fluorescence  
(Nile Red Dye in  
cyclohexane)

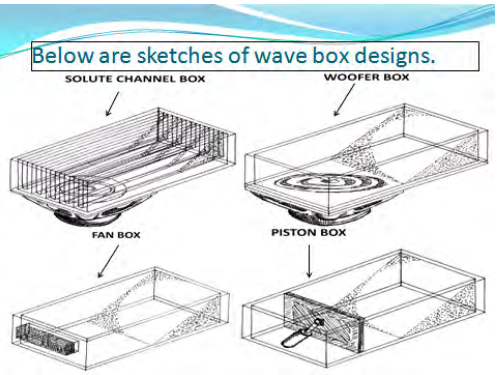
We were asked not to show videos, but laser tweezer videos of air-filled bubbles and oil-filled blobs confirm the contents.

# What we hope to find within the consortium:

- Surface rheology and surface probe diffusion
- AFM mechanical measurements
- Better ways to make waves
- Other hydrophobins
- Recombinant DNA technology to make hydrophobins
- A postdoc (physical/instrumentation/programming)**

# How we hope to serve the consortium:

- DLS/SLS (6 instruments, including fast multiangle/multicorrelator)
- GPC/MALS/Viscosity (3 instruments)
- AF4/MALS/Viscosity/DLS (1 instrument)
- Small-angle X-ray Scattering (at LSU and SSRL)
- Fluorescence photobleaching recovery



# Marina Tsianou & Paschalis Alexandridis

## Advance methodologies that facilitate the reformulation of dispersants

Oil and dispersant experiments in a controlled, aqueous environment at a scale of (i) an individual oil drop and (ii) large populations of drops

- generate data on oil-surfactant interactions at the molecular/nanoscale level
- resolve the contribution to the dispersion of the individual components of the dispersant
- facilitate the optimization of dispersant formulation

## Develop oil dispersants based on mineral particles that have a low impact on the environment

- wetting and adhesion of crude oil on a variety of mineral surfaces (related to sand and sediment) in a variety of conditions
- emulsification of crude oil in the presence of mineral particles and molecular surfactants (seeking synergisms)

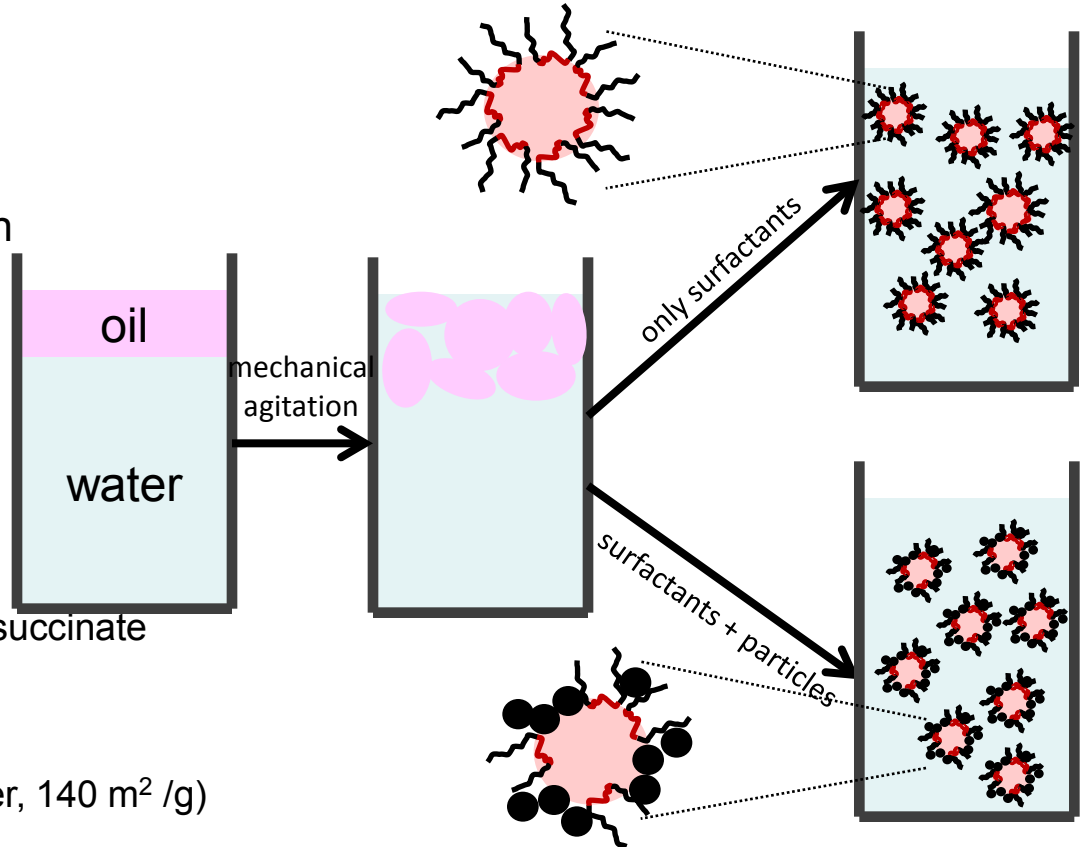
- The University at Buffalo (UB) is a research-intensive public university, and the largest and most comprehensive institution in the State University of New York (SUNY) system.
- UB's more than 28,000 students pursue their academic interests through more than 300 undergraduate, graduate, and professional degree programs.
- Founded in 1846, UB is a member of the Association of American Universities.





