

Formation of Detergent Stabilized Oil-Water Emulsion in Bilge Water and a Method to Thwart the Same

WP18-1074

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Lehigh University**

**In-Progress Review Meeting
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14. ABSTRACT The technical objectives of this project are listed below: <ul style="list-style-type: none"> • Emulsification is a non-equilibrium process. • This research attempts to develop an overarching philosophy with which to tie together physics of equilibrium and non-equilibrium processes and thendevlop appropriate theoretical and computational tools to address the issues of emulsification with increasing complexity. 					
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Formation of Detergent Stabilized Oil-Water Emulsion in Bilge Water and a Method to Thwart the Same

Performers: Monicka Kullappan and Manoj K. Chaudhury

Technology Focus

- *Methods to characterize the spectral properties of turbulence and its role in the emulsification of oil in water*

Research Objectives

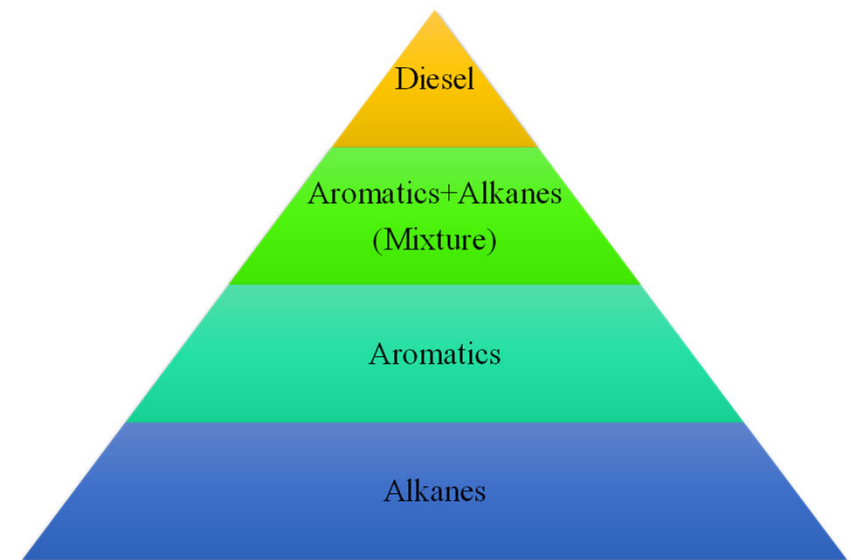
- *Understand the joint roles of fluctuating hydrodynamics and Surface chemistry in emulsification*

Project Progress and Results

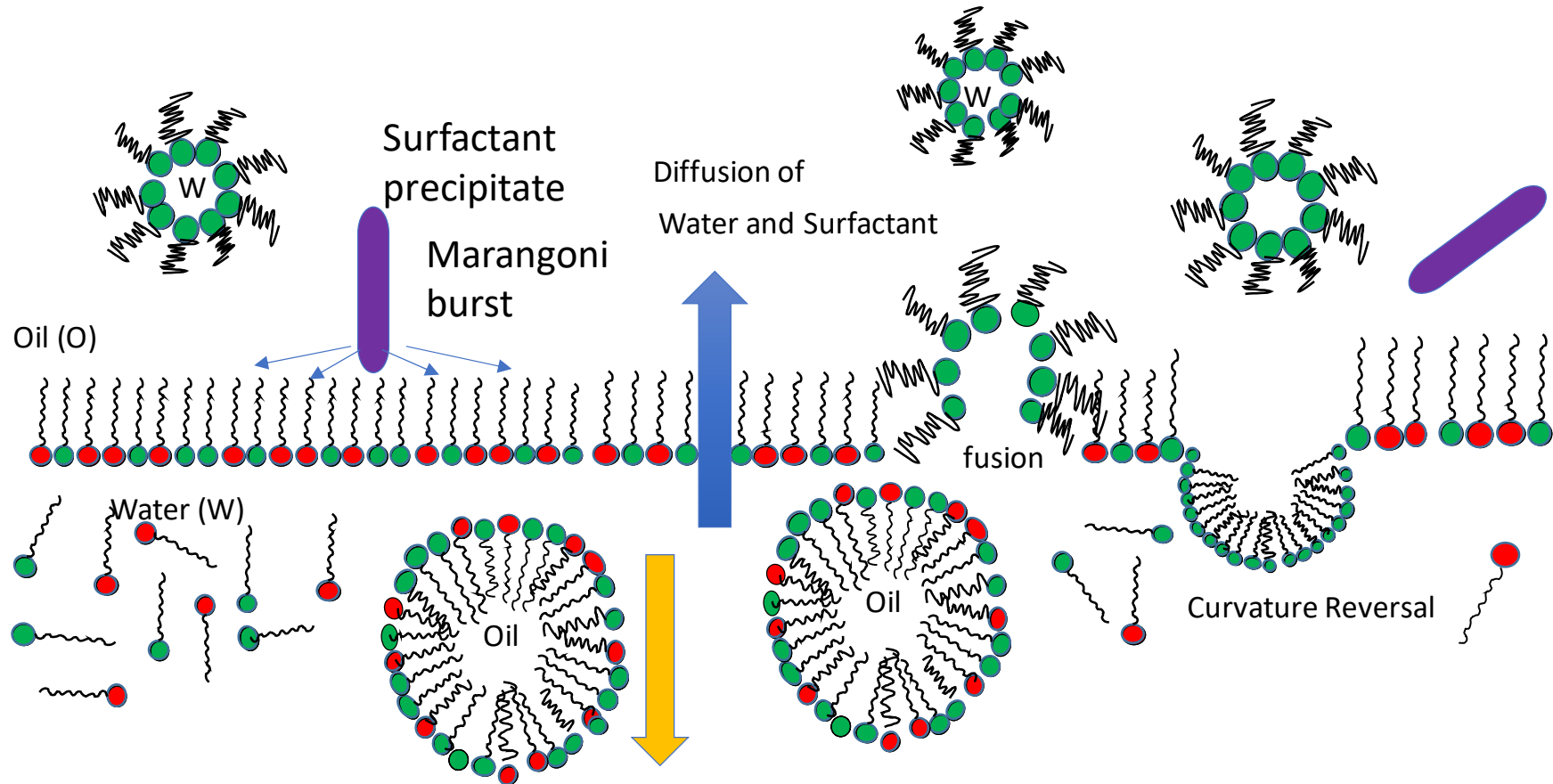
- *Identified certain kinetic pathways underlying spontaneous emulsification*

Technology Transition

- * *Based on the experimental results and a molecular dynamics simulation, we will be able to tackle highly complex scenarios facing bilge water emulsification*



Technical Objective



- Emulsification is a non-equilibrium process.
- This research attempts to develop an overarching philosophy with which to tie together physics of equilibrium and non-equilibrium processes and then develop appropriate theoretical and computational tools to address the issues of emulsification with increasing complexity.

Technical Approach

Task 1

Develop Chemo-hydrodynamic Approach To Emulsification

Task 2

Modify Properties of Turbulence Rheology and Power Input

Task 3

Roles of Interfacial Properties and Additives In Emulsification

Task 4 (redefined)

Consolidation to Bilge Water Formation Complexity with the help of molecular dynamics simulation



Accomplished



Ongoing

Overview of Prior Work

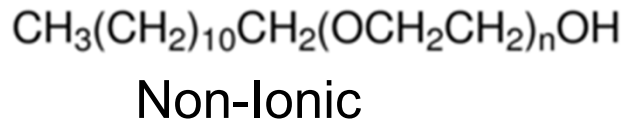
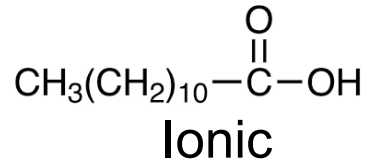
- Developed New Insights into the Role of Hydrodynamic Fluctuation and Emulsification, Both for agitated and unagitated situations
- Elaborated the Roles of various Additives in Emulsification and Microemulsion aging. We learned that emulsification can be delayed or thwarted in many cases.

Results of Current Period

- Detailed Characterization of Emulsification under Unstirred Conditions
- Verification of results using molecular dynamics simulation.

Method

Surfactant



Oil

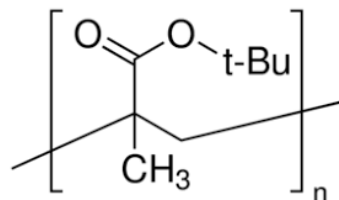
Diesel, Various Alkanes and Aromatics and some Mixtures (every liquid was purified Chromatographically)

