

Understanding Shipboard Oil/Water Emulsions Using Macro- and Micro-scale Flows

WP18-1031

Cari Dutcher
University of Minnesota

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14. ABSTRACT This project directly addresses the objectives of the statement of Need (SON), including the "fundamental knowledge base" of the "generation, stabilization and worsening" of shipboard oil/water emulsion. This work explores the factors including "shear/mixing, salinity, interfacial tension, and water/oil/surfactant ratios" that influences the emulsion dynamics at both micro- and macro- scale.						
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Project Team

- Cari Dutcher (PI, University of Minnesota)
- Yun Chen (Postdoc, University of Minnesota)
- Thomas Neumiller (Graduate student, University of Minnesota)
- Vishal Panwar (Graduate student, University of Minnesota)



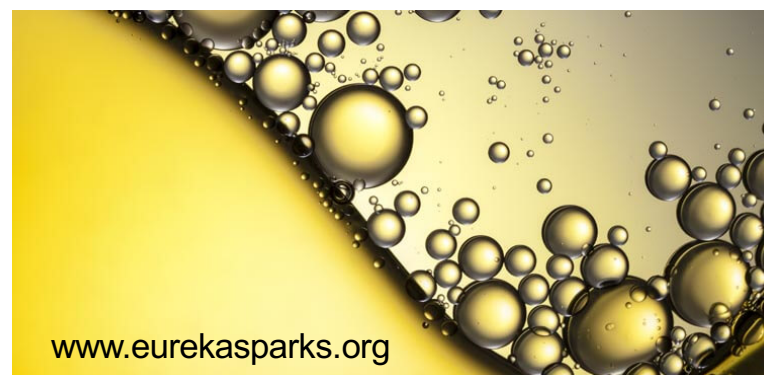
Background

- This project was initiated in 2018
- This project directly addresses the objectives of the statement of Need (SON), including the "fundamental knowledge base" of the "generation, stabilization and worsening" of shipboard oil/water emulsion.
- This work explores the factors including "shear/mixing, salinity, interfacial tension, and water/oil/surfactant ratios" that influences the emulsion dynamics at both micro- and macro- scale.