# Tsianou & Alexandridis: Preliminary Data

- Emulsion formation
  - probe sonication for 1 min.
  - height data by visual observation
  - optical microscopic images of emulsion droplets
- Surfactants:
  - Pluronic F127 block polymer
    - $EO_{100}-PO_{70}-EO_{100}$
  - Aerosol-OT (AOT)
    - Sodium bis(2-ethylhexyl) sulfosuccinate
- Particles:
  - Colloidal silica
    - LUDOX TM 50 (26 nm diameter, 140 m<sup>2</sup> /g)
- Oils evaluated for emulsion stability in water:
  - Aromatic hydrocarbon, **toluene**
  - Aliphatic hydrocarbon, **n-decane**
  - Aliphatic hydrocarbon, **n-hexadecane**

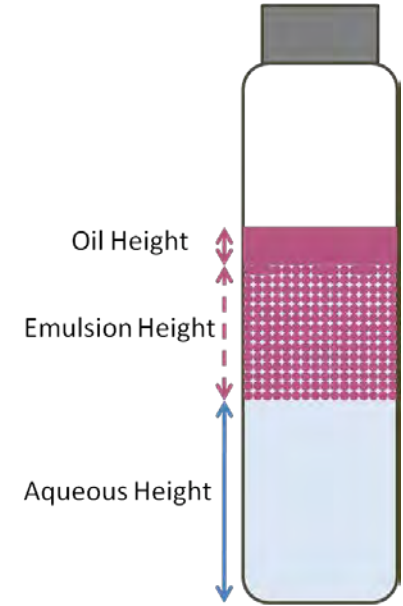
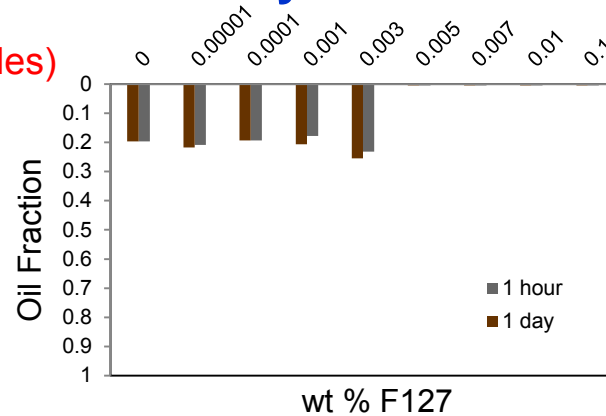
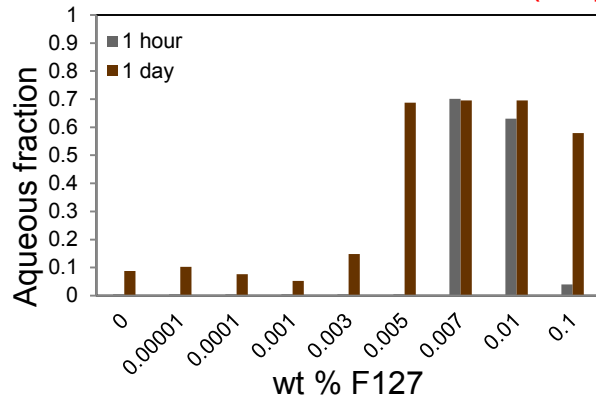