Water

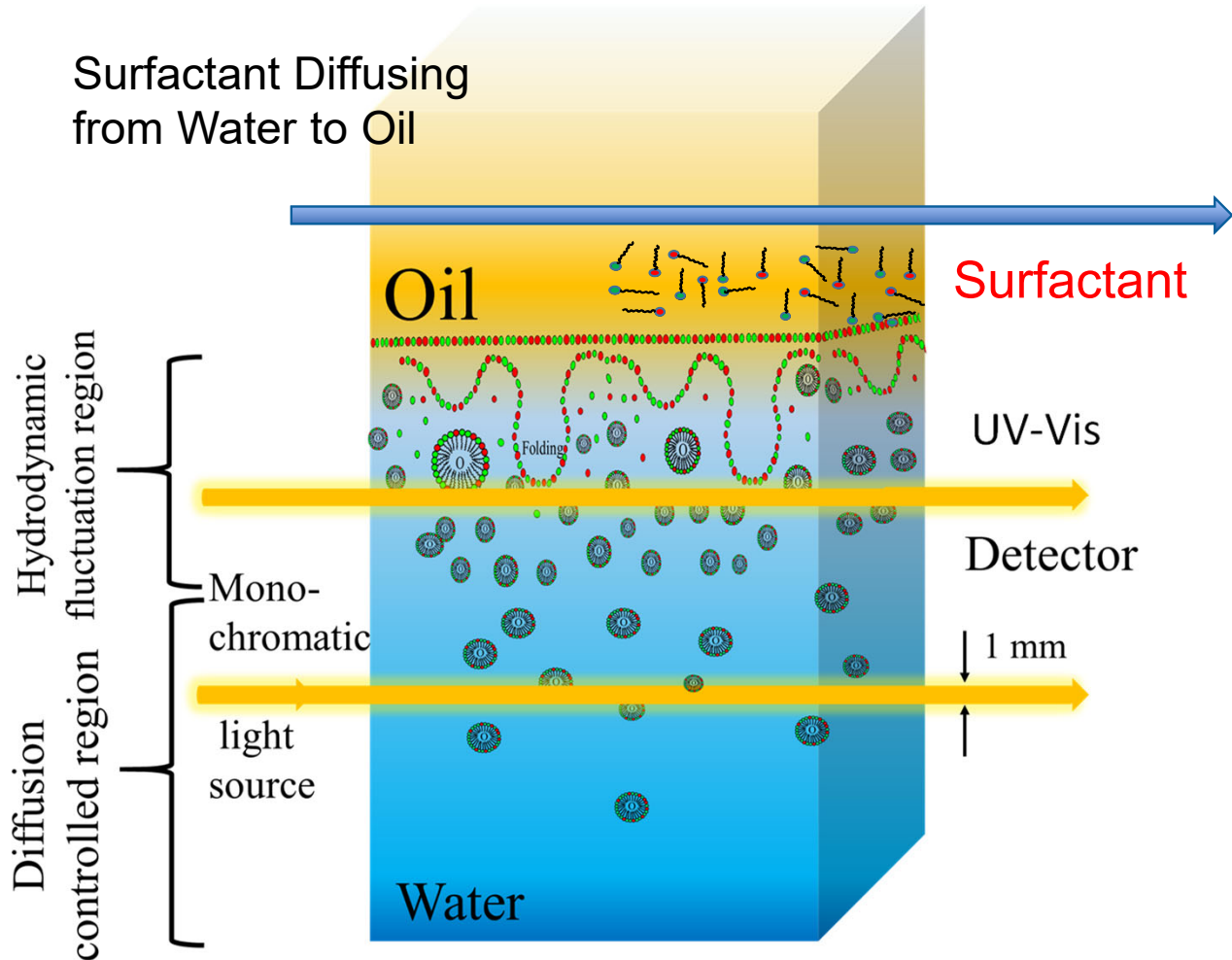
0.6 M NaCl in Distilled Water

Additives

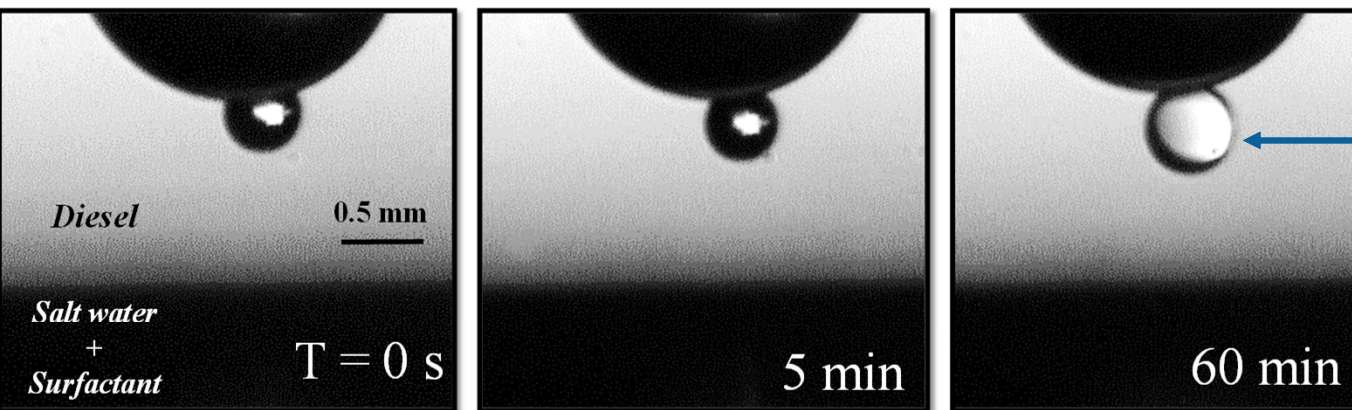
Poly 4-tert butyl styrene



, Polyacrylamide (MW~ 1 MM) , also protein

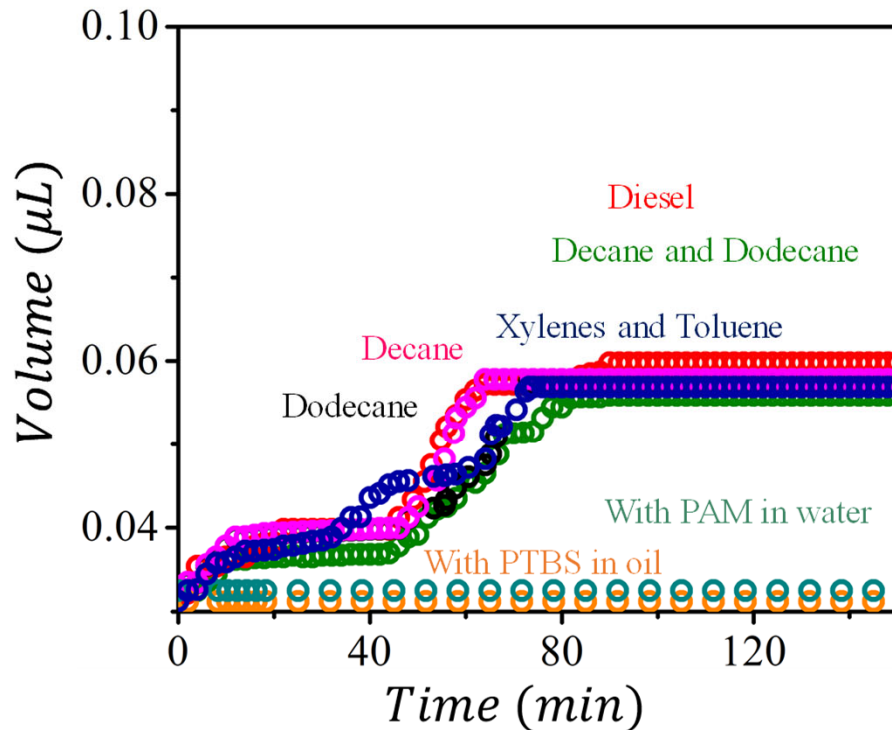


Vapor Phase Osmosis Provides Evidence of Water in Oil

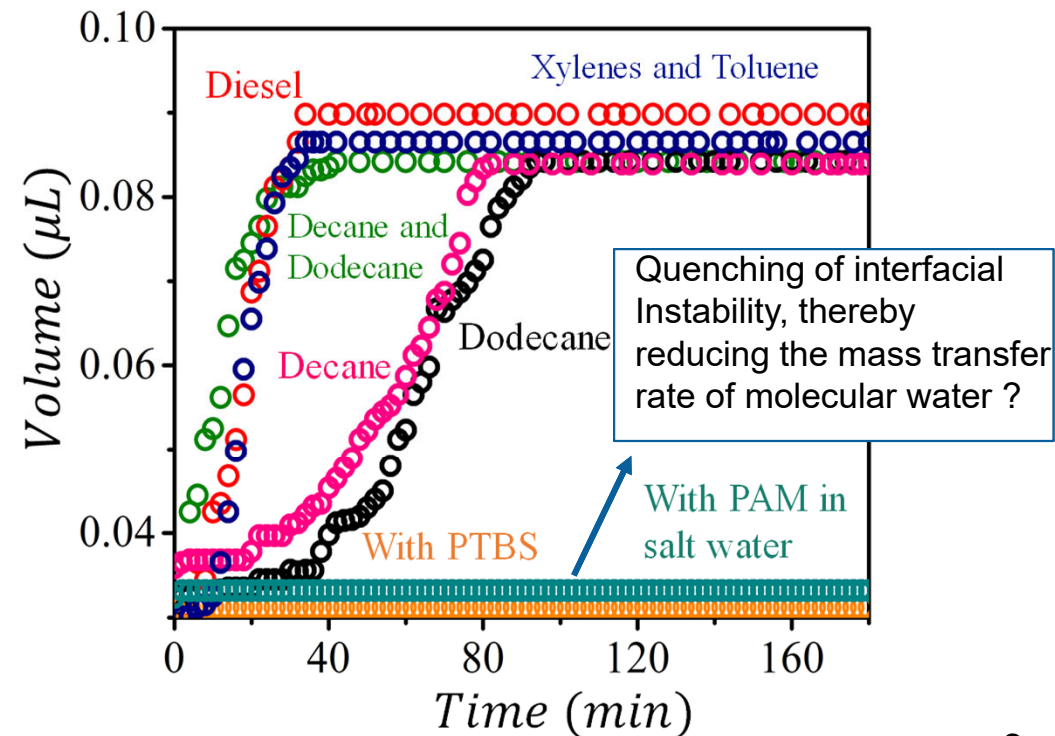


Nectar drop grows by absorbing water present in oil

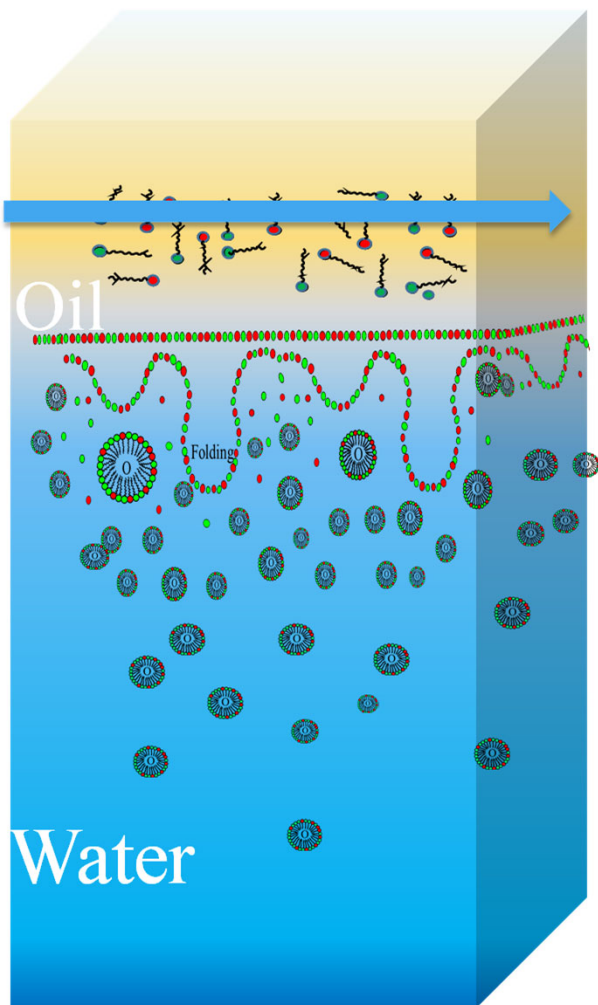
Solvent / Salt water



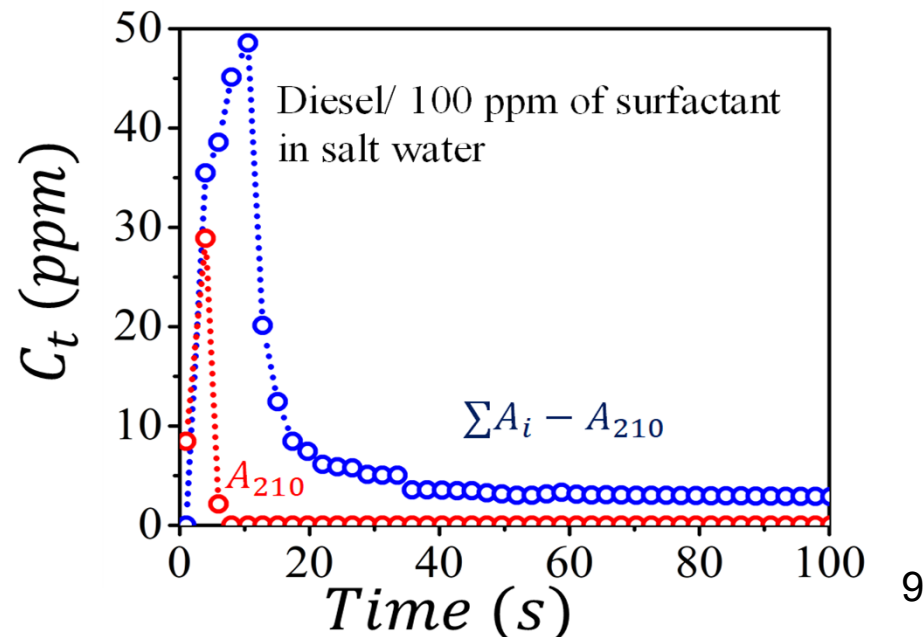
