Anti-deposition as a Strategy To Mitigate the Effect of Oilspills on Near-shore Flora and Fauna

Robert Lochhead, Sarah Morgan, Daniel Savin, Giselle Marks and Lisa Kemp
The University of Southern Mississippi

OIL SPILL WORKSHOP ALAMEDA FEB 24, 2015

Los Angeles Times

June 4, 2010

CLEAN UP METHODS USED

- Dispersants
- Controlled burns
- Boom/sorbents
- Skimming

John Kepsimelis/U.S.Coast Guard via Bloomberg/Getty Images

- **None of the existing methods prevent the oil from fouling coastal flora and fauna!**

Photograph: Gerald Herbert/AP

Saul Loeb/AFP/Getty Images

- Our Goal: Find a Solution for Coastal/Inland Spills
  - Don’t add to the problem
  - Reduce the immediate impact
  - Find ways to enhance removal of the oil from the environment

RECENT SPILL ON MS RIVER – JAN 2013

- Released >1,000 gals of light crude oil
- Clean up:
  - 5,300 ft of boom
  - 159 workers
  - 10 day clean up effort
  - 16 miles of MS River closed for 4 days
    - 1,000 barge queue
  - >250,000 gals of oil/water mix recovered

DISPERSANTS CURRENT TECHNOLOGY

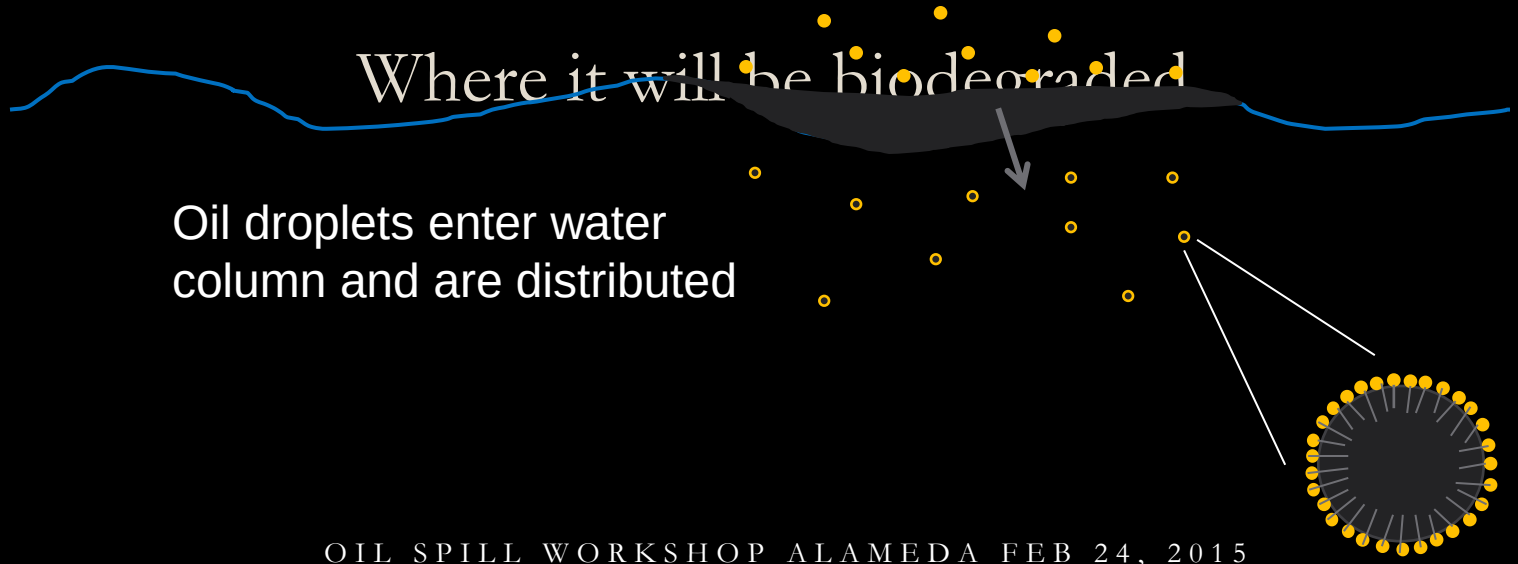
Disperses oil into small droplets and distributes through water column

Petroleum based solvents

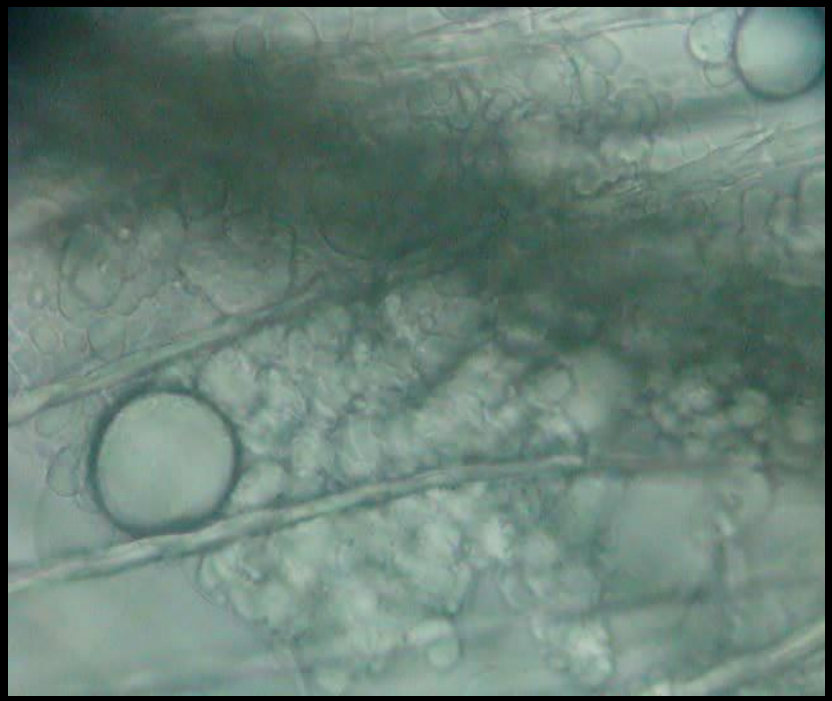
Good wetting agents

The objective is to keep oil at sea

Where it will be biodegraded

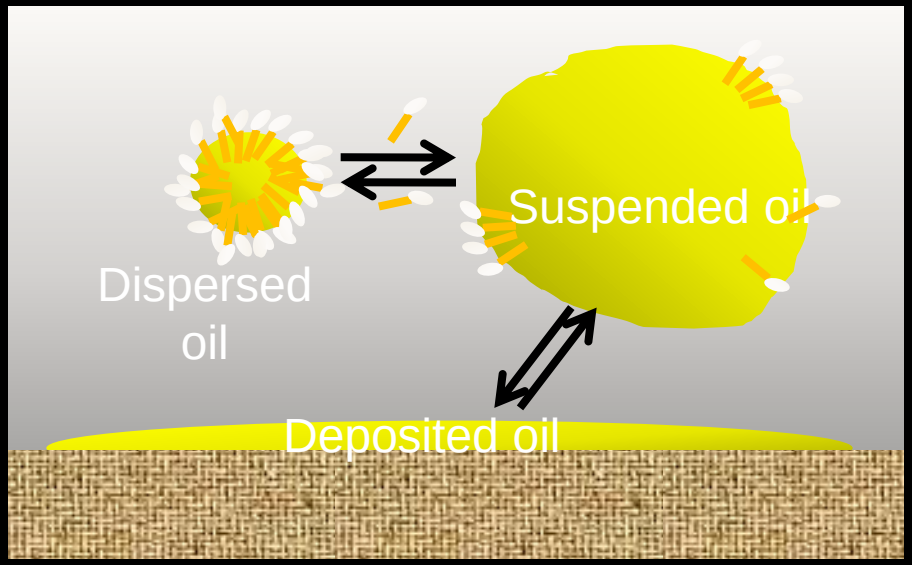


DISPERSED OIL CAN STILL WET FEATHERS



Oil droplets formed using traditional dispersants

INSPIRATION FROM LAUNDRY SOIL ANTI-REDEPOSITION



In the presence of insufficient conventional dispersants, there is a three-way equilibrium between dispersed oil, suspended oil, and oil deposited on adjacent surfaces.

Adsorption of lyophilic polymer on the oil droplets and on the substrate causes repulsion between the droplet and the surface, and mitigates deposition. Sufficient anchoring on the oil droplet can prevent deposition even on 'bare' surfaces.

NSF RAPID PROJECT 1047662
PROOF OF CONCEPT ---INITIAL RESULTS

- Conventional laundry soil anti-redep agents function by electrosteric stabilization
- This mechanism is nullified by ions in sea water
- The most common anti-redeposition agent precipitates in sea water!!!
- NEED RETHINK APPROACH
- …..AND REDEFINE SCOPE
- → Explore nonionic cellulose ethers