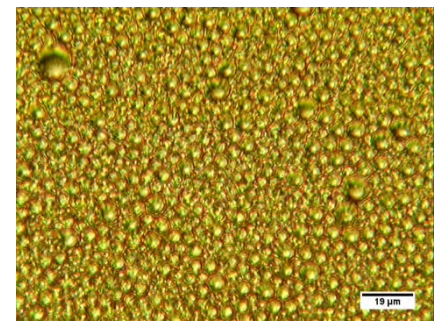
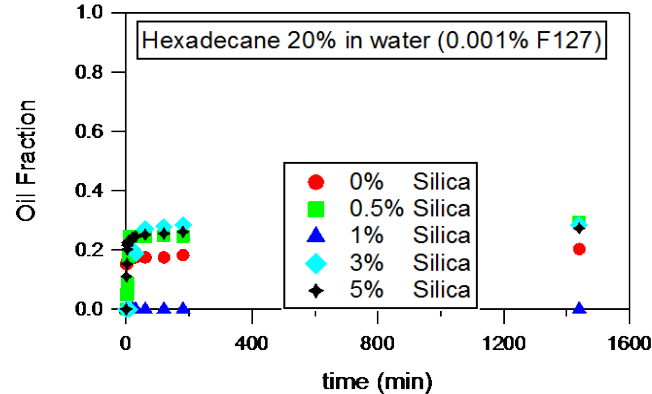
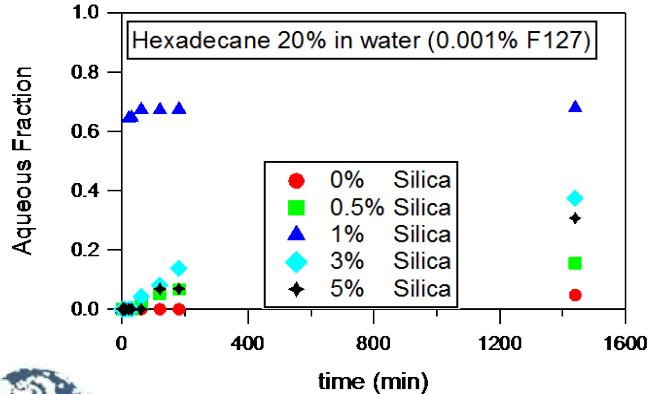
# Tsianou & Alexandridis: Preliminary Data

## Emulsification in Hexadecane-Water System

Addition of Pluronic (no particles)



Addition of Pluronic + Particles



0.000025 wt% AOT  
+0.5 wt% silica  
7 days after sonication

synergistic effect at 0.001 wt% F127 and 1 wt% particles







# Tsianou & Alexandridis: Future Plans

## Advance methodologies that facilitate reformulation of dispersants

Oil and dispersant experiments in a controlled, aqueous environment at a scale of (i) an individual oil drop and (ii) large populations of drops

- generate data on oil-surfactant interactions at molecular/nanoscale level
- resolve the contribution to the dispersion of the individual components of the dispersant
- facilitate the optimization of dispersant formulation