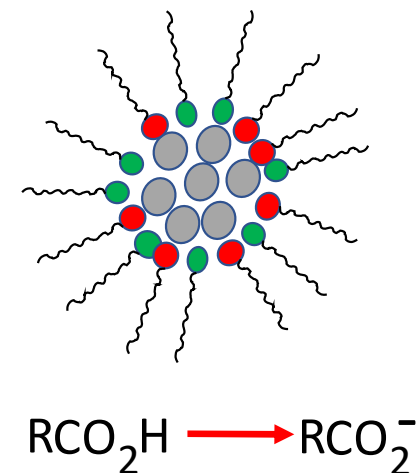
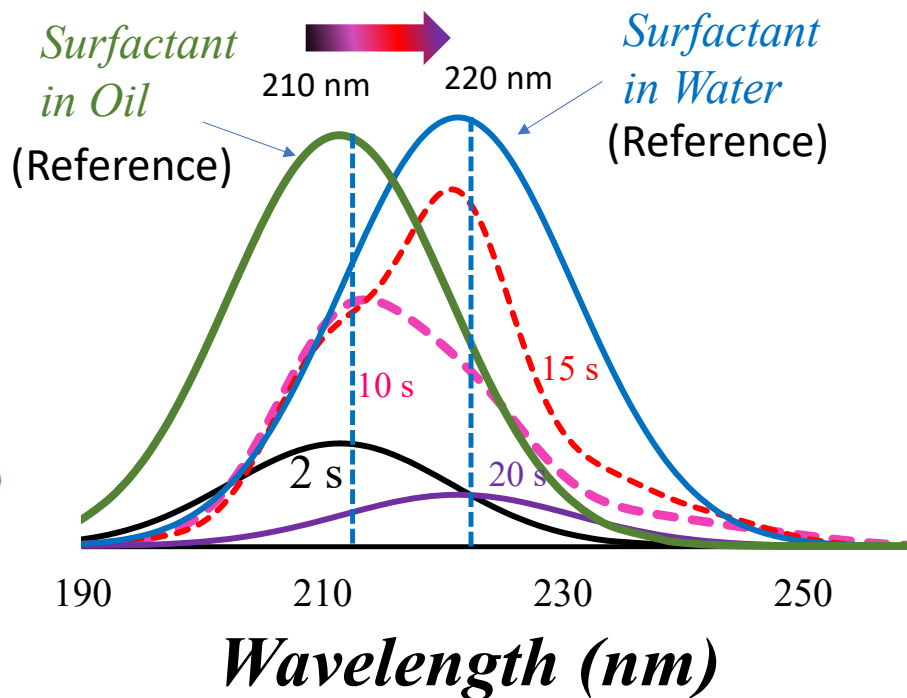
Solvent / 100 ppm Surfactant in Salt water



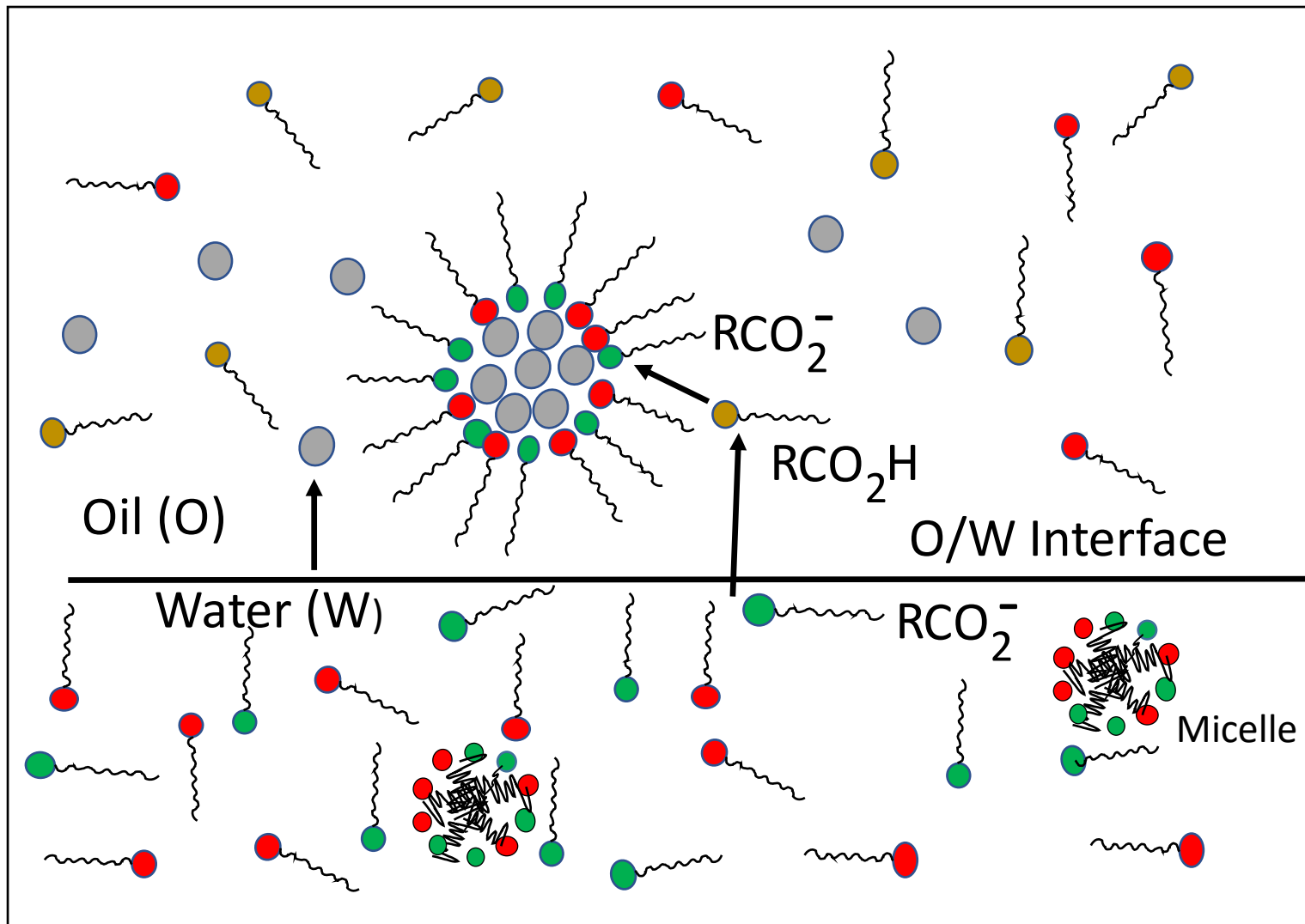
Dodecanoic Acid Diffusing from Water to Diesel



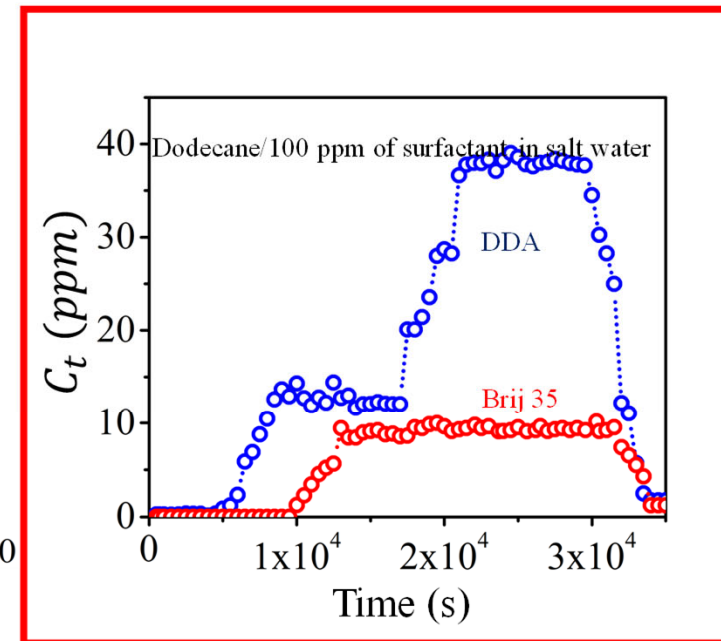
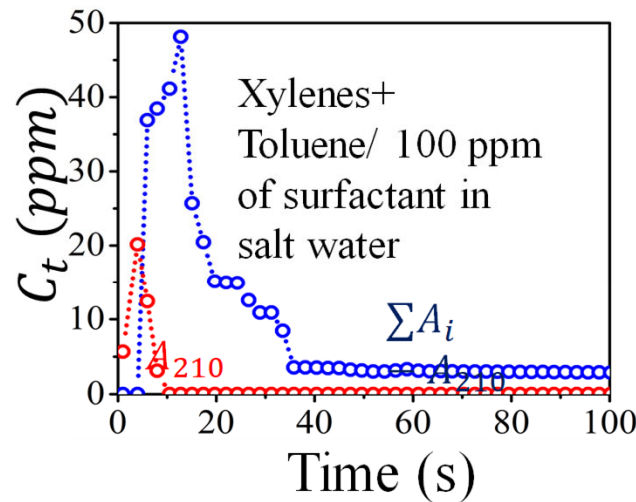
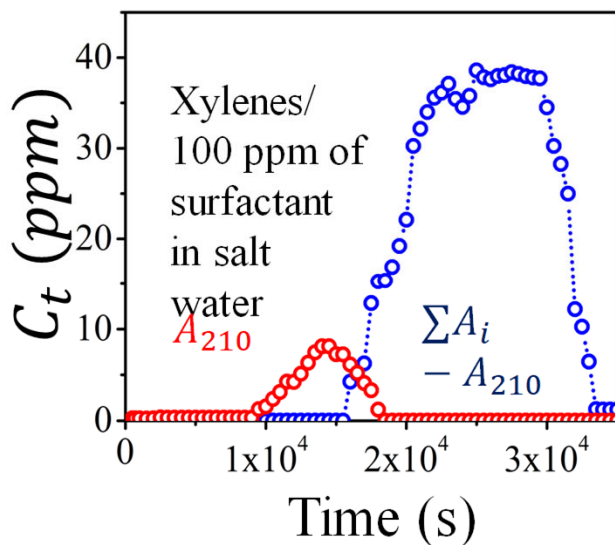
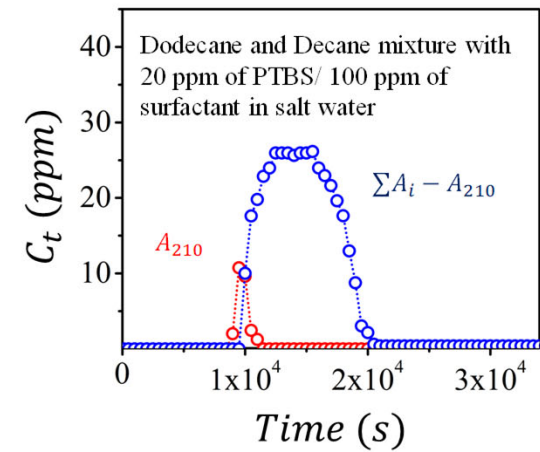
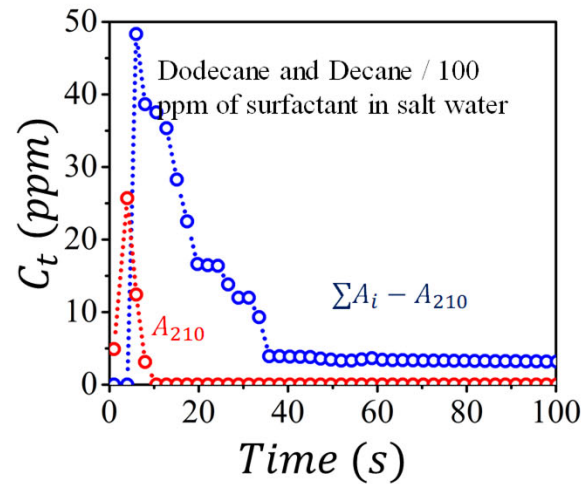
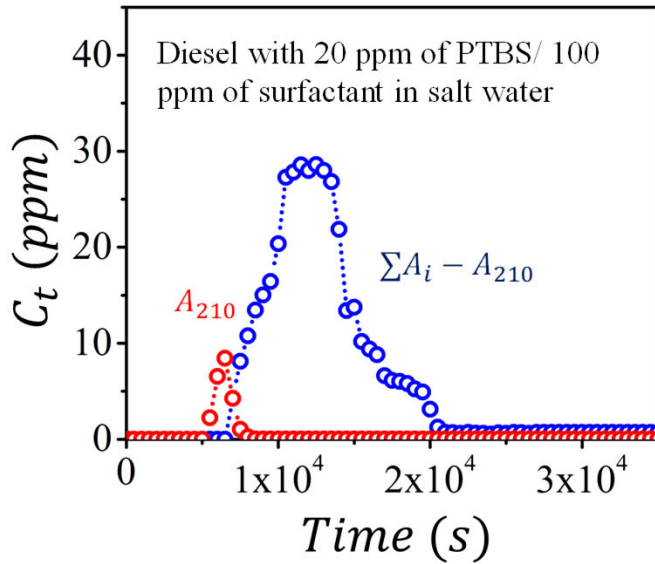
UV Beam
Is passing
through oil