OIL/WATER INTERFACIAL ADSORPTION OF AMPHIPATHIC CELLULOSE ETHERS

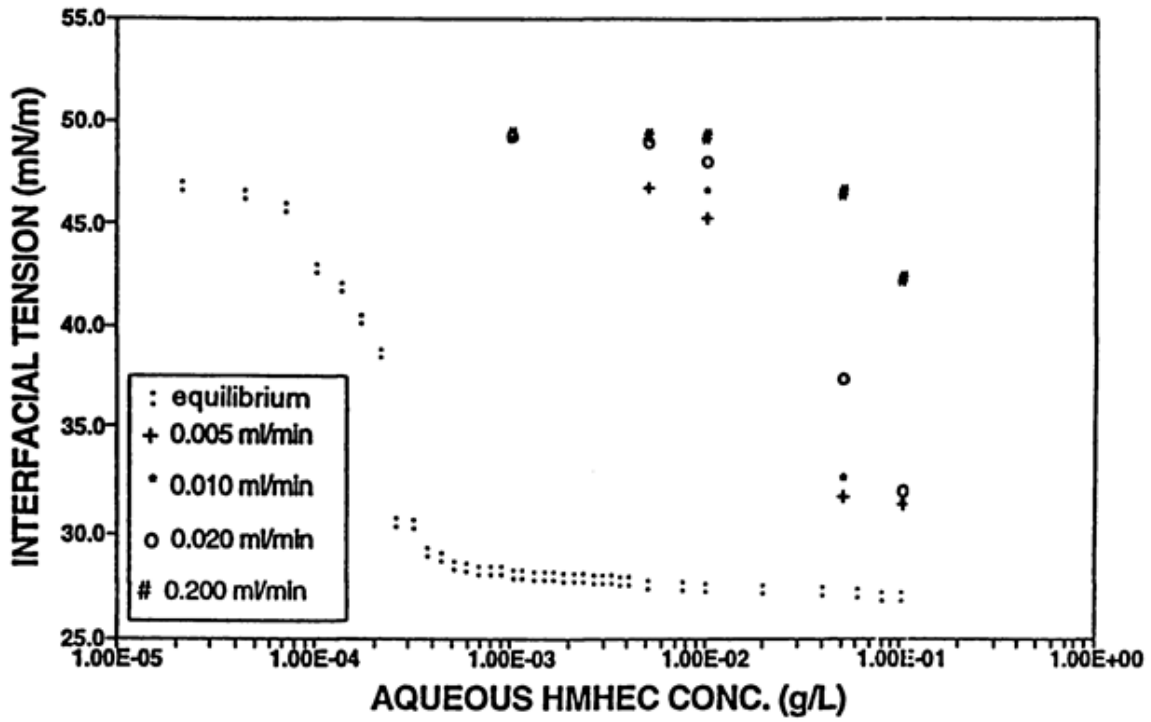
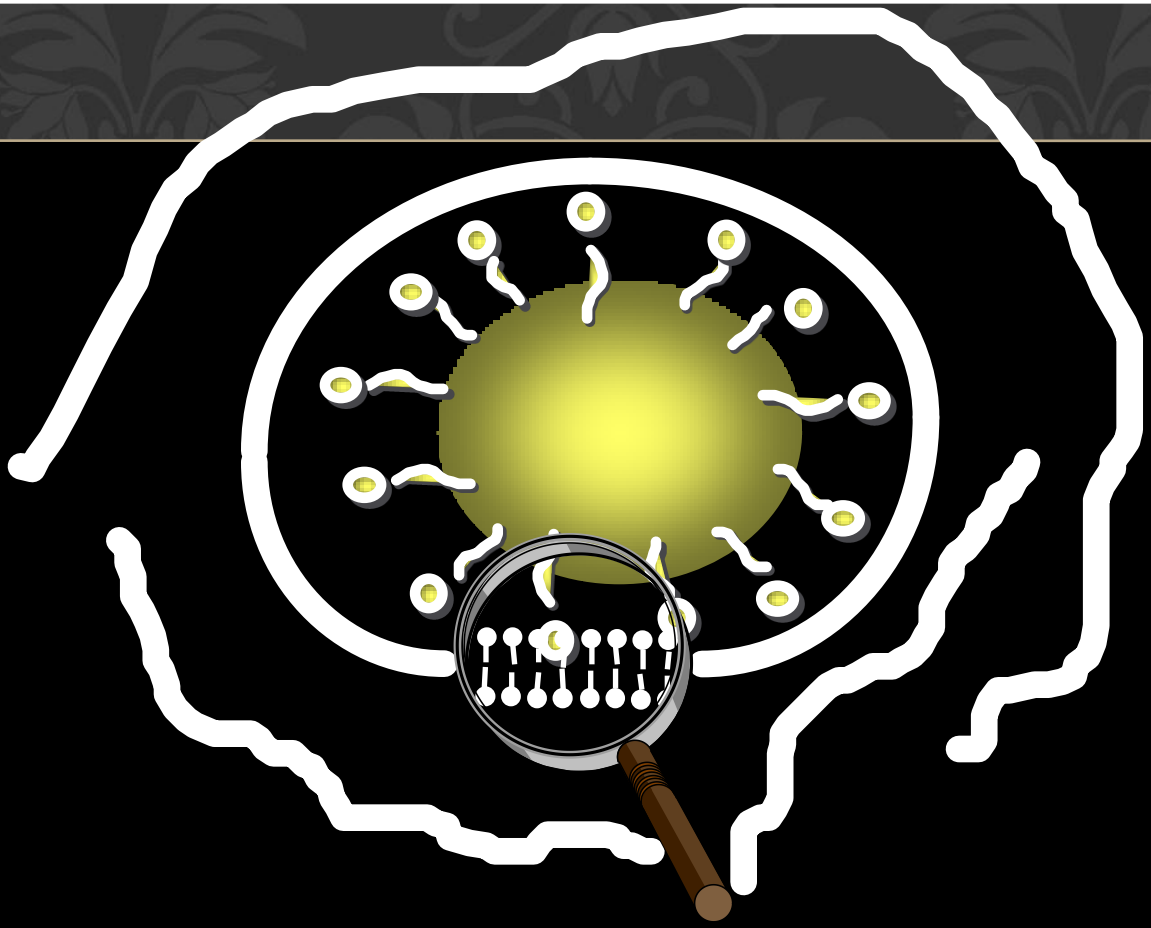


Figure 11. Dynamic Interfacial Tension for Aqueous HMHEC Solution/Mineral Oil

- Adsorption is rapid
- Diffusion limited
- But **no** stable emulsions

Christopher J. Rulison and Robert Y. Lochhead, *Surfactant Adsorption and Surface Solubilization,* Chapter 19, **1996,** pp 280-313; *ACS Symposium Series,* Volume 615

Surfactant Lamellar Phase can Emulsify Oil

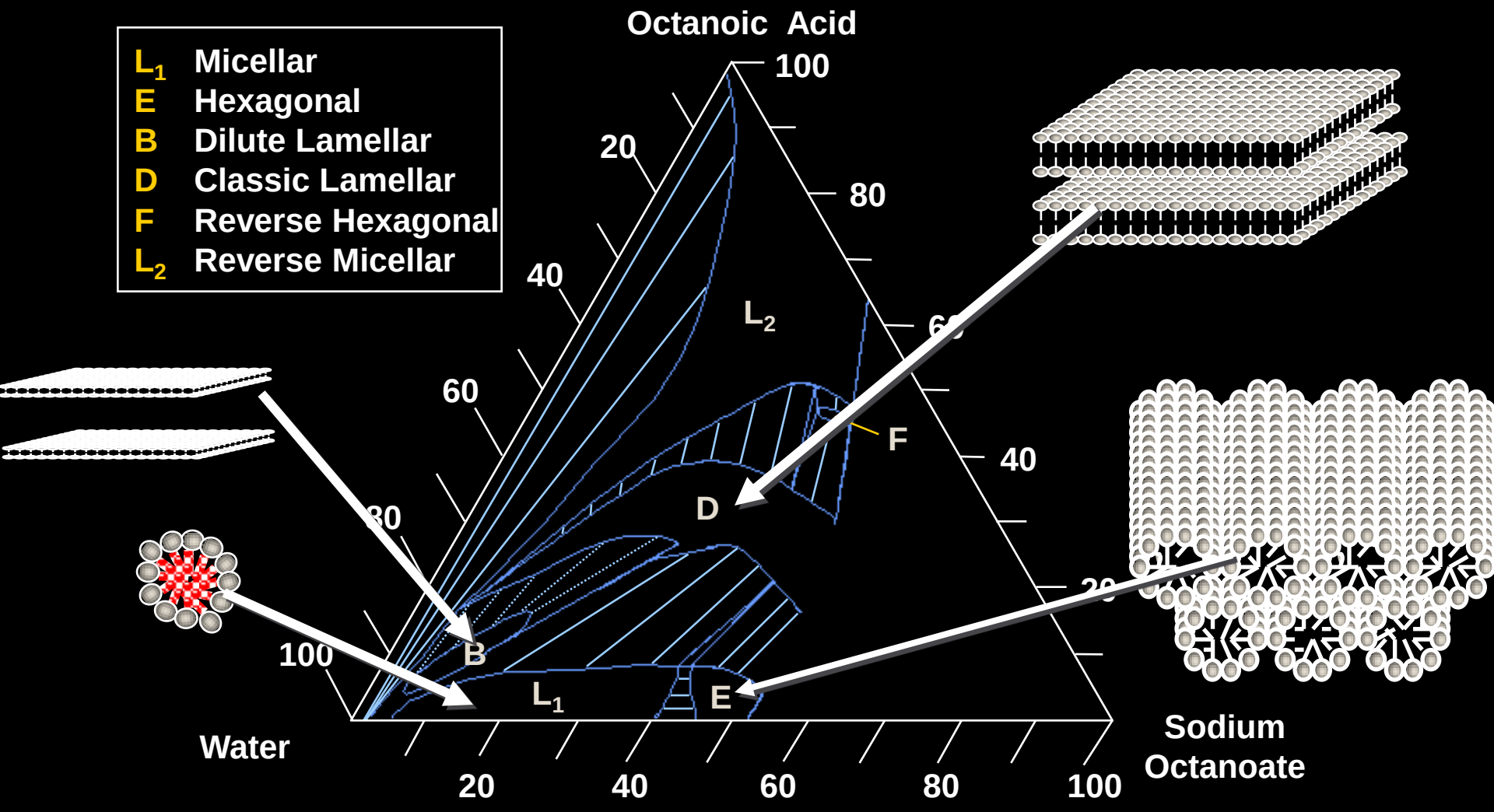


LAMELLAR LIQUID CRYSTAL STABILIZATION

Davies, J. T.; Rec. Progr. Surf. Sci., 2, 129, (1964).