Technical Objective



Shipboard water must be < 15ppm oil to be discharged overboard

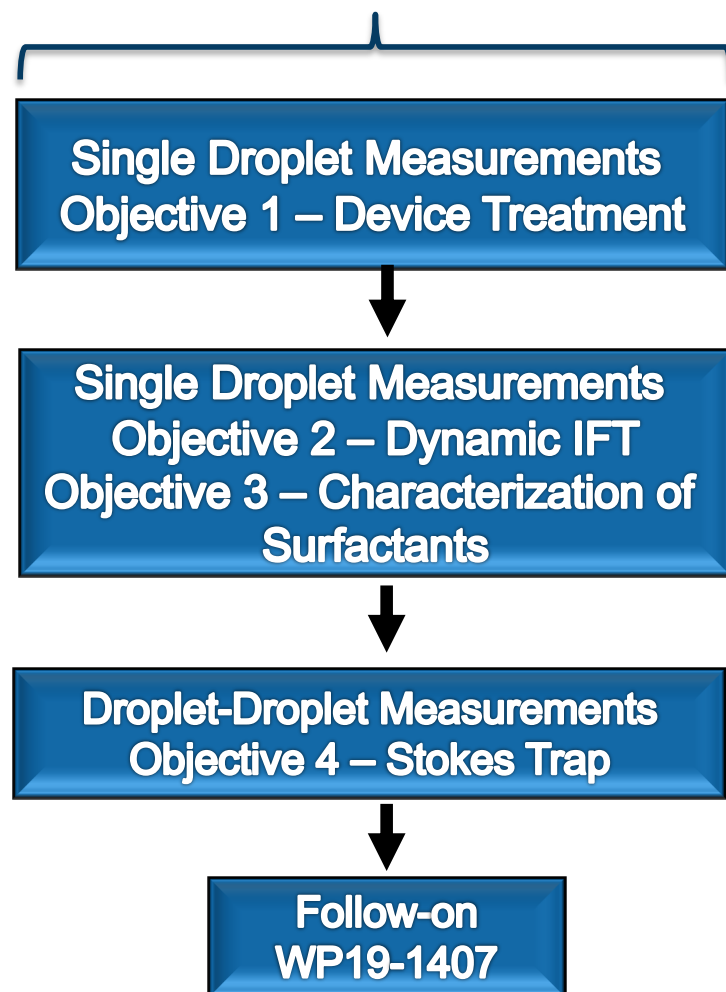


Bilge water is a complex emulsion with oils, fuels, solids, soaps, and solvents

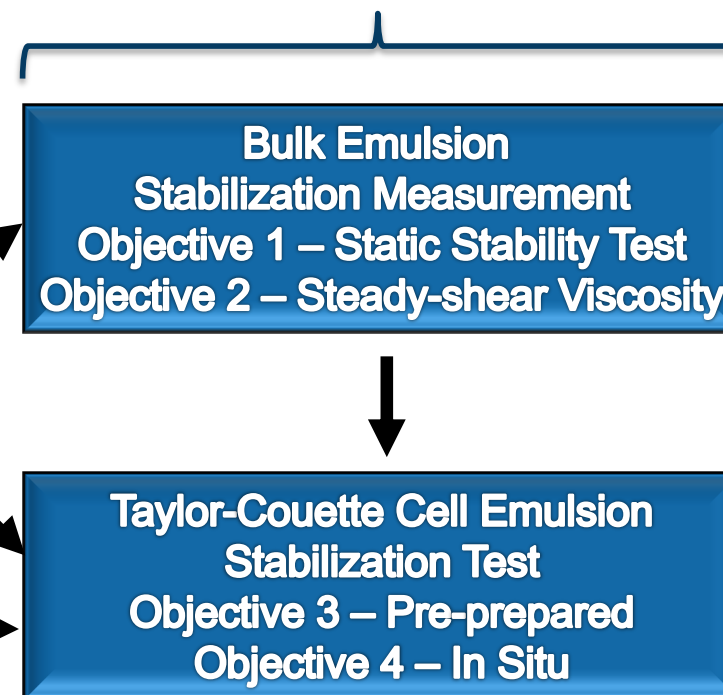
- Provide an understanding of the generation, stabilization, and worsening of shipboard oil/water emulsions in the presence of complex hydrodynamic fields with varied chemical conditions.
- Explore emulsion governing factors, including shear/mixing, interfacial tension, water/oil/surfactant ratios, salinity, and size distribution, in complementary macro- and micro-scale tasks.

Technical Approach

Task 1: Microscale Droplet using Microfluidics



Task 2: Macroscale Taylor-Couette Flows



Results-Task 1

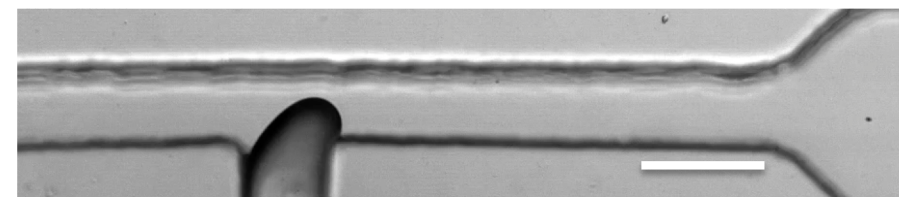
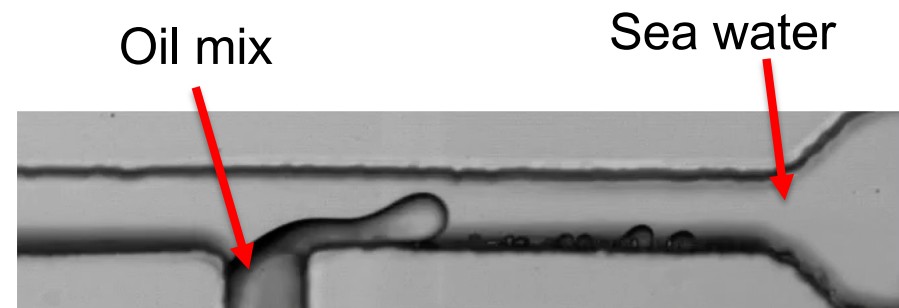
Objective 1 Surface Treatment of Microfluidic Devices



Method 1: Device is treated in 20 W plasma for 15 min prior to use.