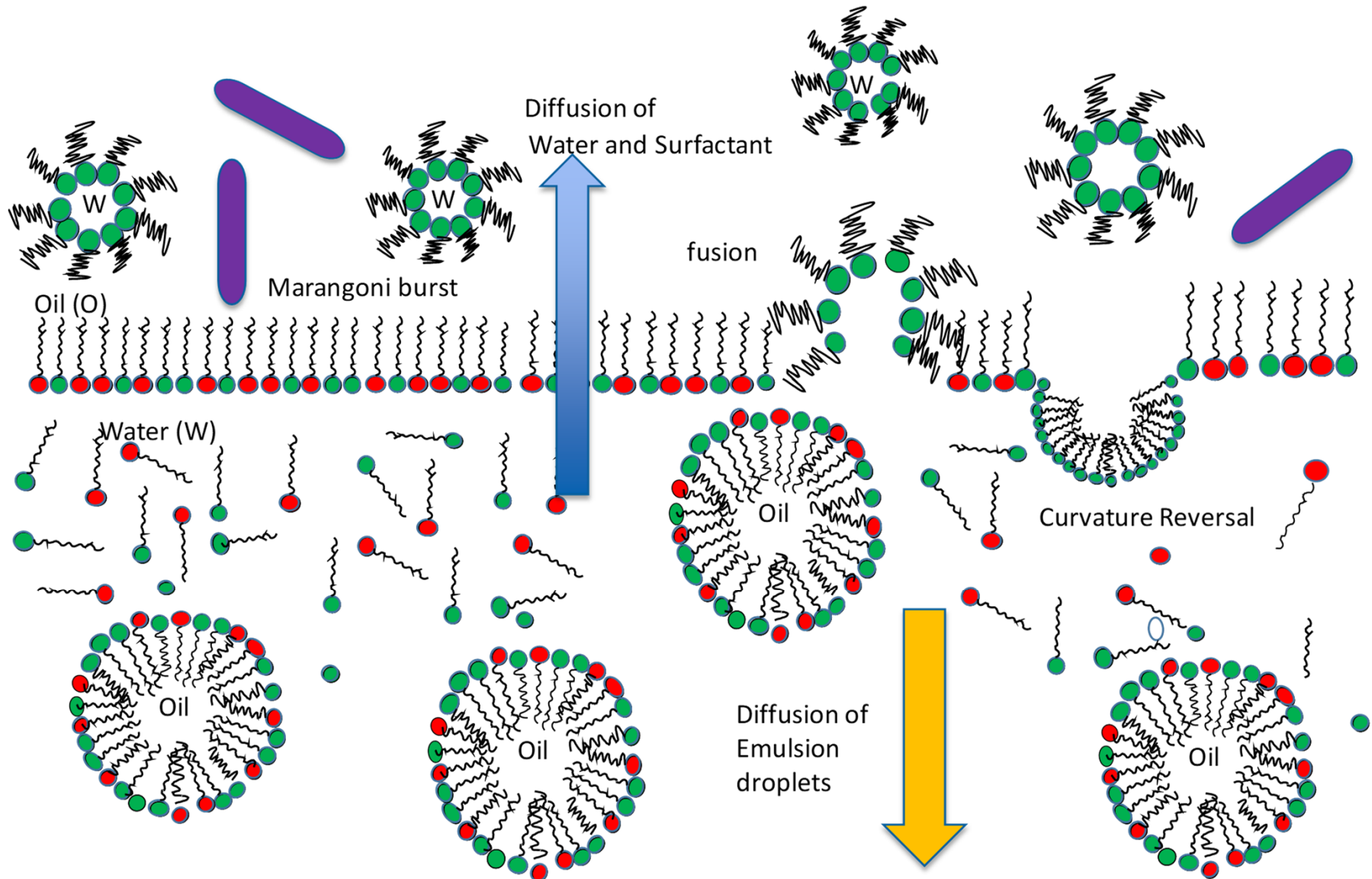
Schematic of the morphological evolution in oil



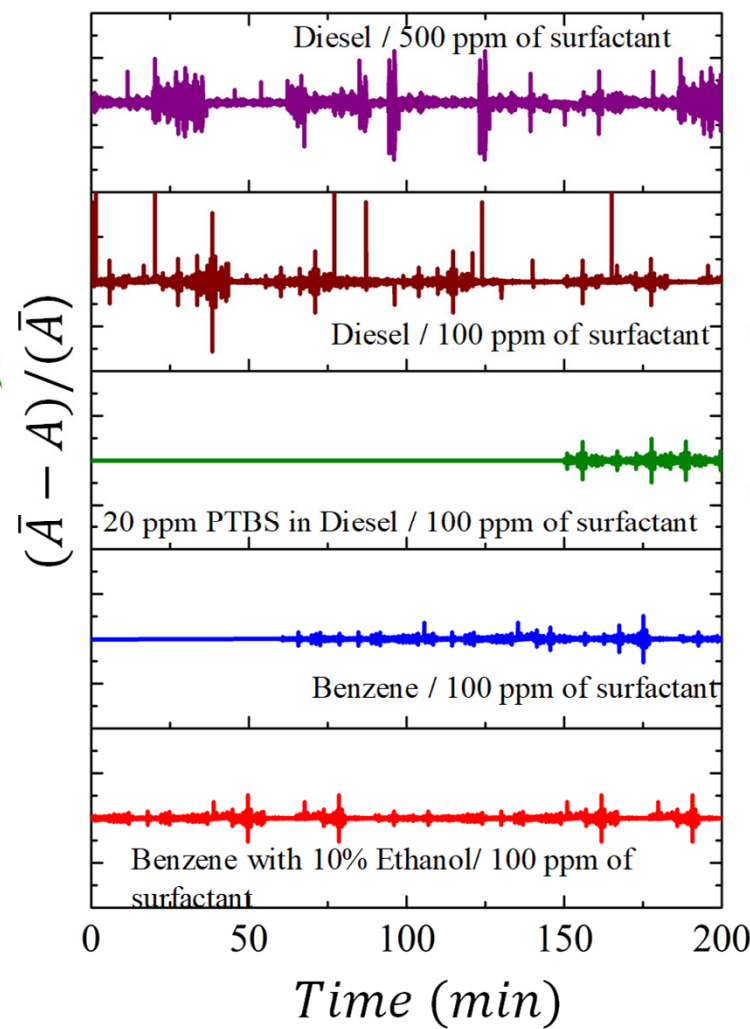
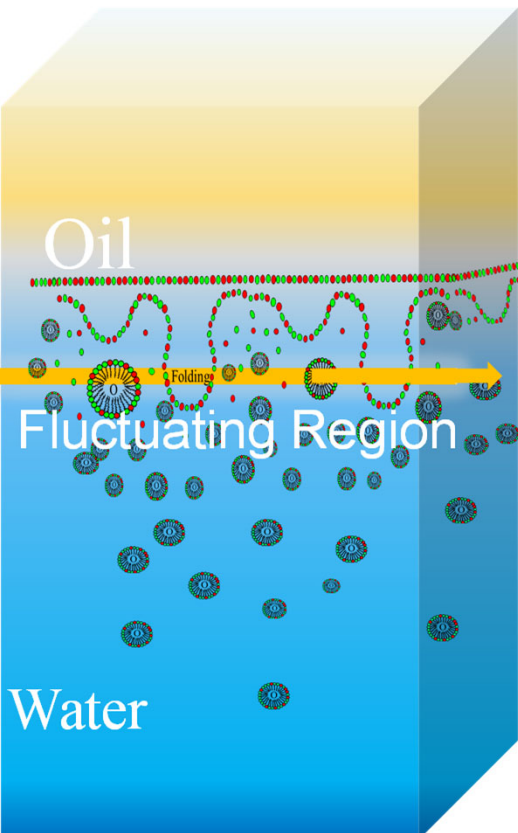
Evolution of the surfactant in oil (note: the time delay varies from one system to another)



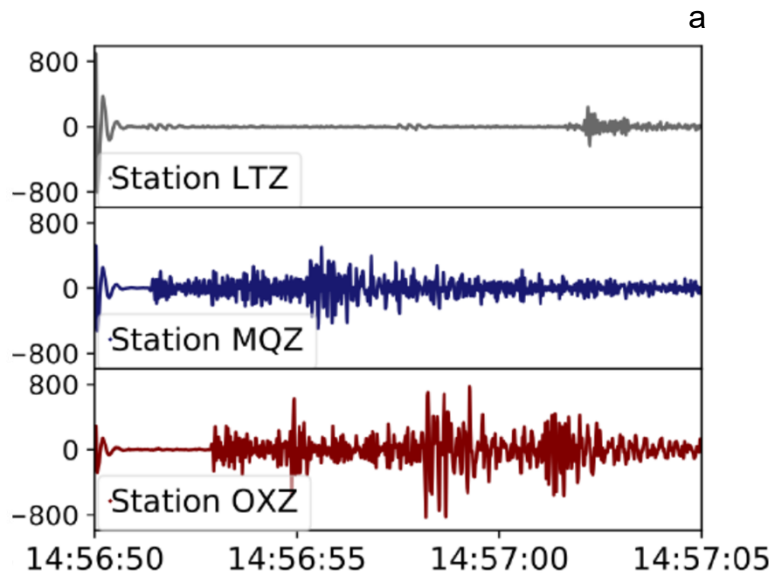
Complex Pathways to Emulsification



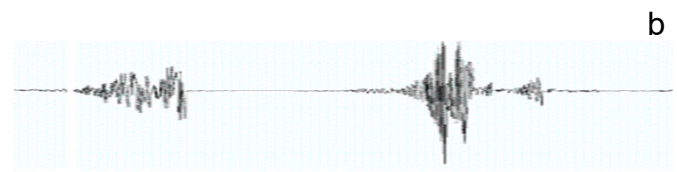
Intermittency and Concentration Fluctuation