Friberg, S.; Larrson, K.; and Mandell, L. *Journal of Colloid and Interface Science*, 29, 155, (1969)

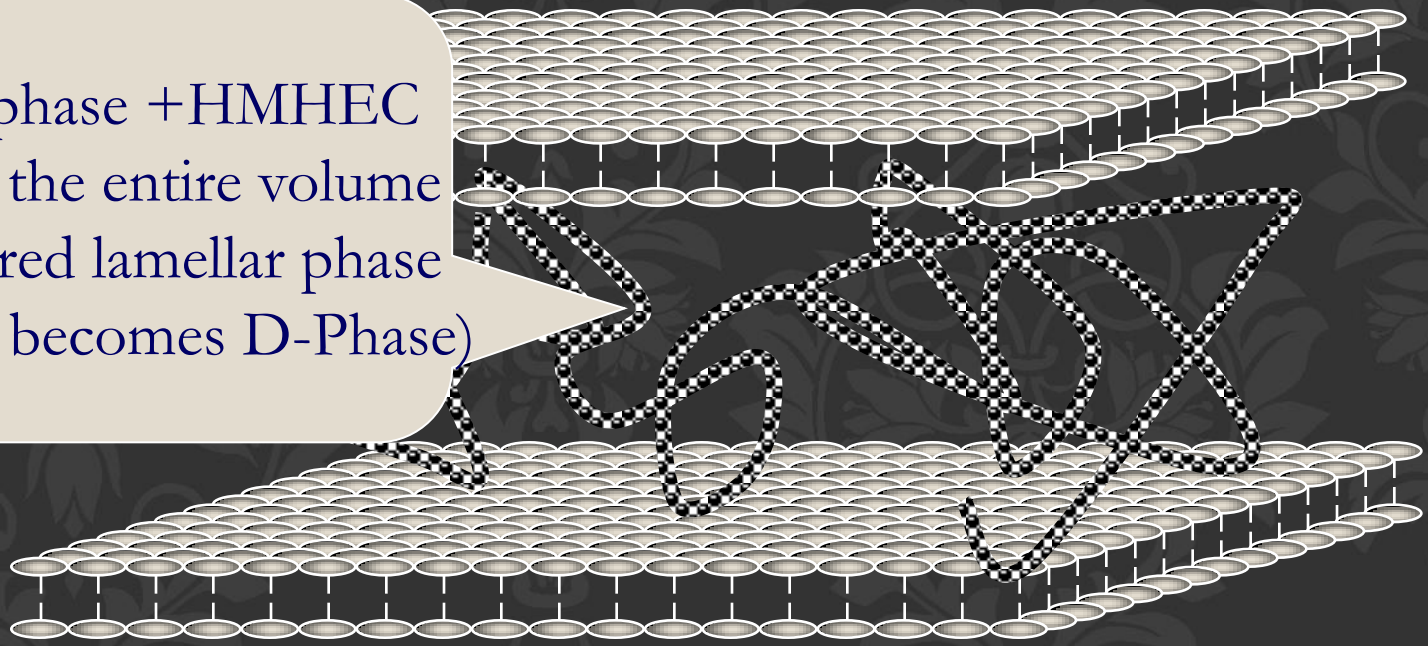
PHASE DIAGRAM FOR OCTANOIC ACID / SODIUM OCTANOATE / WATER



Ekwall, P.; Mandell, L.; *Kolloid ZZ Polymere* 1969, *233*, 938.

Lamellar Phases

The lamellar phase +HMHEC expands to fill the entire volume with well-ordered lamellar phase (that is B-phase becomes D-Phase)



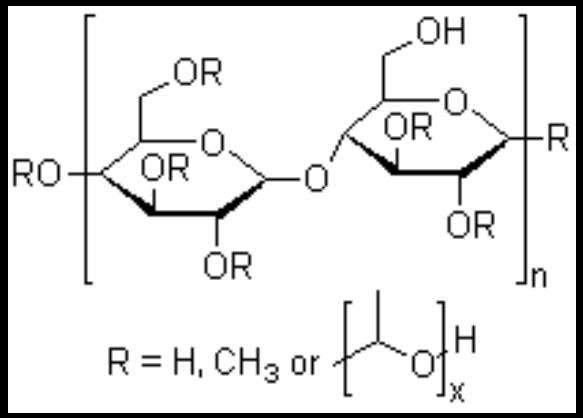
Cynthia F. Welch and **Robert Y. Lochhead** The Effect of Hydrophobically-Modified Hydroxyethylcellulose on the Structure and Rheology of a Model Surfactant System in the Liquid Crystal Regime", Preprints of the Society of Cosmetic Chemists, Annual Scientific Meeting, New York, NY (1999).

CELLULOSIC POLYMERS

Natural polymers with good hydrophilic/hydrophobic balance and no negative impacts on the ecological environment:

Hydroxypropyl methylcellulose

- Readily obtainable commodity
- Variety of molecular weights and side group modifications
- Biodegradable

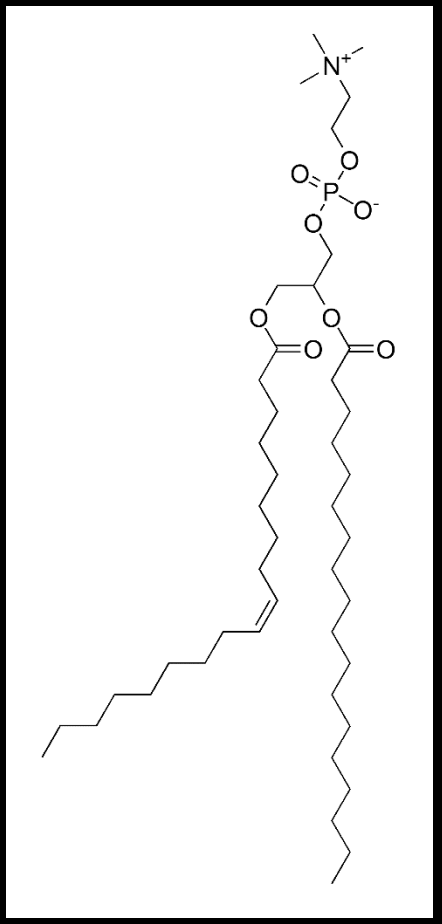


NATURAL DISPERSANT

Alternative biodegradable dispersants with no negative impacts on the ecological environment:

Soy Lecithin

- Easily obtainable commodity
- Readily forms lamellar phase – well known as an emulsion stabilizing phase
- Biodegradable and on the EPA list of acceptable substances for the marine environment



MICROBES ARE THE FIRST RESPONDERS

DAPI-stained bacterial cells attached to oil droplets
from the *Deepwater Horizon* site.

Source: Jay Grimes. Coastal Sciences, University of Southern Mississippi

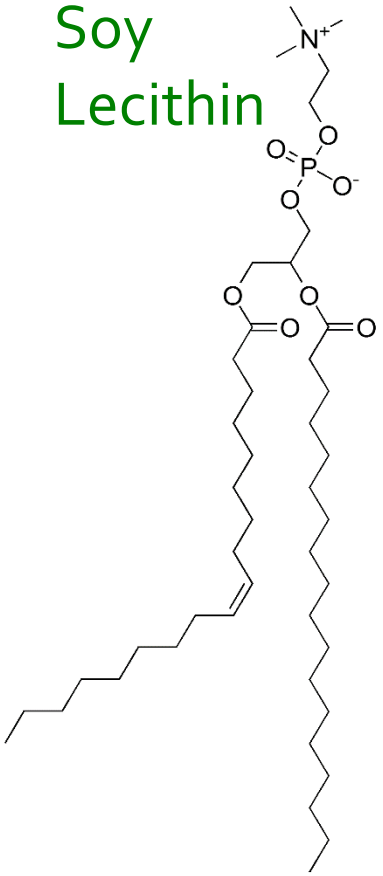
N and P provided by lecithin can help microbes thrive while degrading the oil

Nikolopoulou, M.; Pasadakis, N.; Kalogerakis, N. *Desalination* (**2007**), 211(1-3), 286-295.