**next (2)**  
baffled flask test

## Develop oil dispersants based on mineral particles that have a low impact on the environment

- wetting and adhesion of crude oil on a variety of mineral surfaces (related to sand and sediment) in a variety of conditions.
- emulsification of crude oil in the presence of mineral particles and molecular surfactants (seeking synergisms)

**next (3)**  
AFM & QCM

**ongoing**  
model systems

**next (1)**  
real systems



# Tsianou & Alexandridis Labs: Relevant Expertise

## • fundamental research

- surfactant-water-oil phase behavior and structure
- solvent effects on polymer conformation
- biopolymers
- polymer+surfactant complexes
- interfacial dynamics / surfactant dissolution
- surfactant-nanoparticle interactions
- layer-by-layer assembly
- adsorption of polymers or surfactants on mineral surfaces
- materials synthesis in self-assembled templates

## • in-house characterization capabilities

- light scattering (dynamic & static)
- small-angle X-ray scattering
- rheology (oscillatory & shear)
- optical microscopy (confocal, fluorescence)
- atomic force microscopy (with fluid cell)
- quartz crystal microbalance (with dissipation)

## • formulation & characterization

- microemulsions and emulsions
- inks for ink-jet printing
- waterborne coatings
- pharmaceutical formulations
- gels
- paper
- resins

## • synergistic activities

- Outreach: Tech Savvy (AAUW)  
(American Association of University Women)
- Colloids & Surfaces course @ UB
- Product Design course @ UB
- ERIE @ UB (Ecosystem Restoration  
through Interdisciplinary Exchange )
- AIChE and ACS programming

# Characterization of Dispersant Adsorption Timescales Using a Microscale Tensiometer

PIs: *Lynn M. Walker, Shelley L. Anna*  
Graduate Student: *Matt D. Reichert (Ph.D.)*

Center for Complex Fluids Engineering  
Carnegie Mellon University  
Pittsburgh, Pennsylvania

**Objective:** To characterize the dynamics of adsorption of dispersant components relevant to oil spills by at the oil-water interface at marine-relevant conditions and in the presence of flow

# Concept and Approach

## Timescales matter: Dynamics of adsorption depend on transport mechanisms

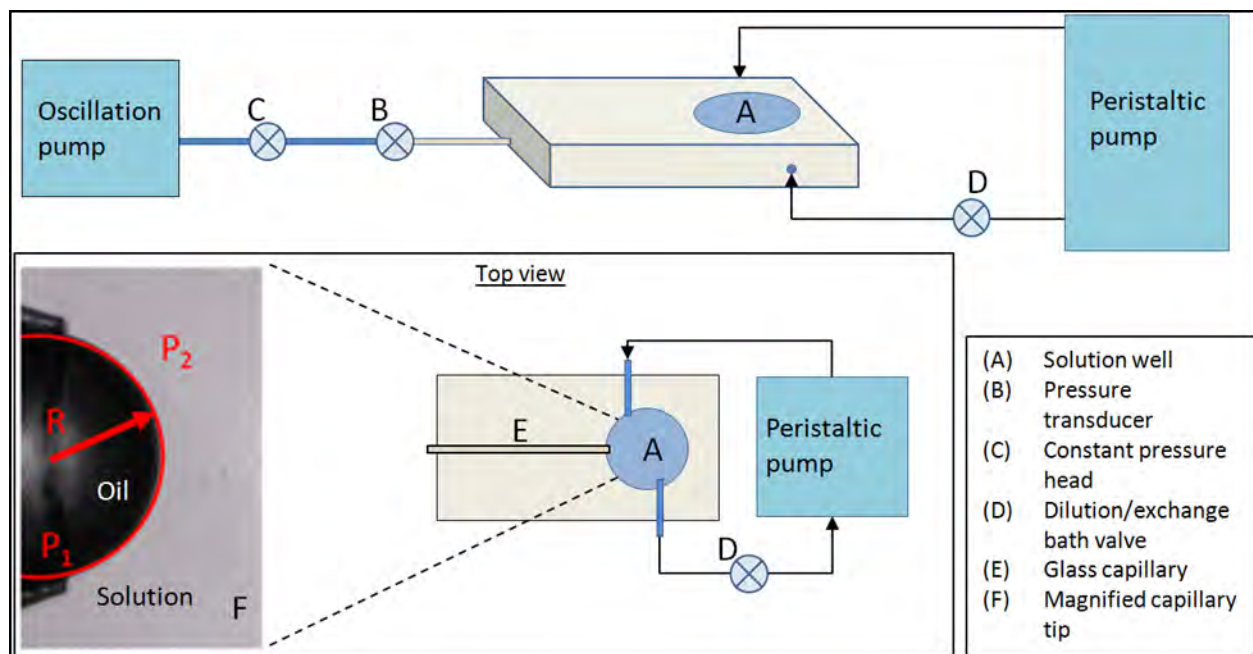
- Diffusion of soluble components
- Kinetic barriers for adsorption & desorption
- Convection near the oil-water interface