Concentration Fluctuation
Near Interface (aqueous phase)



Earthquake



Solar Wind

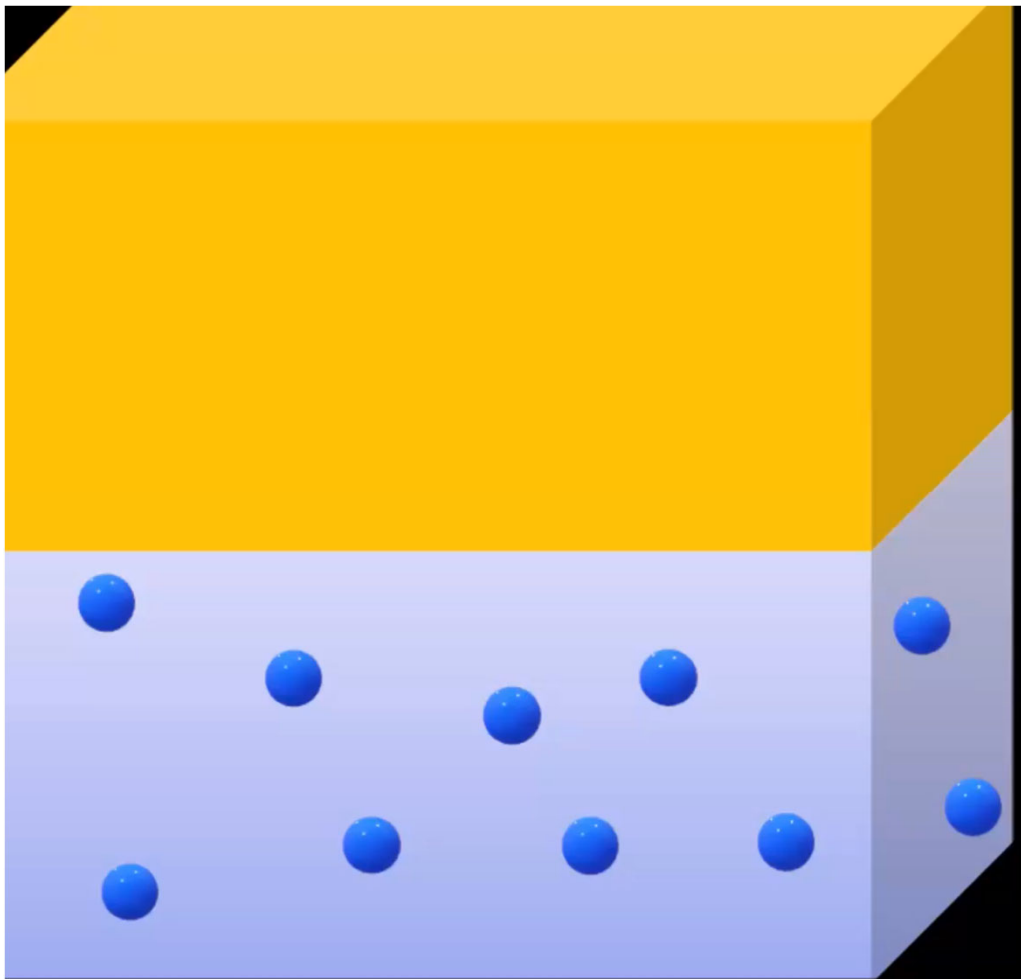


Similar to

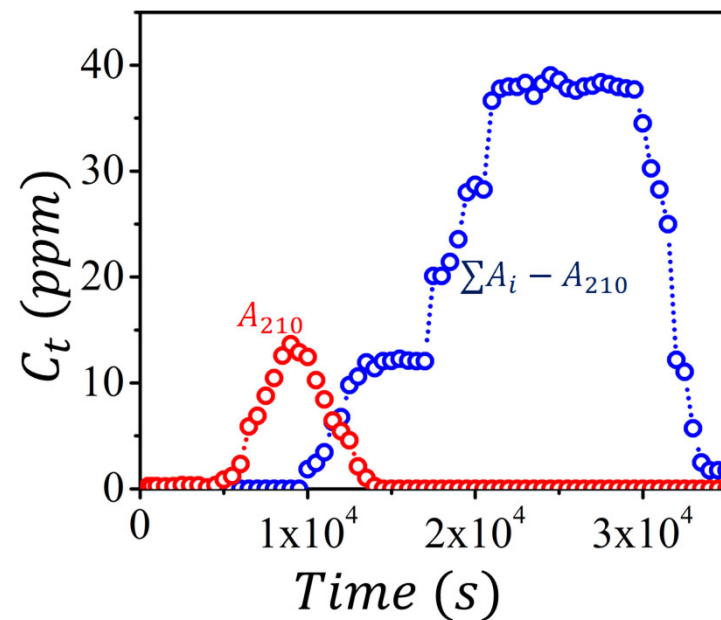
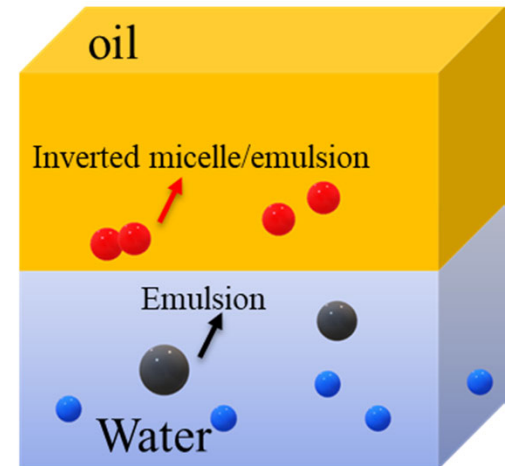
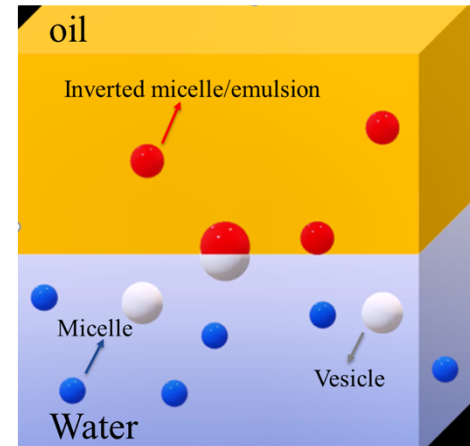
a <https://dawn.cs.stanford.edu/2018/09/05/quake/> Date: 2/4/2022, 1:30PM EST
 b <http://pfusia.cbk.waw.pl/en/topics/intermit.html> Date: 2/4/2022, 2:30PM EST

Molecular Dynamics Simulation of Emulsification

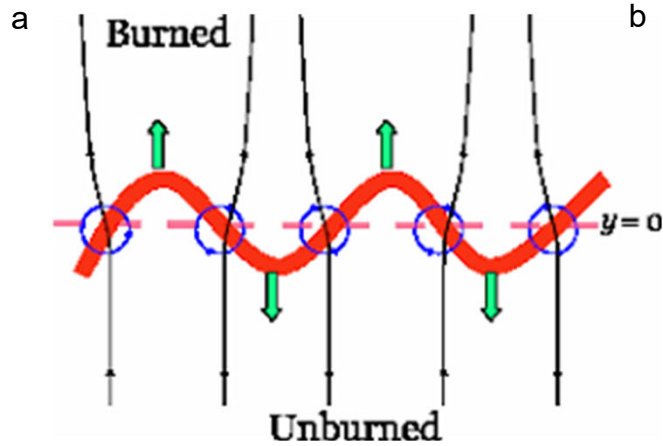
Large-scale Atomic/Molecular Massively Parallel Simulation (LAMMPS)



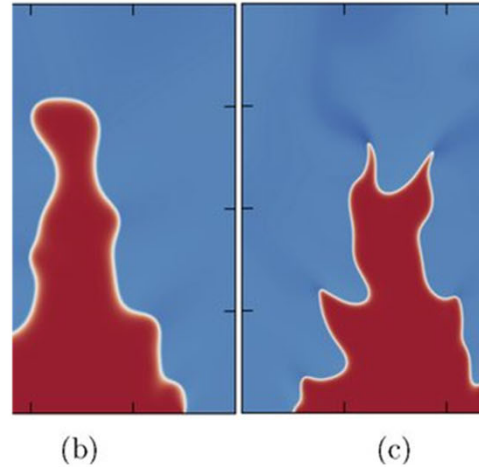
play the movie



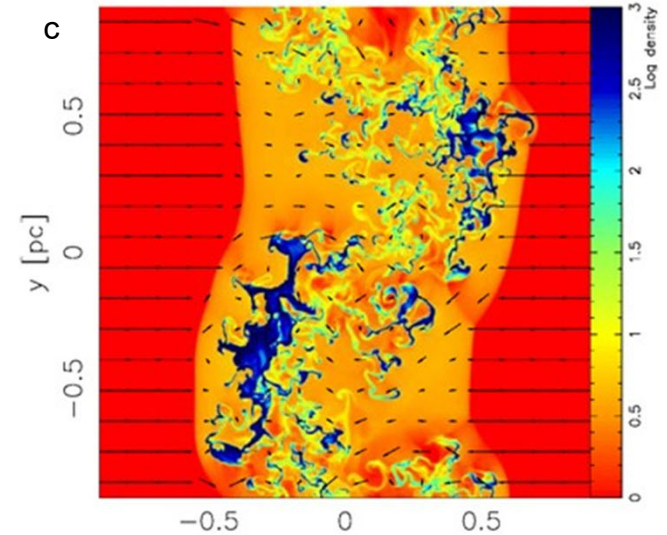
Still New Theory is needed to Elucidate the Origin and Role of Hydrodynamic Fluctuation



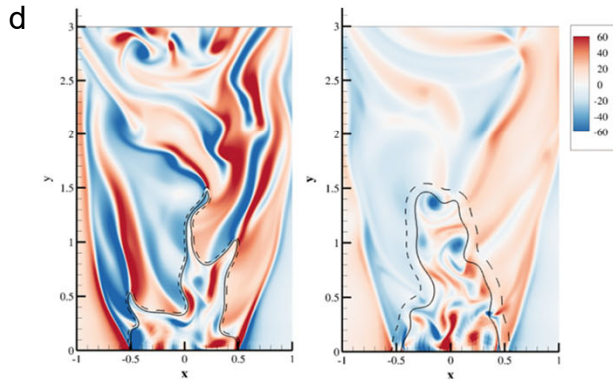
Landau-Darrieus Instability



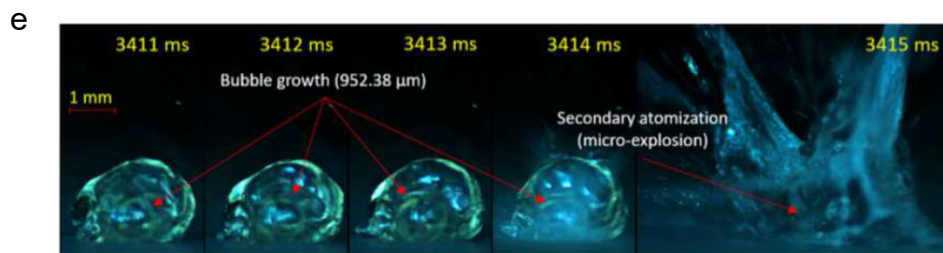
Fractal Flame



Generation of Cloud



Combustion



g. 5 Sequence images of few milliseconds before micro-explosion of water-in-palm oil derived biodiesel 8-8-11 emulsion.