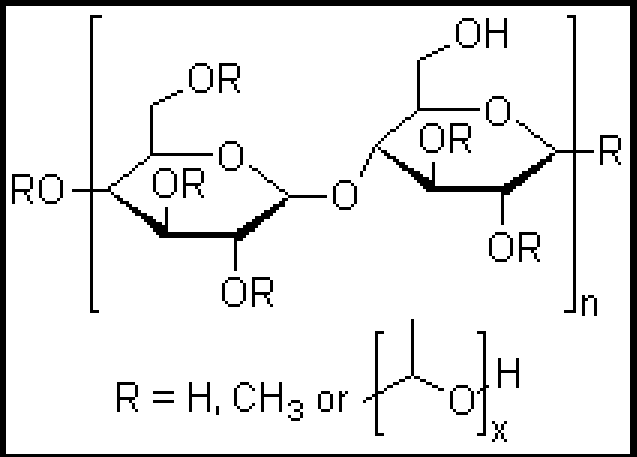
USING SCIENTIFIC INTUITION

NSF RAPID PROJECT 1047662

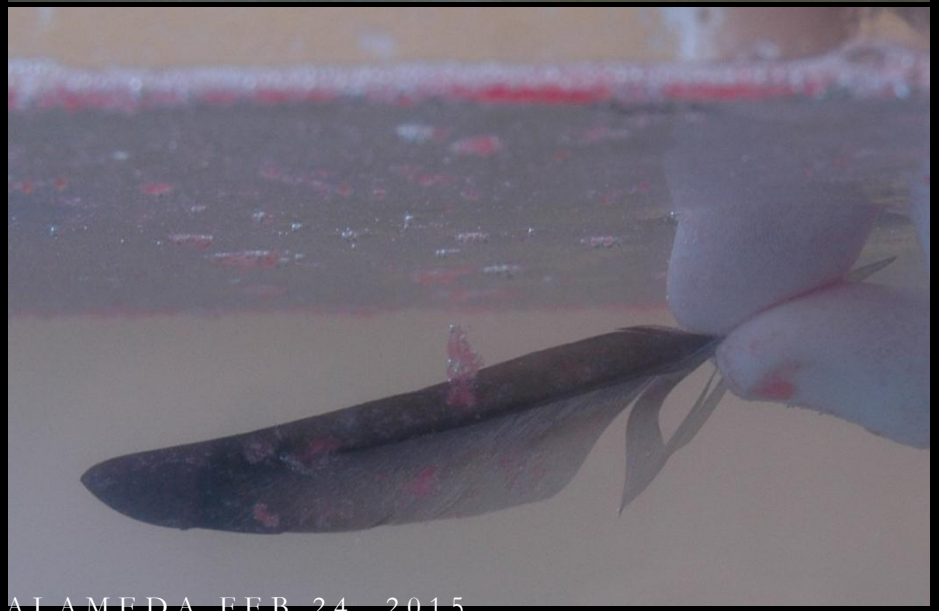
Soy Lecithin



Hydroxypropylmethyl cellulose

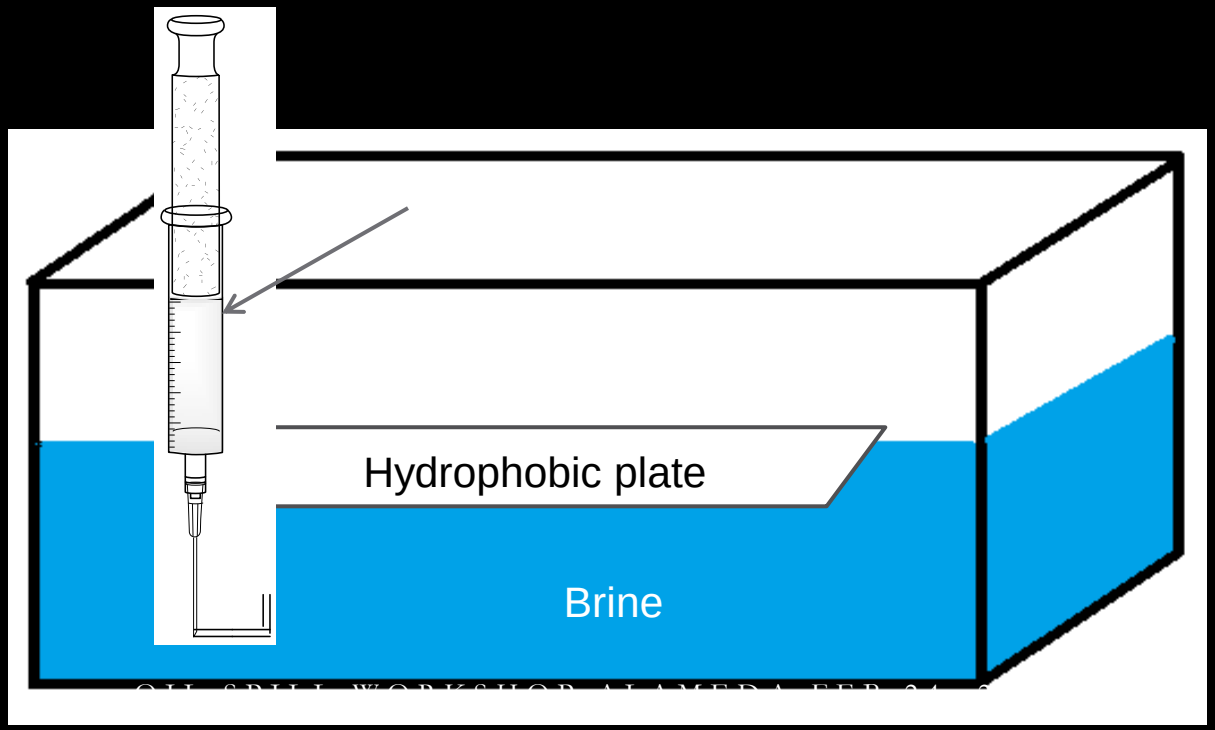


PROOF OF PRINCIPLE
LAB TESTS WITH DUCK FEATHERS

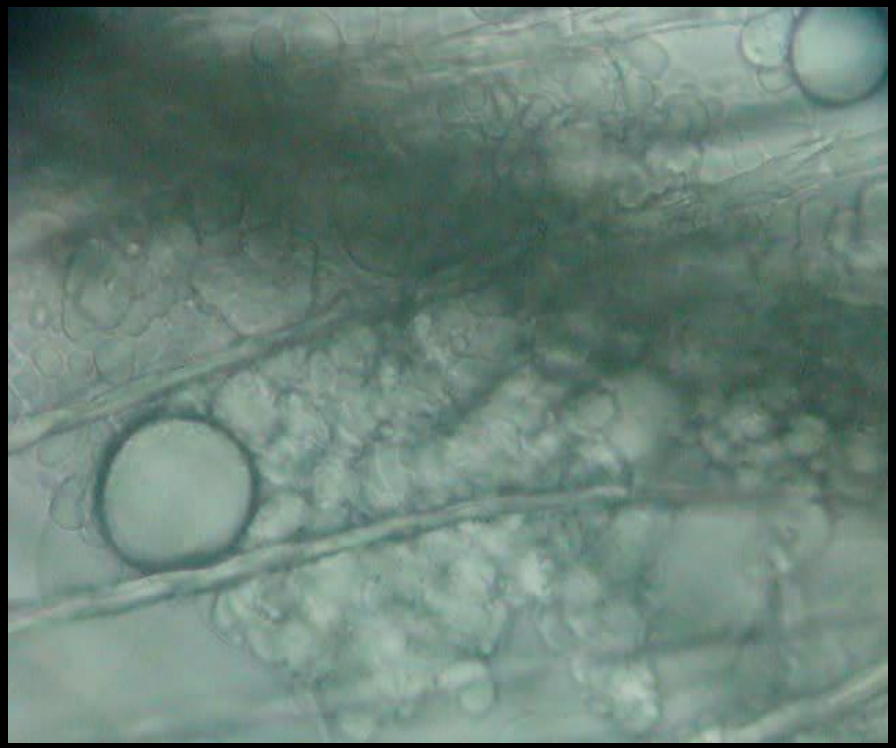


NSF AIR PROJECT 1127846
INVERTED CONTACT ANGLE COMPARISONS



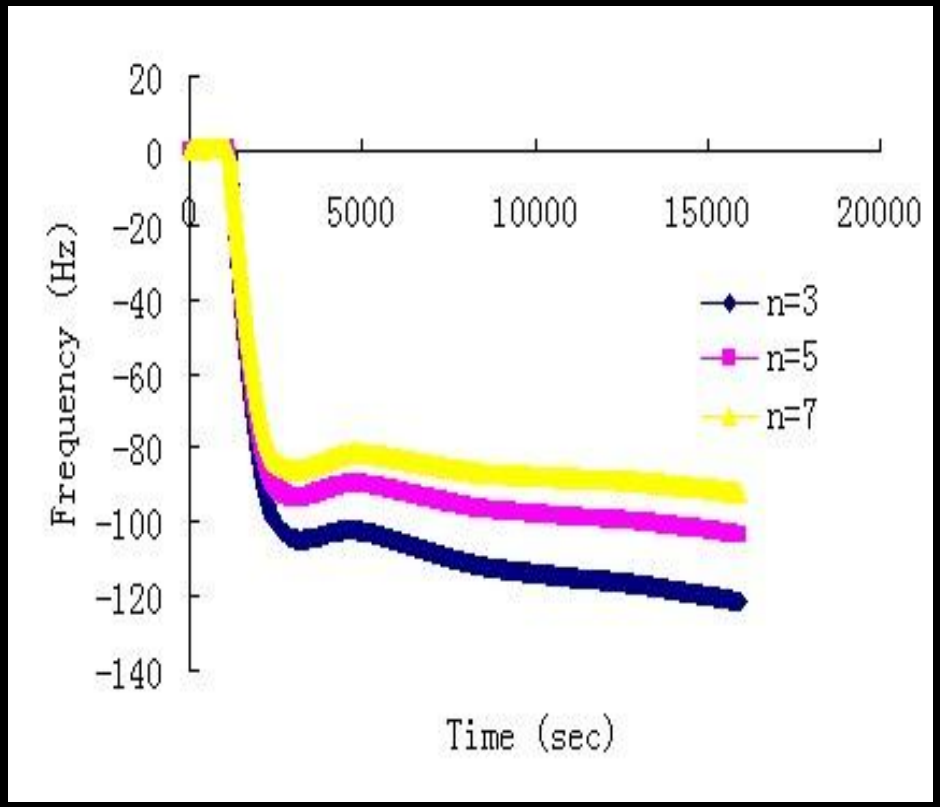
PREVENTION OF OIL WETTING ON FEATHERS