## Model system:

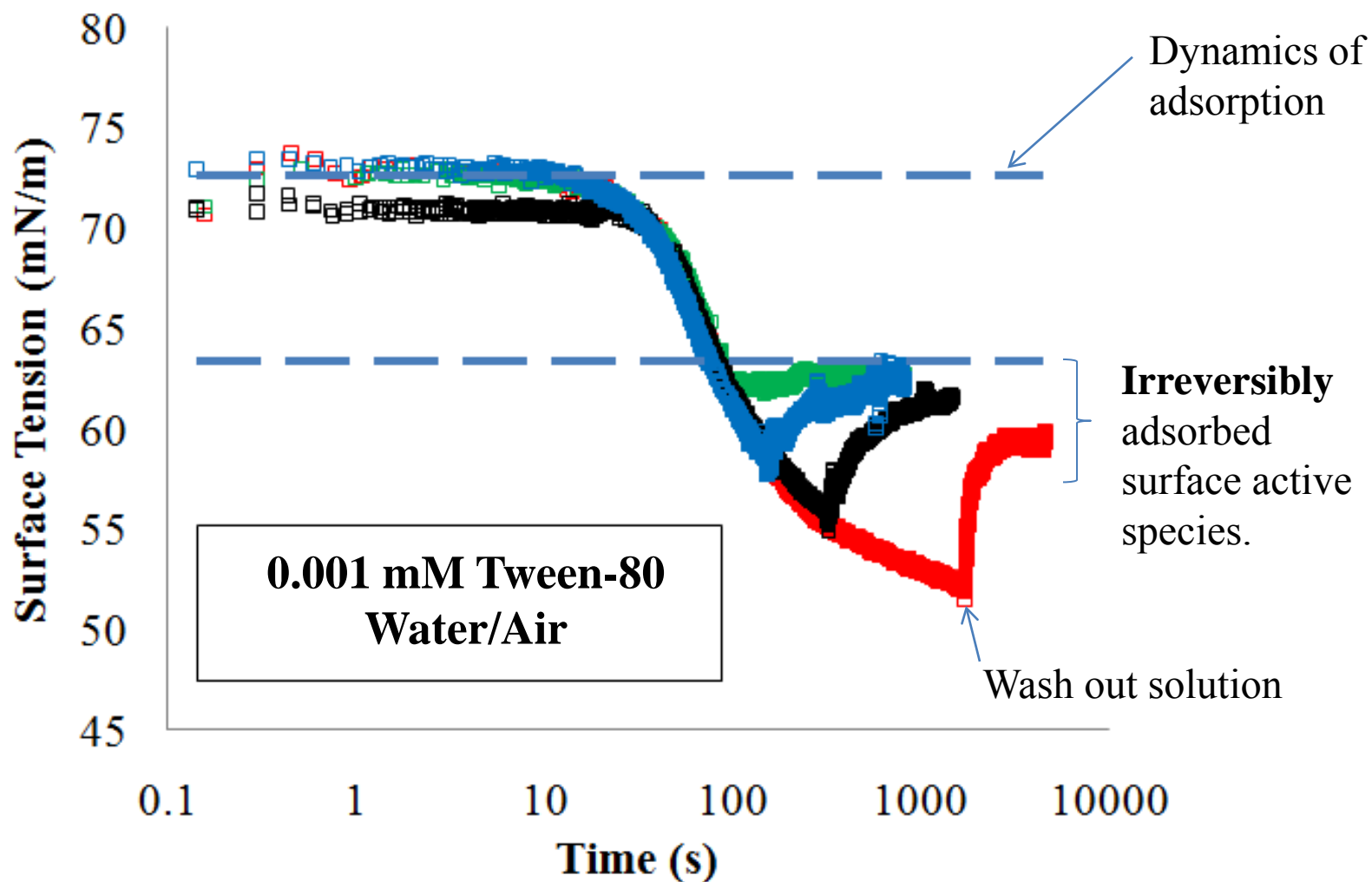
- Dispersant: Tween-80 (main component of Corexit)
- Oil: Squalane
- Aqueous: SSW