Micro-explosion of W/O emulsion

a) Matalon, M. (2008). The effect of background turbulence on the propagation of large-scale flames. *Physica Scripta*, 2008(T132), 014038.

b) Creta, Francesco, et al. "Interplay of Darrieus-Landau instability and weak turbulence in premixed flame propagation." *Physical Review E* 94.5 (2016): 053102.

c) Inutsuka, S. I., Koyama, H., & Inoue, T. (2005, September). In *AIP Conference Proceedings* American Institute of Physics.

d) Lamioni, R., Lapenna, P. E., Troiani, G., & Creta, F. (2018). Flame induced flow features in the presence of Darrieus-Landau instability. *Flow, Turbulence and Combustion*, 101(4), 1137-1155.

e) Masharuddin, S. M. S., Karim, Z. A. A., Said, M. A. M., Amran, N. H., & Ismael, M. A. (2022). The evolution of a single droplet water-in-palm oil derived biodiesel emulsion leading to micro-explosion. *Alexandria Engineering Journal*, 61(1), 541-547.

Summary

- Emulsification under unstirred condition is not a passive process. It is driven by large athermal fluctuations.
- Evidently, the surfactant diffuses from one phase to another that triggers emulsification subsequently. This is a coupled interface and bulk processes.
- Spontaneously created hydrodynamic fluctuations arising from Landau-Darrieus instability could play a role (under investigation).

Action Items

- A no cost extension of the project till the end of 2022 was granted. Many Thanks.

Issues

- Some delay occurred due to COVID relate lab shut down.
- Our lab was moved in November from one building to another. This also interrupted our progress.

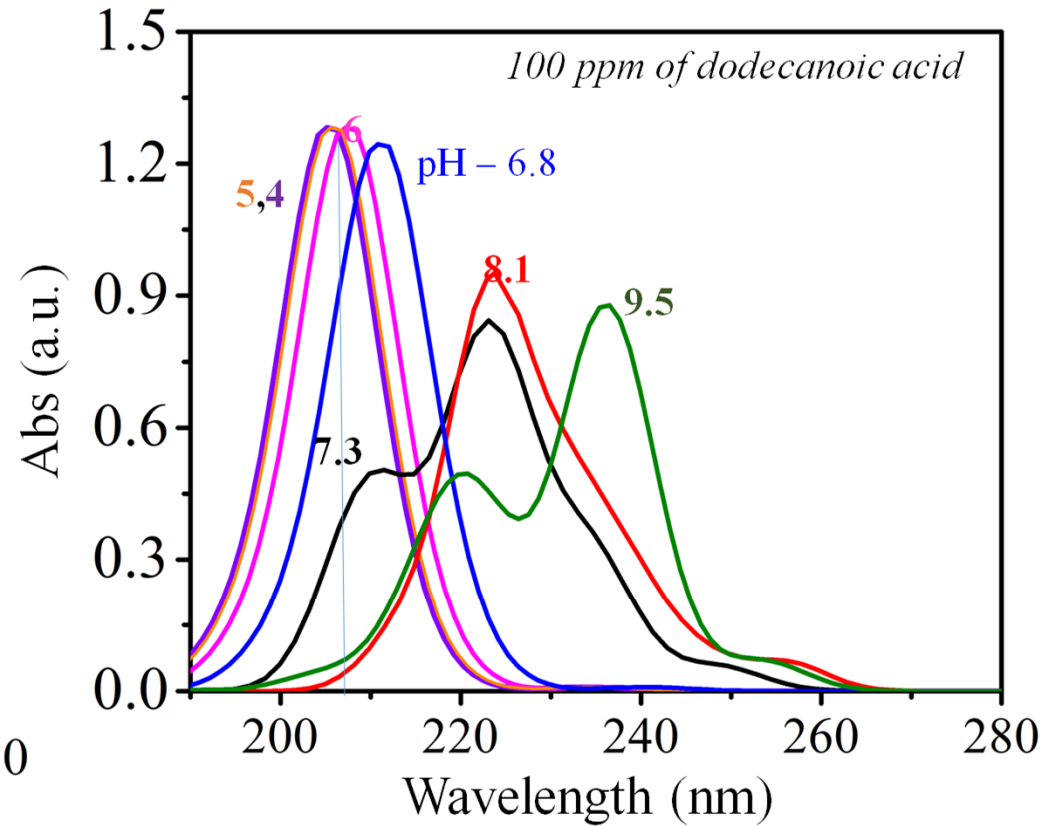
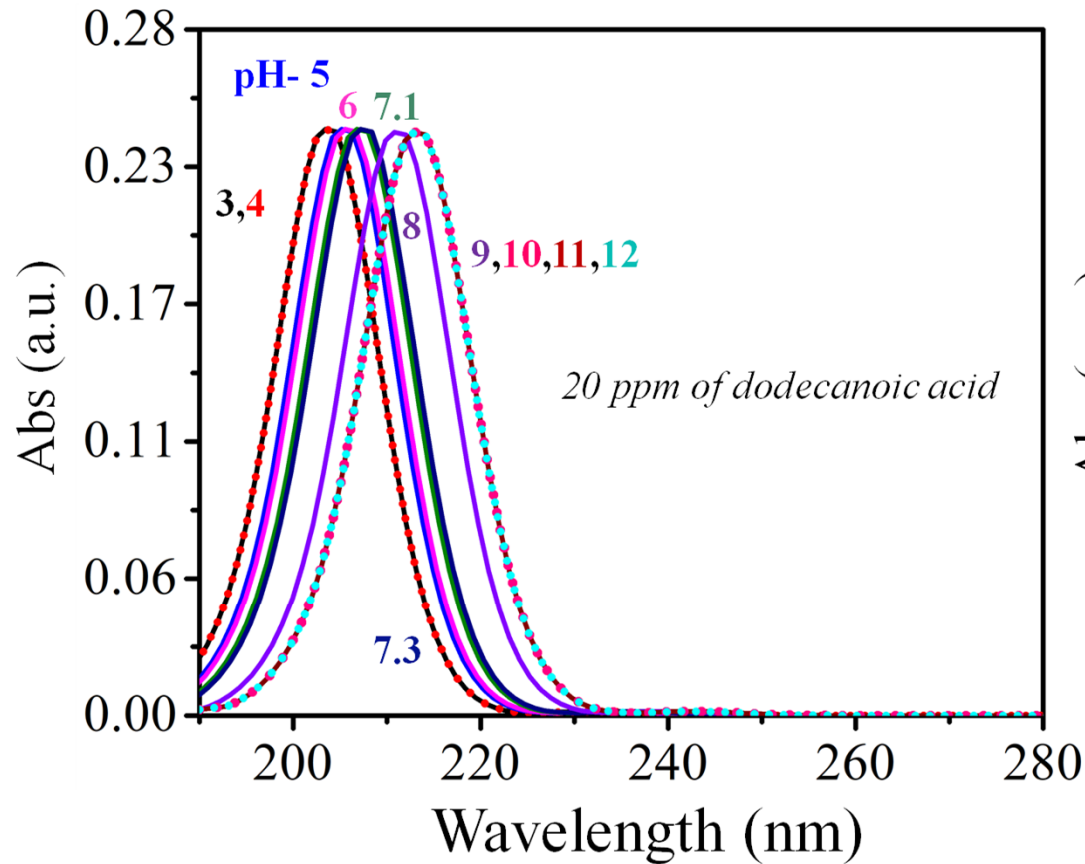
Transition Plan

- Studies on microemulsion synthesis and stability finds broad applicability in pharmaceutical, coatings and other industries.
- Thwarting the emulsification process both at macro and nano scales could find applications in the management of Bilge water.
- Hopefully the experimental, theoretical and computational approaches , which are being developed would be of value to DoD and/or DOE user communities.

BACKUP MATERIAL

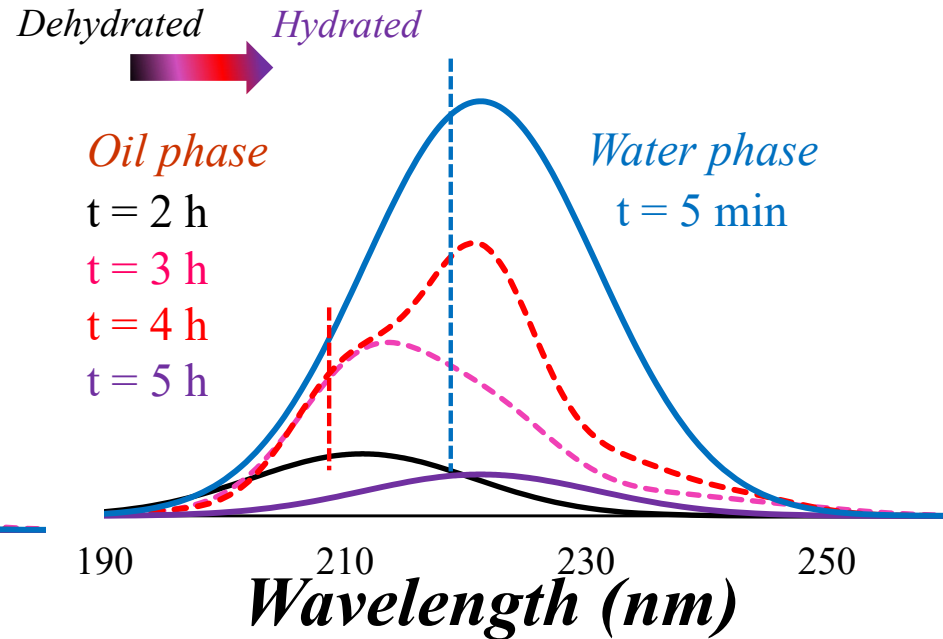
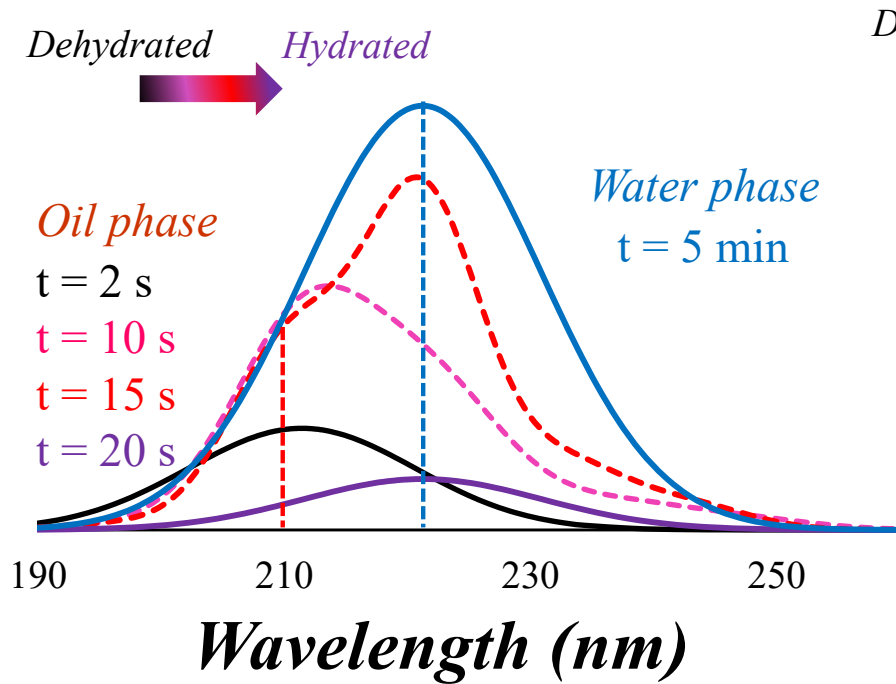
These charts are required, but will only be briefed if questions arise.