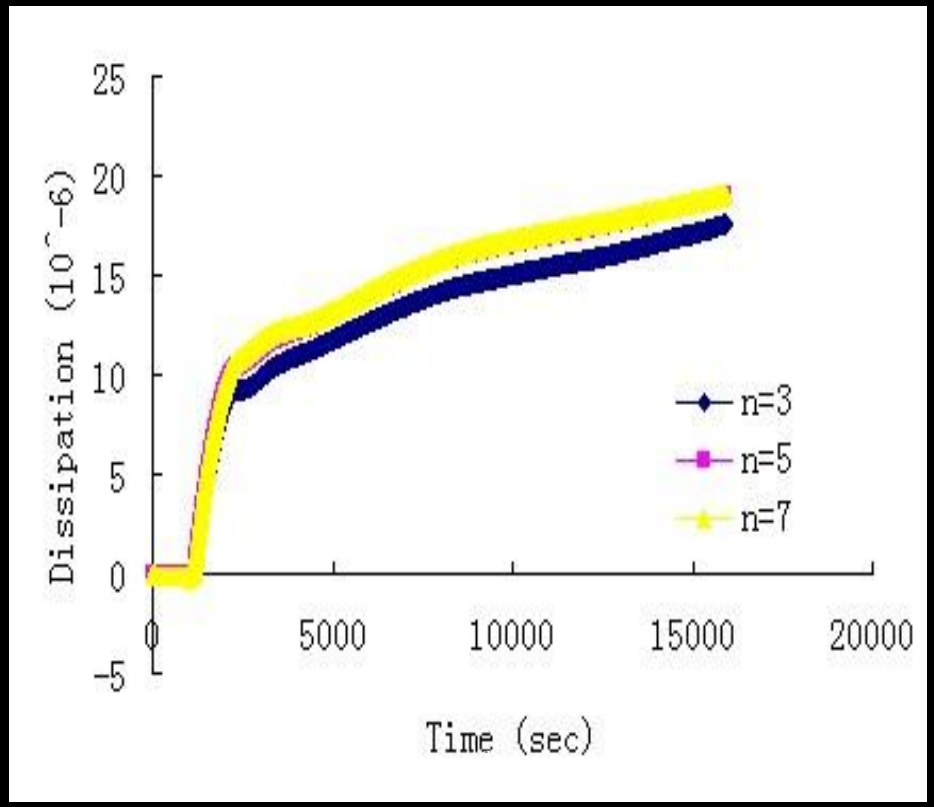


Oil droplets formed using traditional dispersants

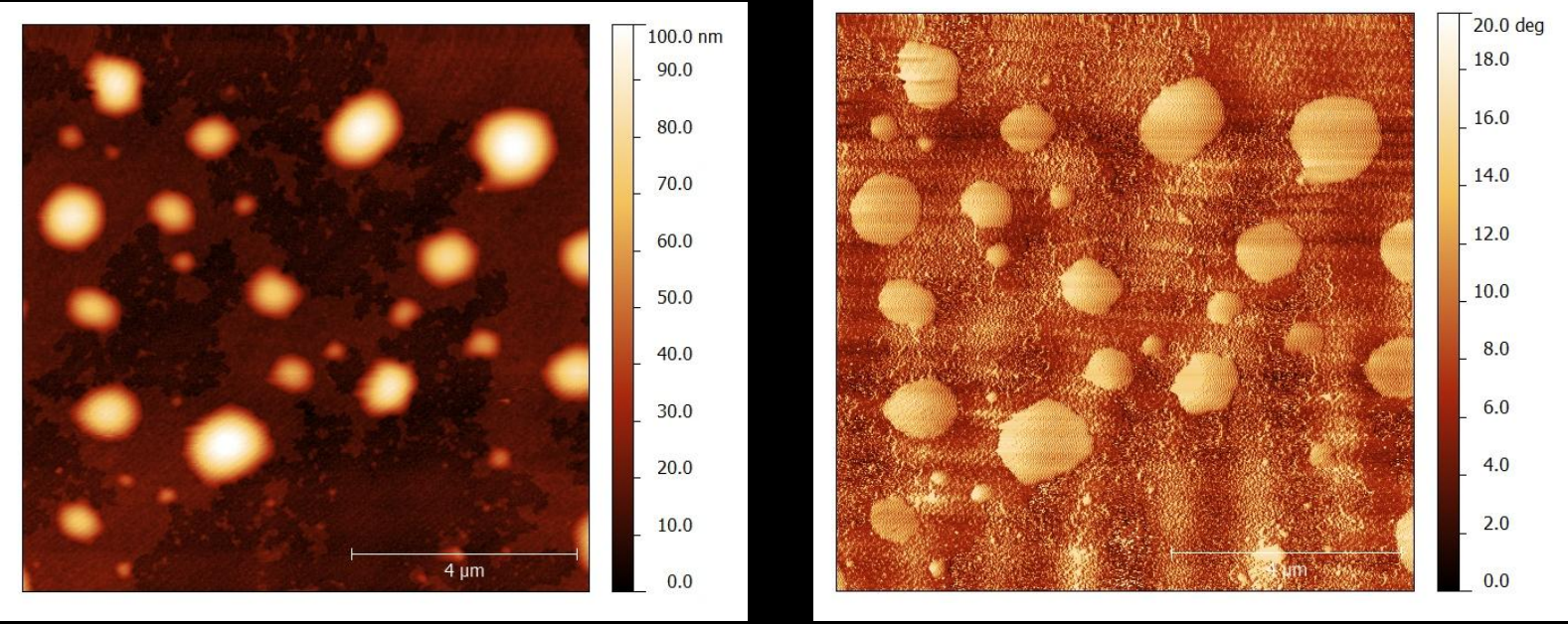
Oil droplets using our anti-deposition agent

QUARTZ CRYSTAL MICROBALANCE STUDIES OF ADSORPTION OF OIL AND LECITHIN



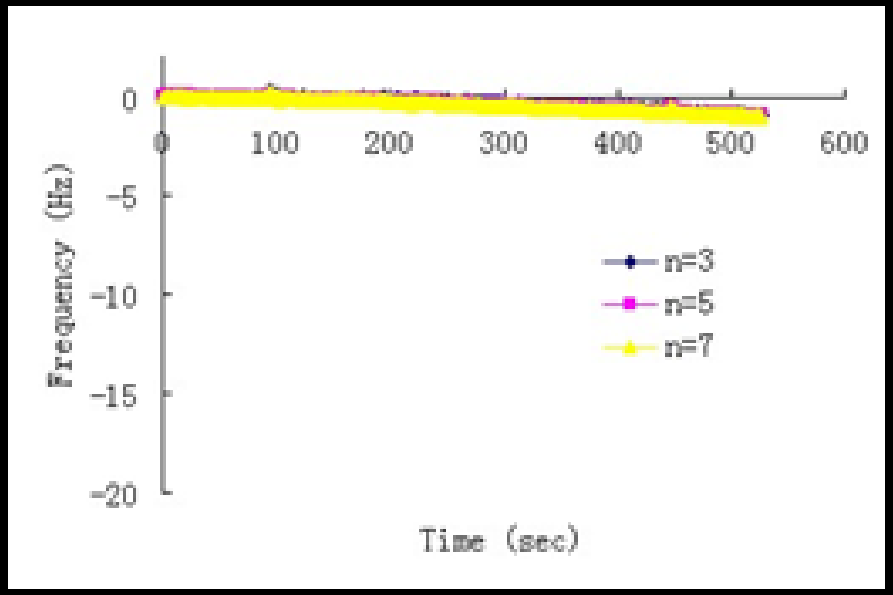


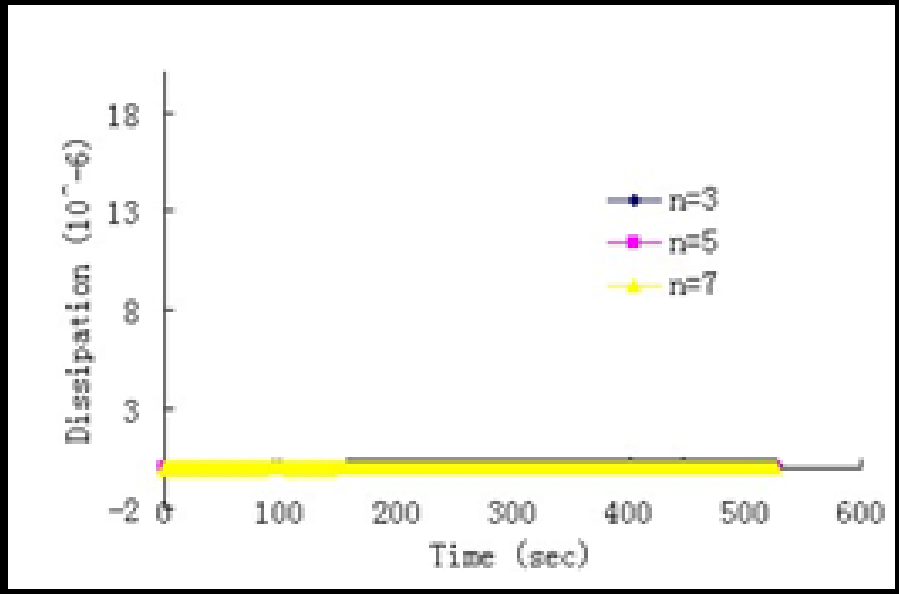
AFM – OIL AND LECITHIN



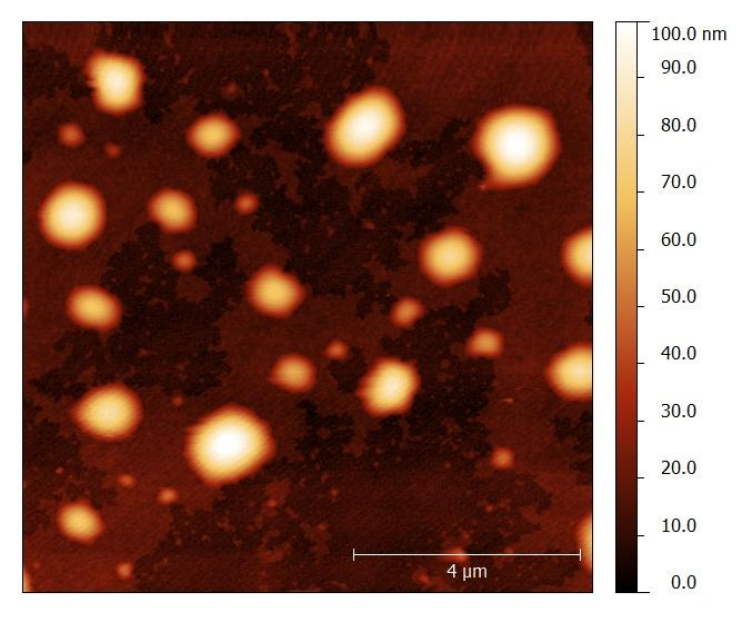
AFM images of oil and lecithin on the QCM sensor in height mode (left) and phase mode (right)