Method 2: Device is treated in 100 W plasma, with high continuous oxygen flow, for 10 min, and is stored in DI water under vacuum for 7 days prior to use.

Hydrophilic Treatment of PDMS Micro Device for Oil-in-water



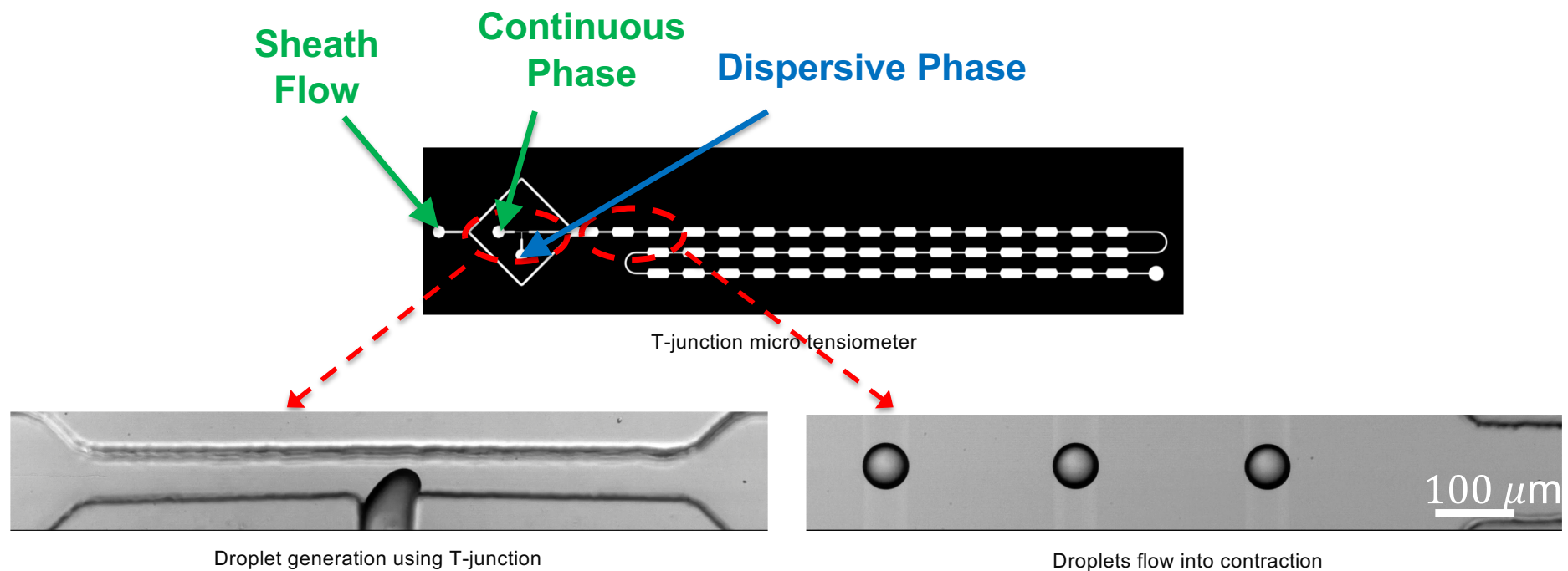
SERDP oil mix droplet generated in sea water
(Scale bar is 100 μm)

Key Result

- Successful generation of microscale oil-in-water droplets for IFT measurements.