Effect of pH in the deprotonation of dodecanoic acid in salt water



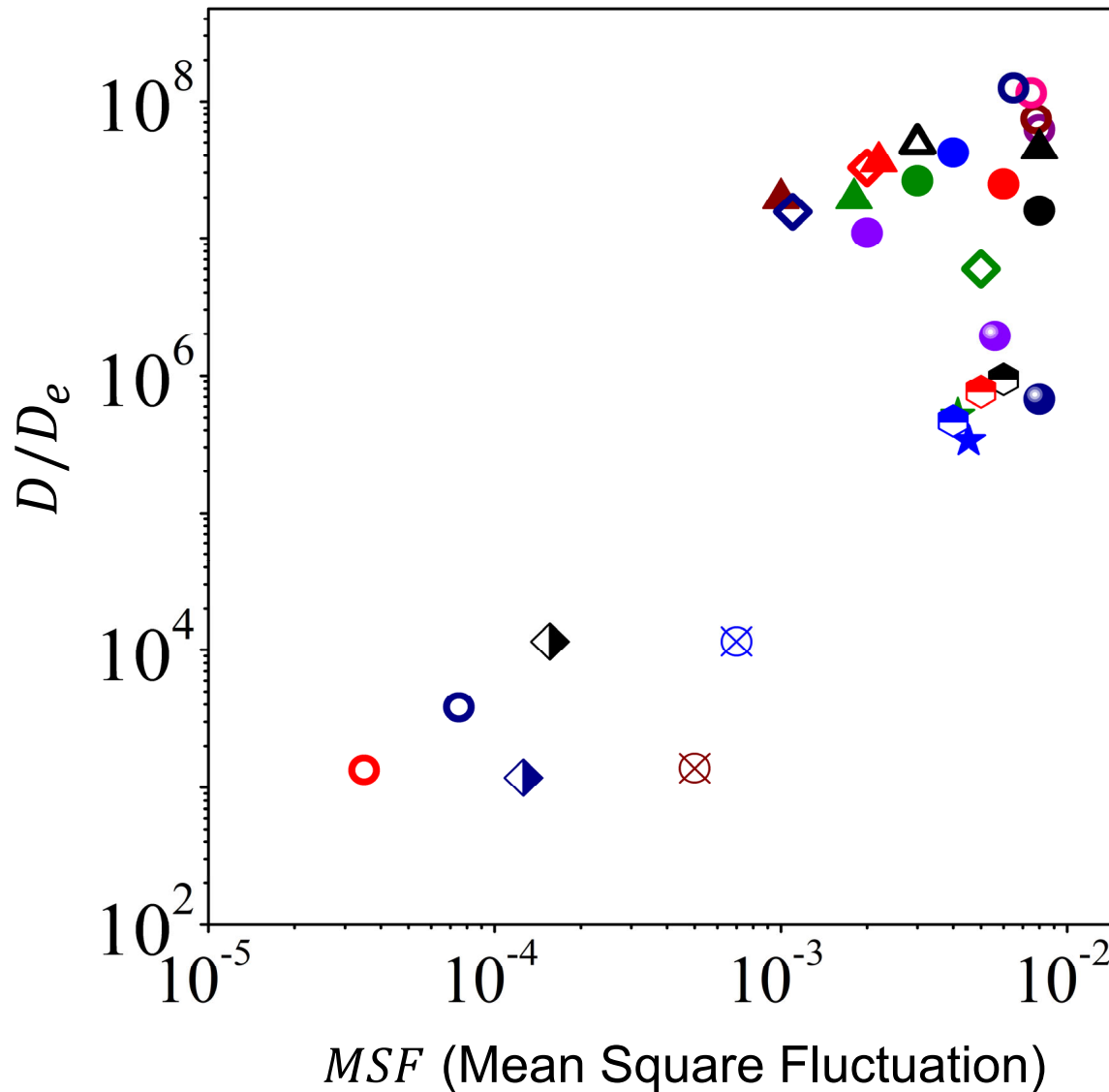
Deprotonation Kinetics of Surfactant

Diesel with 20 ppm PTBS /100 ppm of DDA in salt water



No hydration even after 2 hr.

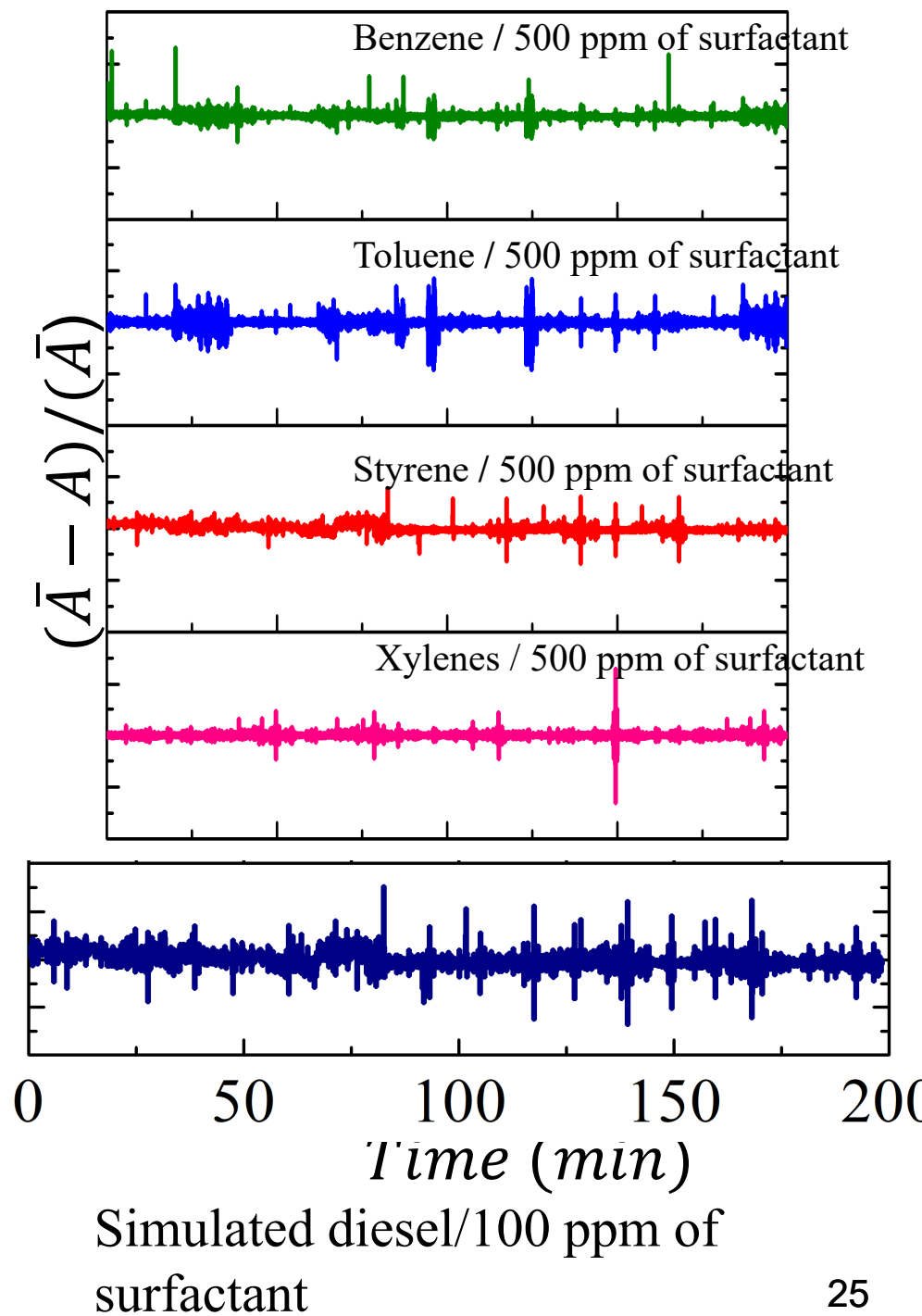
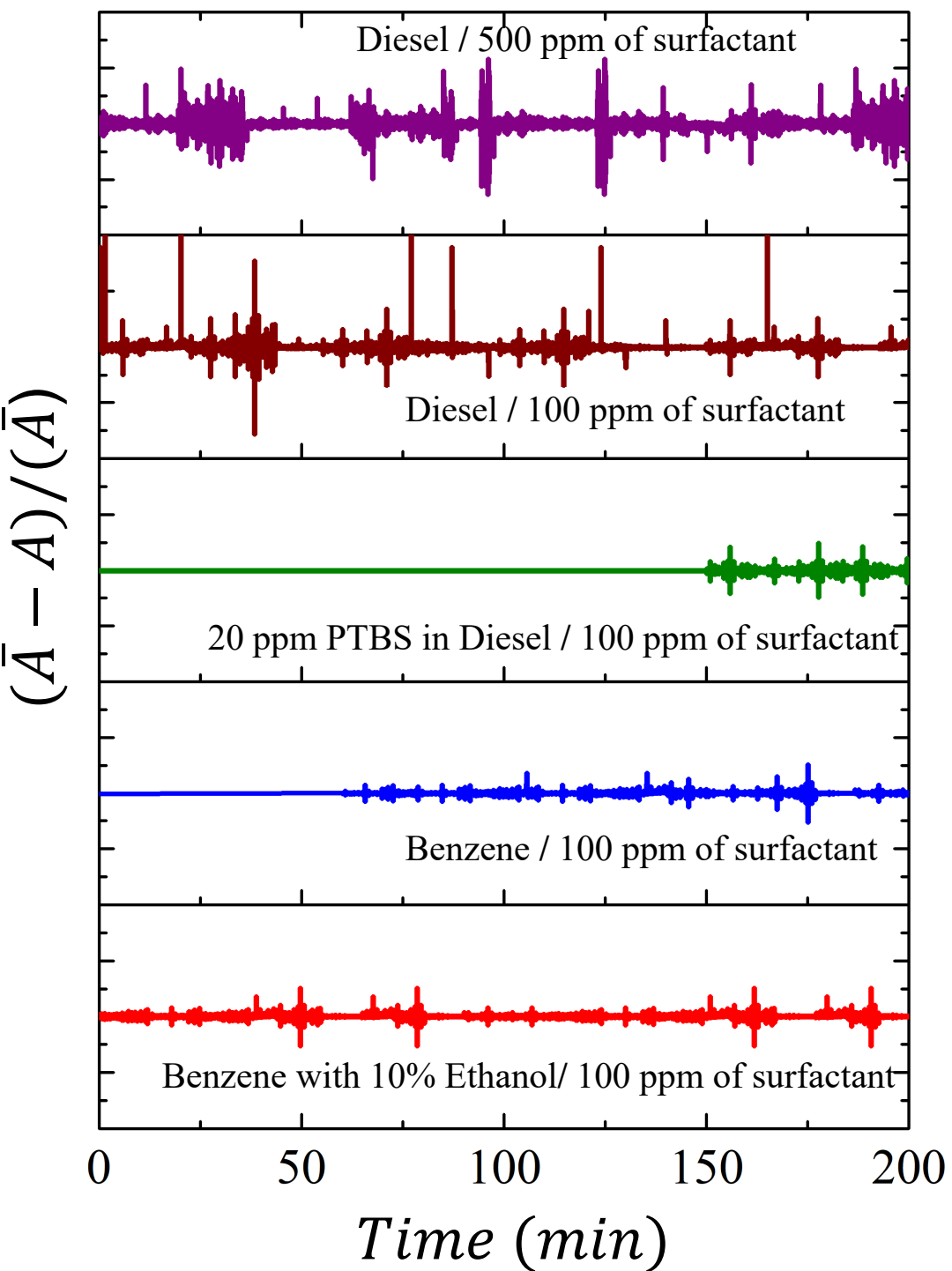
emulsion droplets diffuse away from the interface, which are much faster than the Stokes-Einstein diffusion.