## Microtensiometer:

- Microscale interface
- Rapid testing
- Small volume
- Environment control



# Preliminary Data

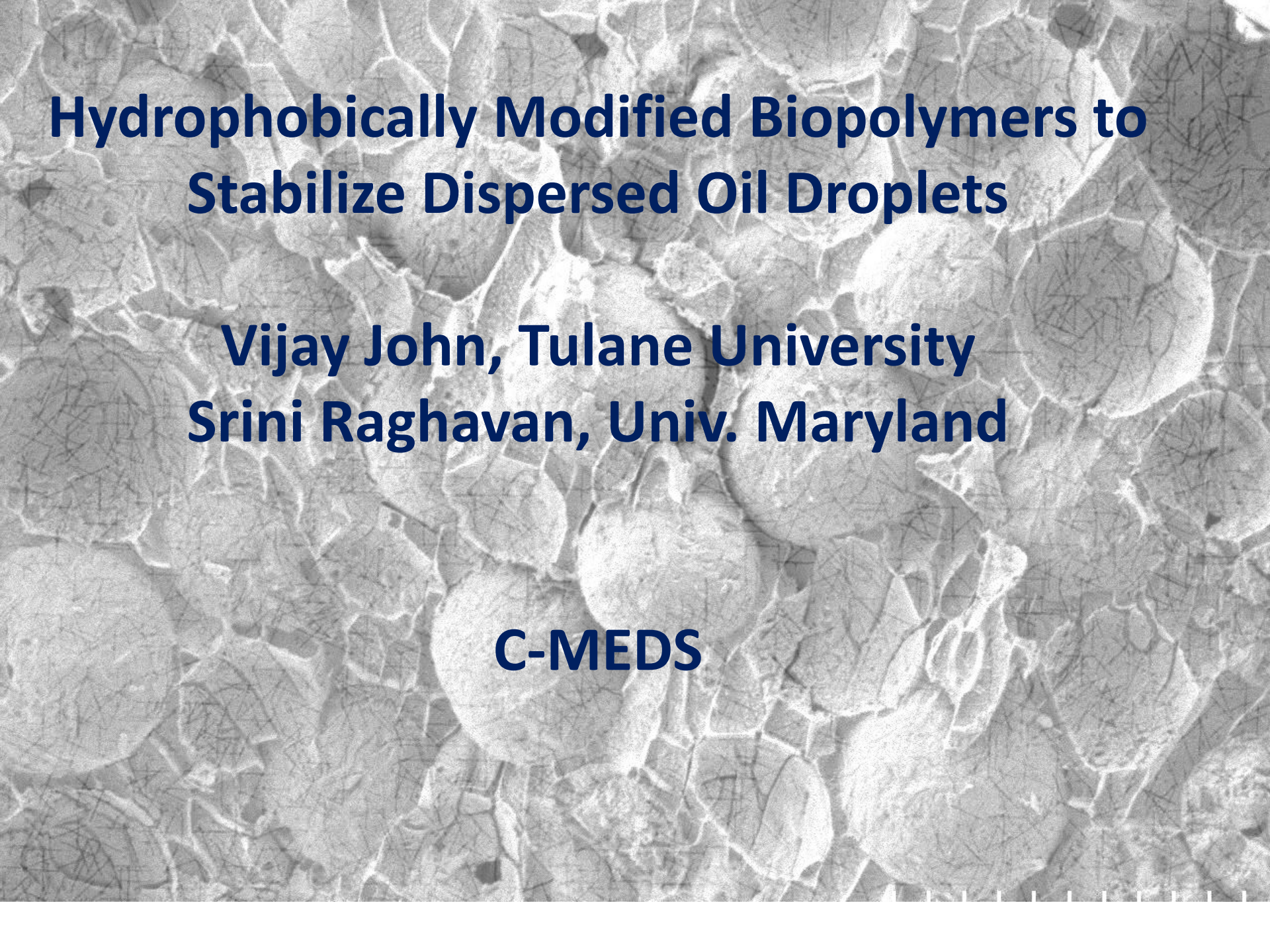


**Initial results:** Isotherm for the model system has been characterized. Tween-80 appears to be a multicomponent material with at least one species that does not desorb easily from the interface.

# Implications

---

- The microtensiometer allows for the separation of timescales of diffusion, convection, and kinetics
  - Important parameters to feed into multiscale simulation of oil spill scenarios
- This capability will allow us to quantify appropriate parameters that are needed to inform rational application of dispersants in oil spills