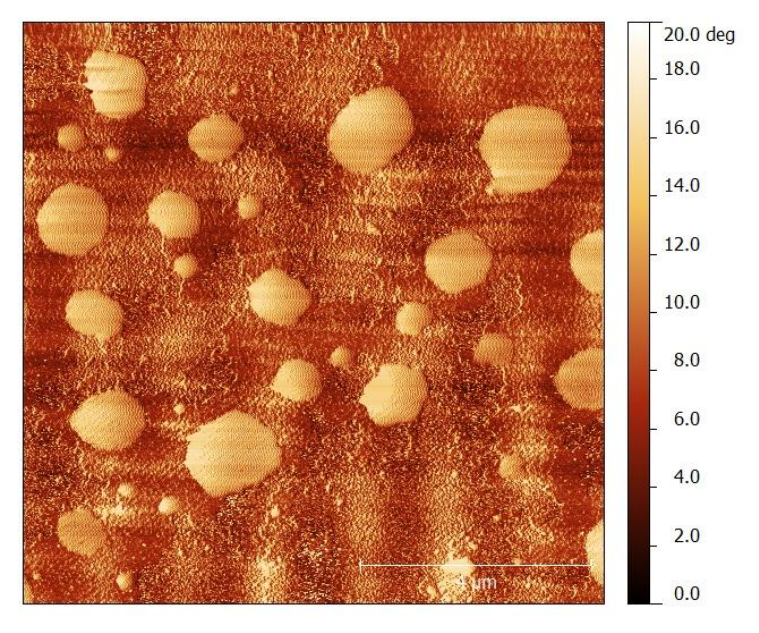
QCM - OIL AND CELLULOSE





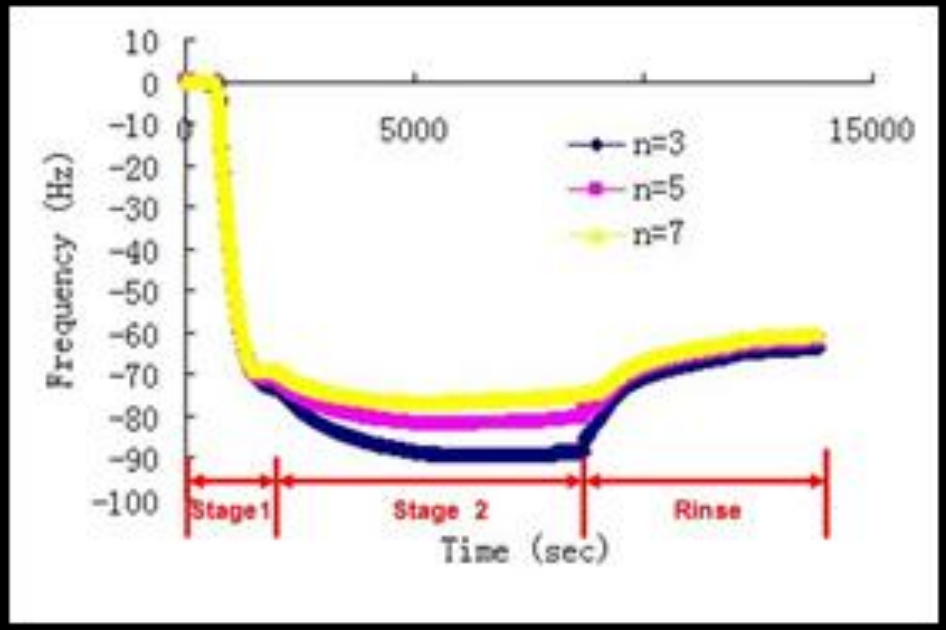
AFM – OIL AND LECITHIN

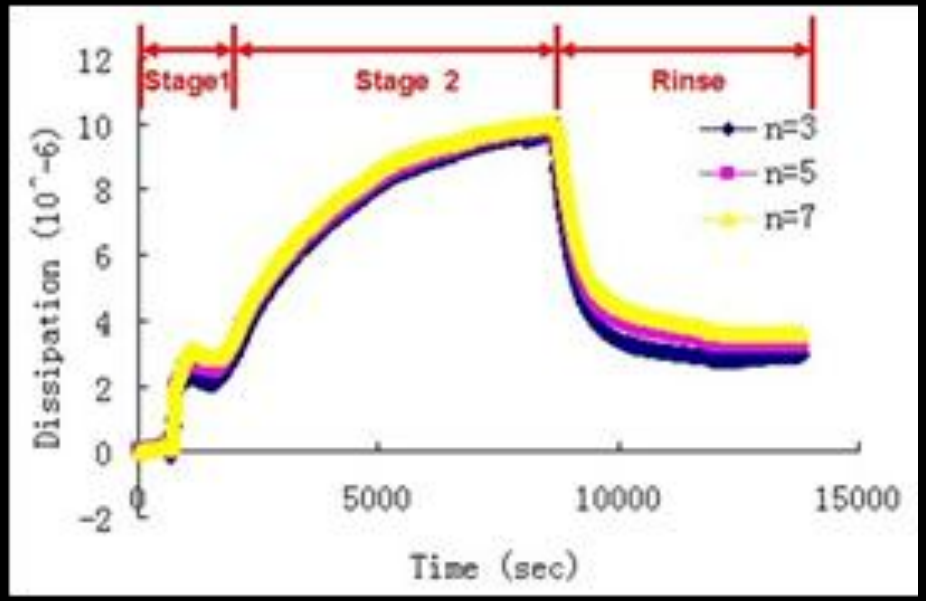




AFM images of oil and lecithin on the QCM sensor in height mode (left) and phase mode (right)