- Diesel/500ppm surfactant in salt water
- Diesel/300ppm surfactant in salt water
- Diesel/200ppm surfactant in salt water
- Diesel/100ppm surfactant in salt water
- Diesel/50ppm surfactant in salt water
- Diesel + 20 ppm PTBS/100 ppm surfactant in salt water
- Diesel + 40 ppm PTBS/100 ppm surfactant in salt water
- Diesel + 20 ppm PTBS/500ppm surfactant in salt water
- Diesel + 40 ppm PTBS/500ppm surfactant in salt water
- Diesel + 80 ppm PTBS/500ppm surfactant in salt water
- Diesel + 100 ppm PTBS/500ppm surfactant in salt water
- ▲ Benzene / 500 ppm surfactant in salt water
- ▲ Toluene / 500 ppm surfactant in salt water
- ▲ Styrene / 500 ppm surfactant in salt water
- ▲ Xylenes / 500 ppm surfactant in salt water
- ◇ octane/500 ppm surfactant in salt water
- ◇ Decane/500 ppm surfactant in salt water
- ◇ Dodecane/500 ppm surfactant in salt water
- ▲ Benzene/100 ppm surfactant in salt water
- ★ Cyclohexane / 100 ppm surfactant in salt water
- ★ Cyclohexane + Dodecane/ 100 ppm surfactant in salt water
- ⊗ Diesel / 20 ppm PAM in 100 ppm of surfactant in salt water
- ⊗ Diesel / 40 ppm PAM in 100 ppm of surfactant in salt water
- ⊗ Benzene + Toluene/ 100 ppm surfactant in salt water
- ⊗ Benzene + Styrene/ 100ppm surfactant in salt water
- ⊗ Benzene + Xylenes/100 ppm surfactant in salt water
- ⊗ Simulated mixture/100 ppm surfactant in salt water
- ⊗ Equal volume mixture/100 ppm surfactant in salt water
- ▲ Benzene+ 10% Ethanol/100 ppm surfactant in salt water
- ▲ Toluene+ 10% Ethanol/100 ppm surfactant in salt water
- ▲ Styrene+ 10% Ethanol/100 ppm surfactant in salt water
- ▲ Xylenes+ 10% Ethanol/100 ppm surfactant in salt water
- Octane+10% Ethanol/100 ppm surfactant in salt water
- Decane+ 10% Ethanol/100 ppm surfactant in salt water
- Dodecane+10% Ethanol/100 ppm surfactant in salt water
- ◇ Dodecane+10% Cyclohexane/20 ppm PAM in 100 ppm surfactant in salt water
- ◇ Dodecane+10% Cyclohexane/40 ppm PAM in 100 ppm surfactant in salt water
- ◇ Dodecane+10% Cyclohexane+20 ppm PTBS/100 ppm surfactant in salt water
- ◇ Dodecane+10% Cyclohexane+40 ppm PTBS/100 ppm surfactant in salt water
- ◇ Dodecane/100 ppm surfactant in salt water
- ◇ Decane/100 ppm surfactant in salt water
- ◇ Octane/100 ppm surfactant in salt water
- Toluene/100 ppm surfactant in salt water
- Styrene/100 ppm surfactant in salt water
- Xylenes/100 ppm surfactant in salt water

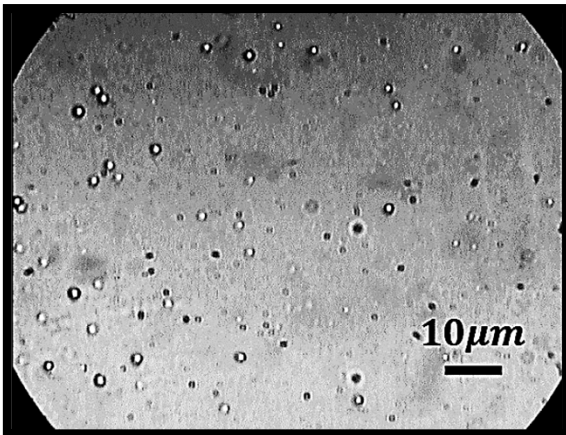
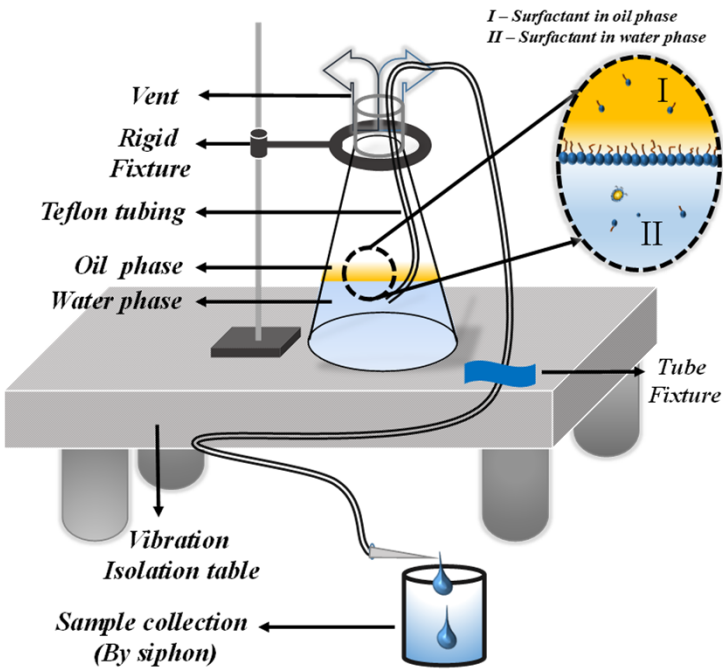
$D_e = k_B T / 6\pi\eta R$ Stokes-Einstein Diffusivity

D Experimental Diffusivity

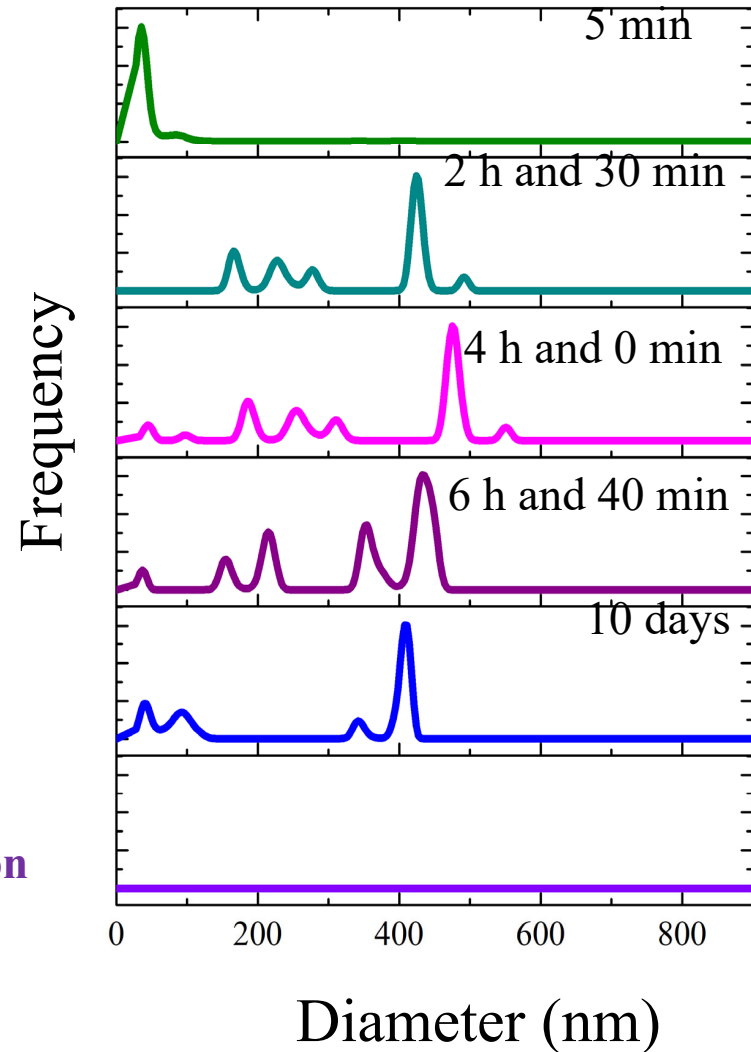


Droplet size from CHDF

Time for emulsification – 5 min



PTBS/ No emulsion formed!!



Social Media Content

- * [https://www.linkedin.com/in/please /manoj-chaudhury-26338089/](https://www.linkedin.com/in/please/manoj-chaudhury-26338089/)
- Appointed to Senior Editor of the ACS Journal *Langmuir*
- We will provide more information about research accomplishments after the manuscript is submitted

Publications

- **Thermodynamic and Kinetic Pathways to Agitated and Spontaneous Emulsification**

Monicka Kullappan and Manoj K. Chaudhury

Langmuir 2020, 36, 34, 10218–10237

Publication Date: August 6, 2020

- **Intricacies of spontaneous emulsification**

Monicka Kullappan, Wes Patel and Manoj K. Chaudhury

(manuscript under preparation)

Editorships

- ❑ ACS renewed my Senior Editorship to *Langmuir*
- ❑ Associate Editor of *Biointerfaces*
- ❑ Editorial Board Member of *Surface Innovations* and *Droplet* (A new journal/ Wiley to be published in 2022)