# **Hydrophobically Modified Biopolymers to Stabilize Dispersed Oil Droplets**

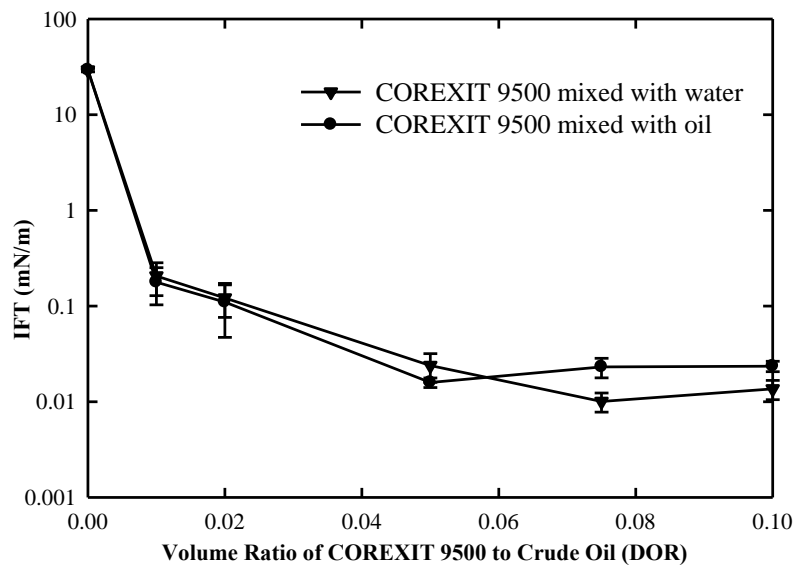
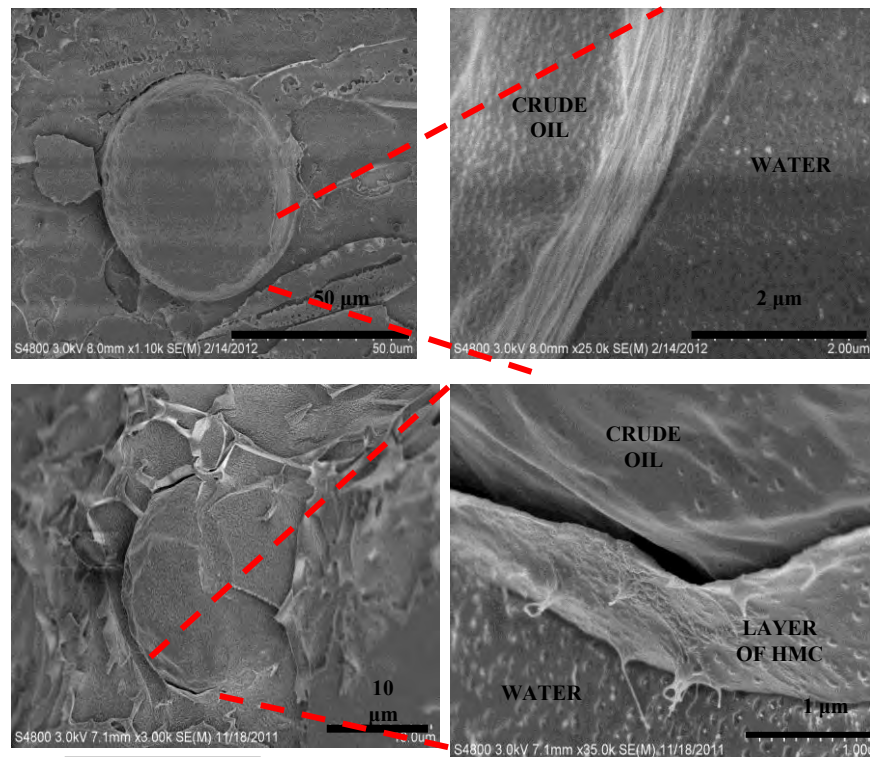
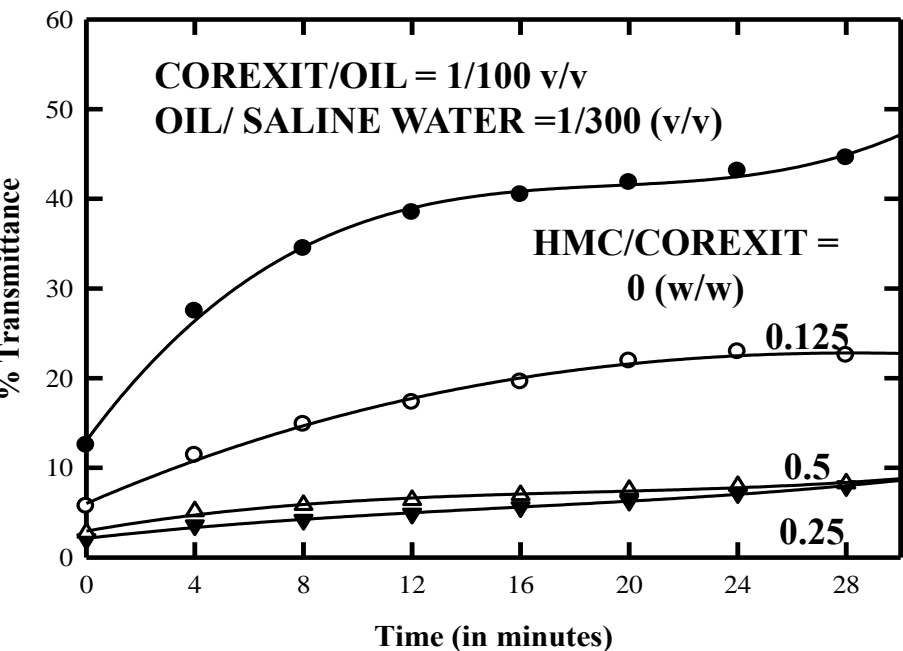
**Vijay John, Tulane University  
Srini Raghavan, Univ. Maryland**

**C-MEDS**





# Droplet Stabilization with hydrophobically modified chitosan



**T = 0 min**



**T = 5 min**



**T = 30 min**



**T = 0 min**



**T = 5 min**



**T = 30 min**

## Broad Topics

1. Stabilization of drops using surfactants/hydrophobically modified biopolymers/particles. Can systems be designed to suspend or precipitate oil droplets?
2. Dispersant design and interfacial tension effects.
3. Gas hydrates in gas expanded systems. The role of dispersant components in hydrate formation.