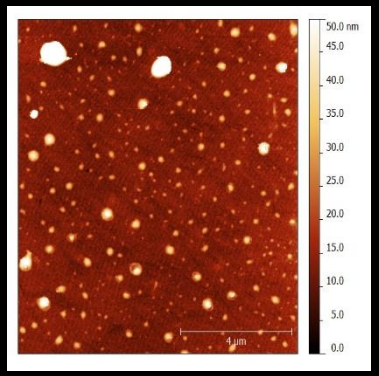
QCM – OIL, LECITHIN, AND CELLULOSE

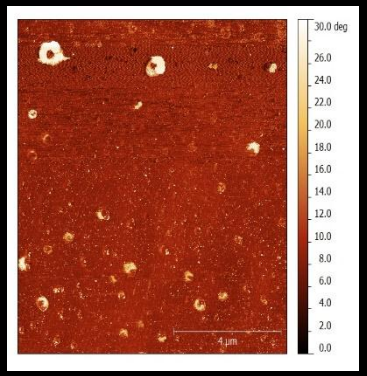


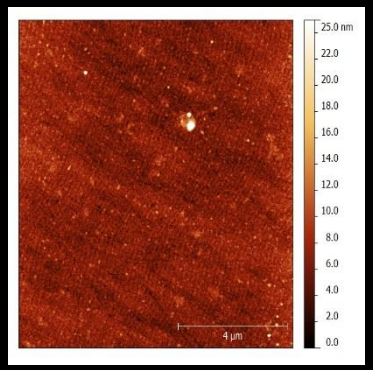


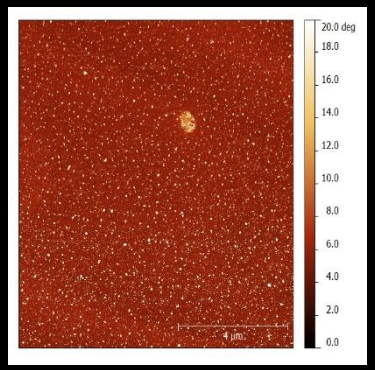
AFM – OIL, LECITHIN, CELLULOSE

After rinse



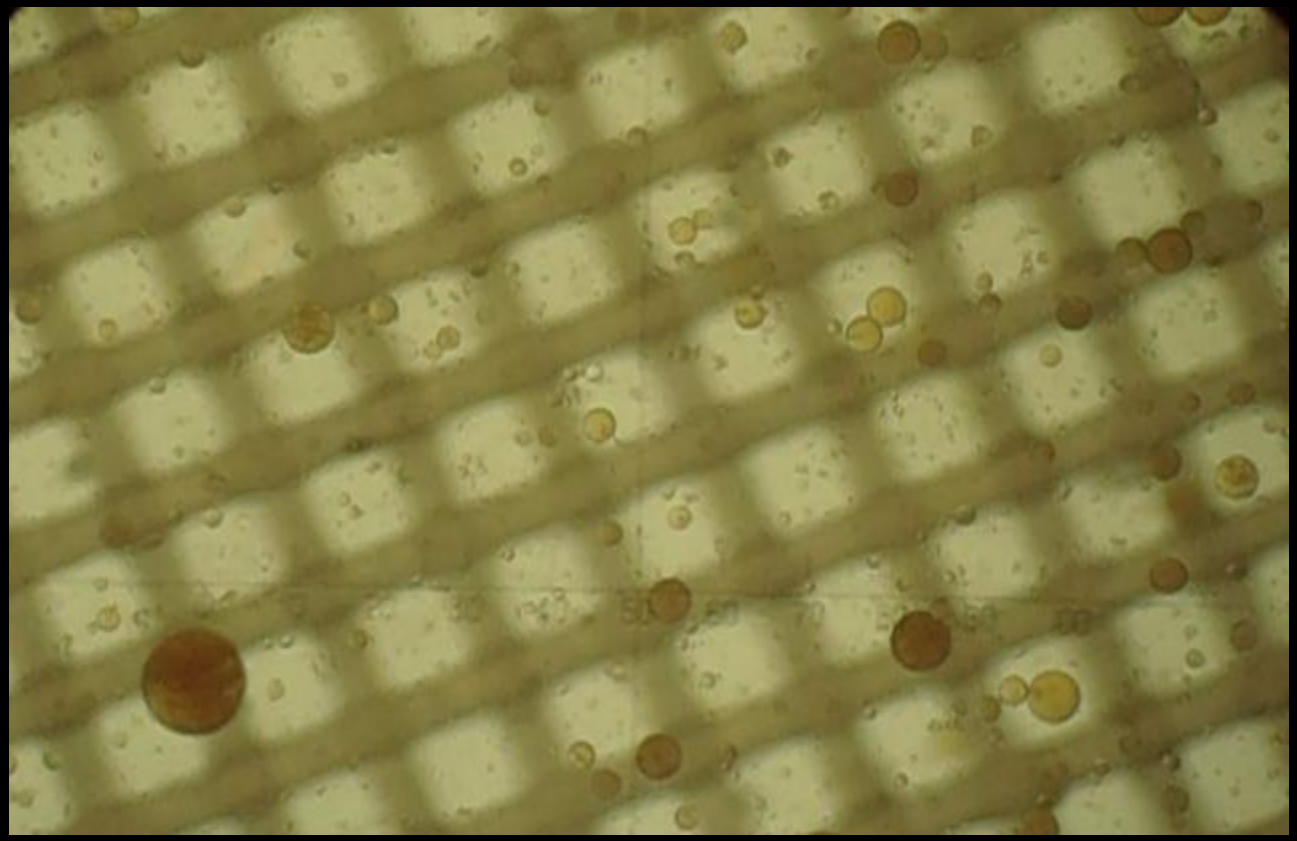




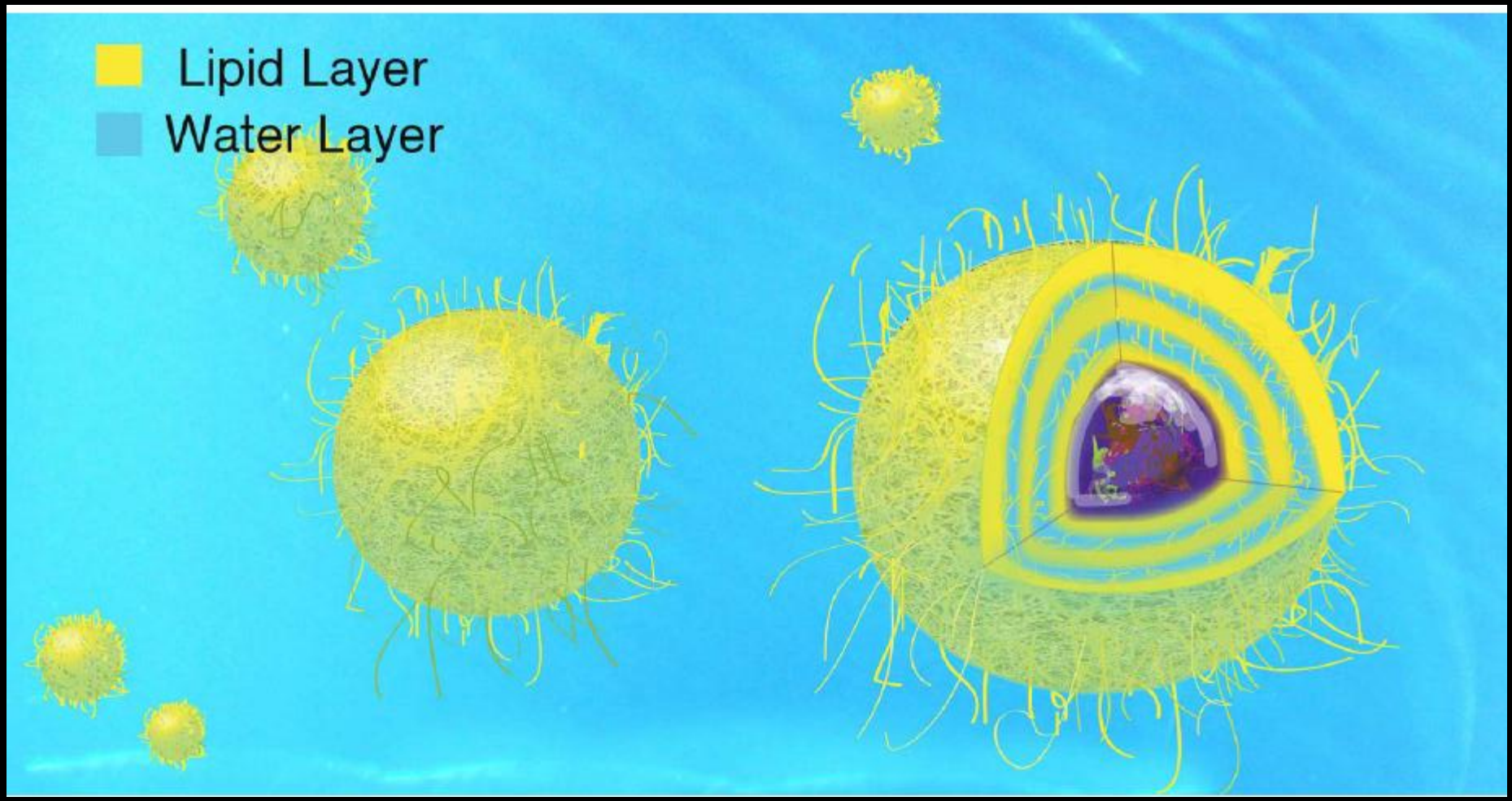


“NON-STICK” IN ACTION

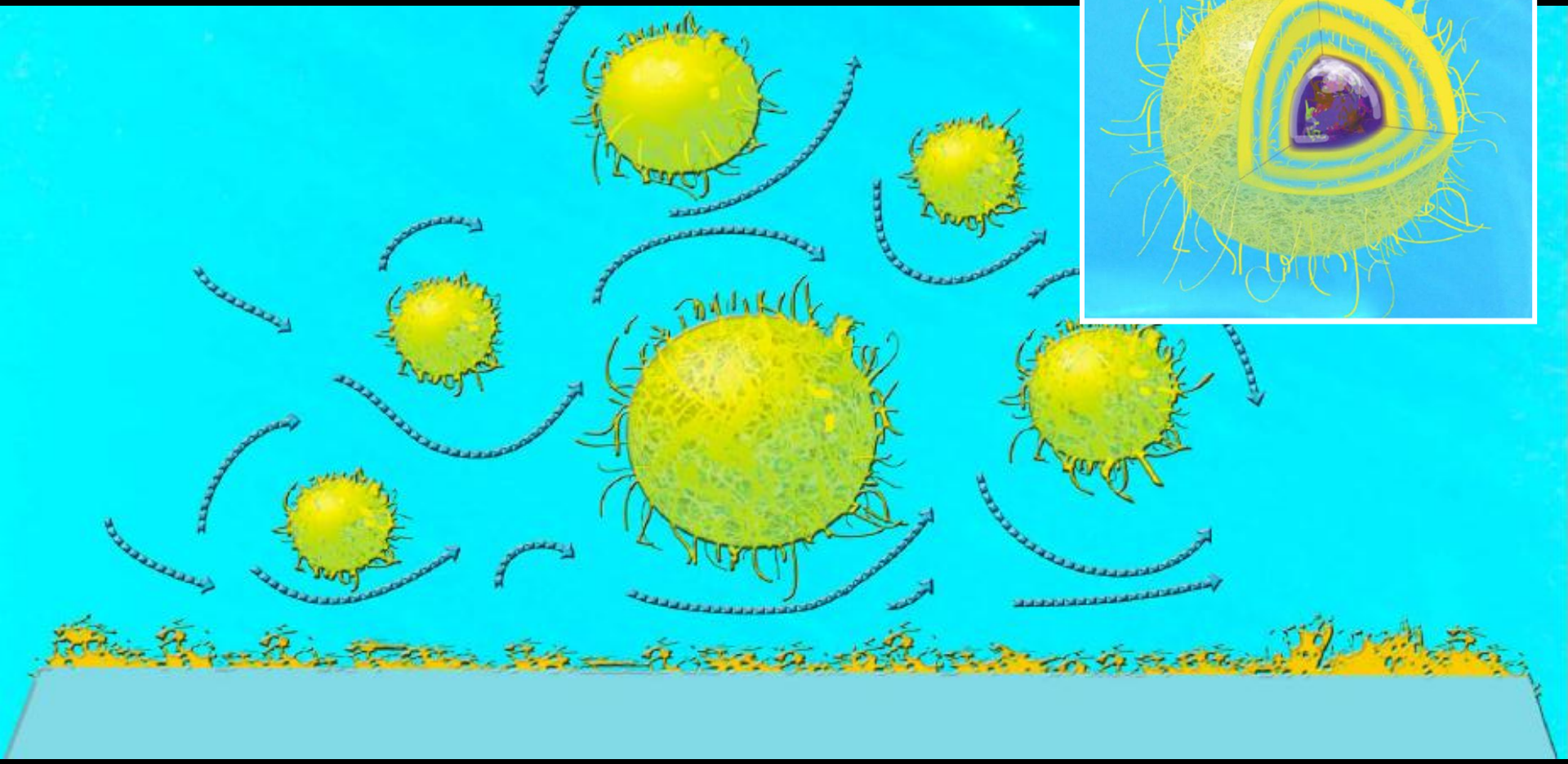
Crude oil from Deepwater Horizon on model, woven fabric



HOW DOES IT WORK?



"NON-STICK" OIL DROPLETS PROPOSED MECHANISM



READILY SCALABLE

- 10 Scaled up batches
- 11 lb each batch
- Reproducibility confirmed

RELATIONSHIPS

Suppliers

ADM

Dow

CRODA

Partners

Ohmsett

ORTEC INC.

MISSISSIPPI POLYMER INSTITUTE

Enabling introduction of new technology

CALIFORNIA DEPARTMENT OF FISH and WILDLIFE

BOEM Bureau of Ocean Energy Management

United States Environmental Protection Agency

POWERPLUS CLEANING SOLUTIONS

Chevron

Interagency Coordinating Committee on Oil Pollution Research — United States of America

Department of Energy — United States of America

NOAA

United States Fire Administration

U.S. Department of the Interior — March 3, 1849

NOFO

bp

ExxonMobil

Maritime Administration — United States of America

U.S. Fish & Wildlife Service

PHMSA — U.S. Department of Transportation — Pipeline and Hazardous Materials Safety Administration

Governor of California — United States Navy

NASA

NIST

United States Coast Guard — 1790

WHAT IS NEEDED TO QUALIFY A PRODUCT FOR USE IN OIL SPILL EMERGENCIES

Environmental Regulations

- EPA Toxicity Testing
- NCP Product Listing

Larger Scale Manufacturing/Testing

- Scale-up Material (Toll Manufacturing)
- Small field test
- Ohmsett Wave Tank

SOME QUESTIONS THAT NEED TO BE ANSWERED

For existing and new technologies

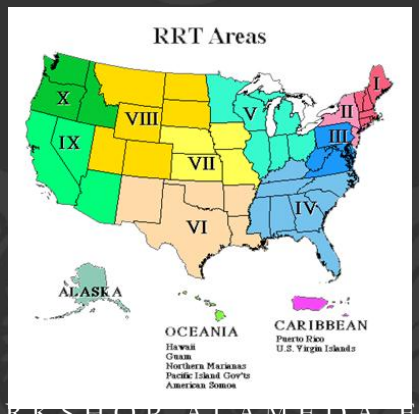
Coastal Response Research Center at the University of New Hampshire
Center for Spills in the Environment

Nancy E. Kinner

The Coastal Response Research Center is focused on developing new approaches to spill response and restoration in marine and estuarine environments through research and synthesis of information.

Amy Merten, NOAA

Investigating the effect of oil spills on the environment and human health.



CASE STUDY: SPILL ON MS RIVER

~1,000 gal of light crude

Clean up:

5,300 ft of boom

159 workers

10 day clean up effort

16 miles of MS River closed for 4 days

1,000 barge queue

>250,000 gals of oil/water mix recovered

"Clean-up workers can damage habitat"

STANDARDIZING TESTING

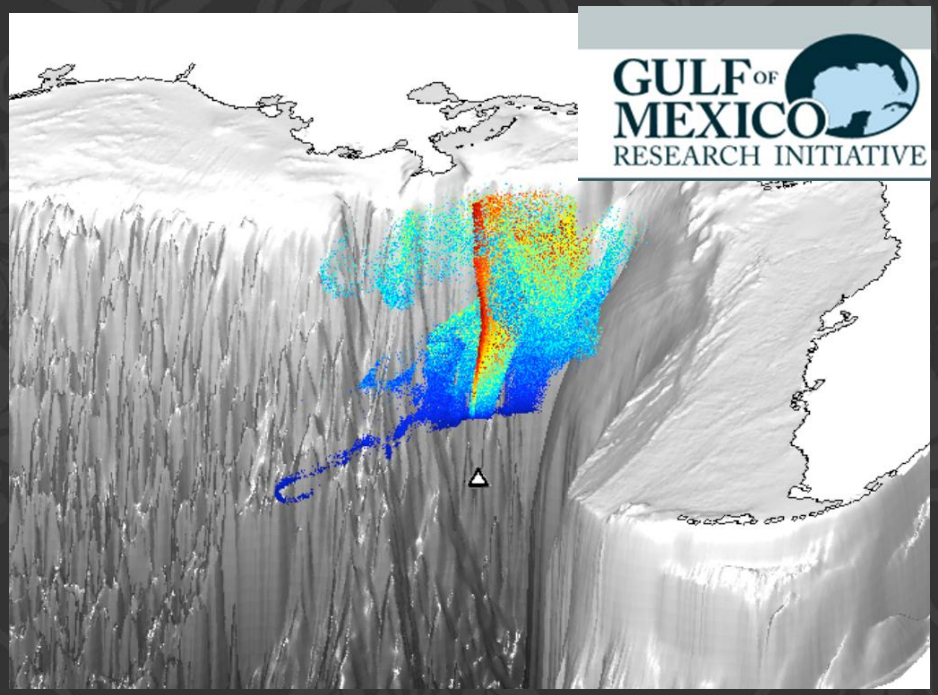
- What are the best oil models to use for standardization?
- During Deepwater Horizon – Southeastern Louisiana Crude
- Now- Alaska North Slope

- BUT THE OIL CHANGES DAY BY DAY!

Is spraying the best method of applying dispersants?

- Sprays drift and overspray can be a problem
- Liquids can 'roll off' of viscous oils
- The existing infrastructure is based on spraying
- Would solids/smart solids be better for dispersal from surface platforms?
  - Better targetting
  - Application at night
- How would they be applied?

Modeling Study Suggests Dispersants Used at Wellhead had Marginal Effect on Oil Reaching Surface Waters



Will modeling provide the basis for better design of sub-surface remediation methods?

Claire B. Paris, Matthieu Le Hénaff, Zachary M. Aman, Ajit Subramaniam, Judith Helgers, Dong-Ping Wang, Vassiliki H. Kourafalou, and Ashwanth Srinivasan (*Environmental Science & Technology* 2012 *46*(24), 13293-13302).

Saving the World with Magic Bacteria

National Science Foundation
WHERE DISCOVERIES BEGIN

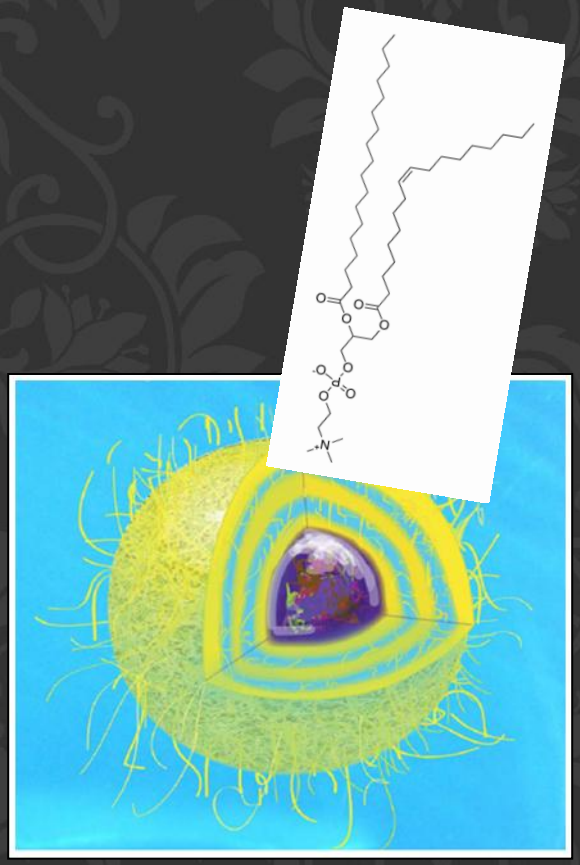
There are so-called 'magic' bacteria in there that eat the oil—that's true. There are also bacteria that eat the waste that's thrown out by the bacteria that eat the oil. There are bacteria that provide food for the others, and then bacteria that provide food to those bacteria, and so forth. We have to try to dismantle this complexity and make sense of it so we can predict these processes. Jack Gilbert, University of Chicago

"If the oil is in very small droplets, microbial degradation is much quicker," Kenneth Lee, director of the Center for Offshore Oil, Gas and Energy Research with Fisheries and Oceans Canada.

Fertilizers, such as iron, nitrogen and phosphorus, were used to stimulate the growth of oil-degrading after the *Exxon-Valdez* spill. "We saw a three to five times increase in rate of biodegradation," Ronald Atlas, University of Louisville

In the ocean, how do you keep the nutrients with the oil? Kenneth Lee.

Biodegradability of [14C]methylcellulose by activated sludge.
F A Blanchard, I T Takahashi, and H C Alexander;
Appl Environ Microbiol. 1976 October; 32(4): 557–560.



- Will the nutrient favor the growth of the wrong genus/species of bacteria?
  - Will it cause unwanted differentiation?
- Will the nutrient in the ocean result in algal bloom?
- Will the nutrient cause eutrophication?

I think the lecithin base and potential for eutrophication is just something you would list as an "other possible hazards" we might need to consider at the time of incident-specific use. If application is on well-circulated or open water bodies (e.g., open offshore waters, near river banks), maybe it's not a problem. Application in more limited water bodies (e.g., lakes, lagoons, ponds, wetlands) might warrant a different look.

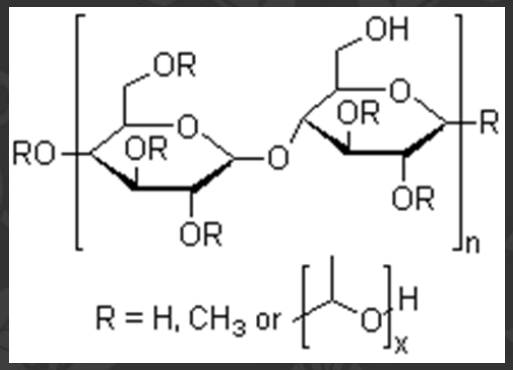
Possible eutrophication might not be a limit to EPA listing, but instead, with that knowledge of its potential, we'd make an incident-specific decision about whether it's use would benefit the situation, or whether we should save it for another day and type of use.

Study Finds Carbon from Deepwater Horizon Entered Food Web

J.P. Chanton at Florida State University (FSU), J. Cherrier at Florida A&M University (FAMU), R.M. Wilson at FSU, J. Sarkodee-Adoo at FAMU, S. Bosman at FSU, A. Mickle at FSU, and W.M. Graham University of Southern Mississippi. **November 2012** ***Environmental Research Letters***

- Will the dispersed oil be mistaken as food pellets by birds and fish?
  - Reduce particle size to < 1 μm
  - Plan to recover the oil

- Buoyancy
- Herders
- Stimuli-responsive polymers



REMAINING OBJECTIVES

- EPA toxicity testing
- Listing on the NCP Product Schedule
- Liquid complement to current product
- Larger scale testing
  - Small field test
  - Ohmsett Wave Tank

SUMMARY

- We have developed an anti-redeposition remediation treatment for spilled oil
- …….To protect coastal flora and fauna from the ravages of oil-fouling
- Deepwater Horizon revealed gaps in our knowledge of the fate of spilled oil, the chemicals used as treatment, and the ecological effects
- NSF responded with RAPID and AIR funds
- The BP funds will greatly leverage NSF funding to shed light on our ignorance of the real effects of oil spills
- .. And to build the scientific infrastructure that is necessary for the emergence of innovative solutions to the oil-spill challenges.

ACKNOWLEDGEMENT

Sincere Gratitude to the National Science Foundation

Without NSF support our advances would be unrealized.

Thank you

NSF PFI 0917730

NSF RAPID 1047662

NSF AIR 1127846

ACKNOWLEDGEMENTS

Additional contributions to the project:

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Chase Thompson

Yan Zong

Dr. Samy Madbouly

Dr. Laura Anderson

Kelly McLeod

Ethan Hoff

Corporate Sponsors:

Dow Chemical

Archer Daniels Midland

Croda International

??? QUESTIONS ???

The National Formulation Science Laboratory