Results-Task 1

Objective 2 Dynamic IFT of Microscale Droplet using Microfluidics



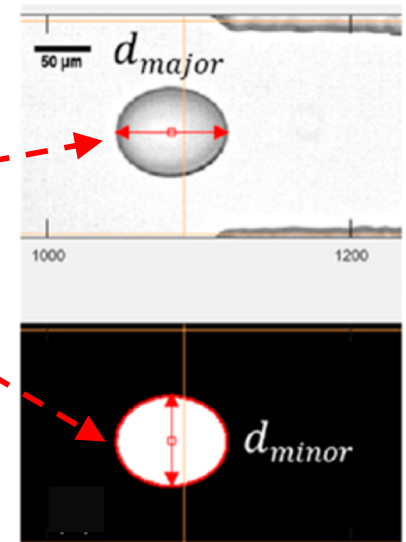
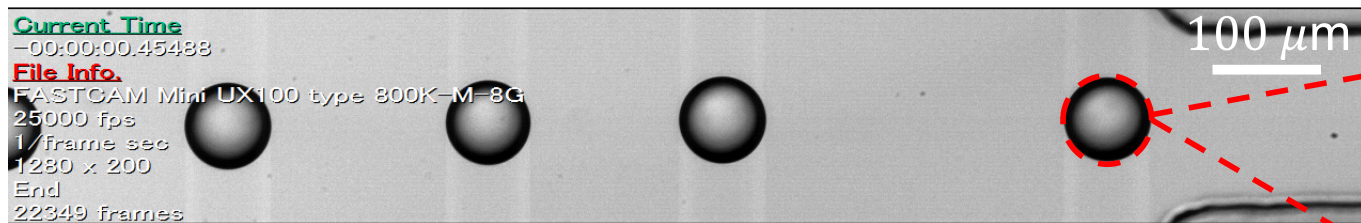
Motivation

- Micrometer sized droplets are **particularly challenging to separate in bilgewater.**
- Interfacial Tension (IFT) is directly related to how easy it is to coalesce/cream and separate oil from water.

Chen & Dutcher, Soft Matter (2020)

Results-Task 1

Objective 2 Dynamic IFT of Microscale Droplet using Microfluidics



→ x Chen & Dutcher, Soft Matter (2020)

$$D(x) = \frac{d_{major}(x) - d_{minor}(x)}{d_{major}(x) + d_{minor}(x)}$$

Deforming force
from the flow

Material change
in deformation

Restoring force from
interfacial tension

$$\alpha \eta_c \left(\frac{5}{2\hat{\eta} + 3} \dot{\epsilon}(x) - u(x) \frac{\partial D(x)}{\partial x} \right) = \gamma \frac{D(x)}{a_0}$$

(G. I. Taylor 1934, Hudson et. al 2005)

Interfacial Tension (IFT)

a_0 : equilibrium droplet radius

u : velocity of droplet

$\dot{\epsilon}$: extension rate ($\dot{\epsilon} = du/dx$)

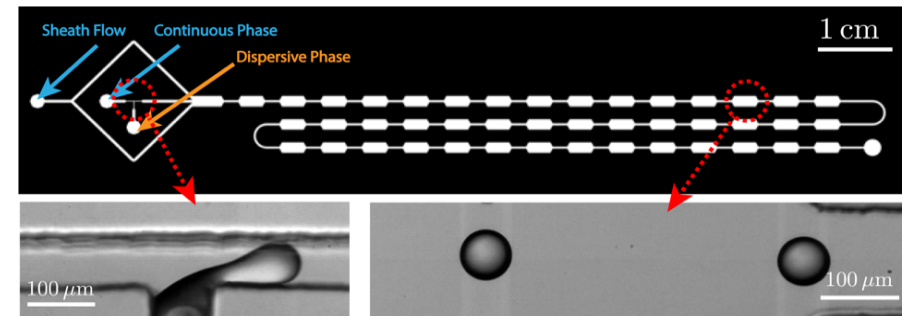
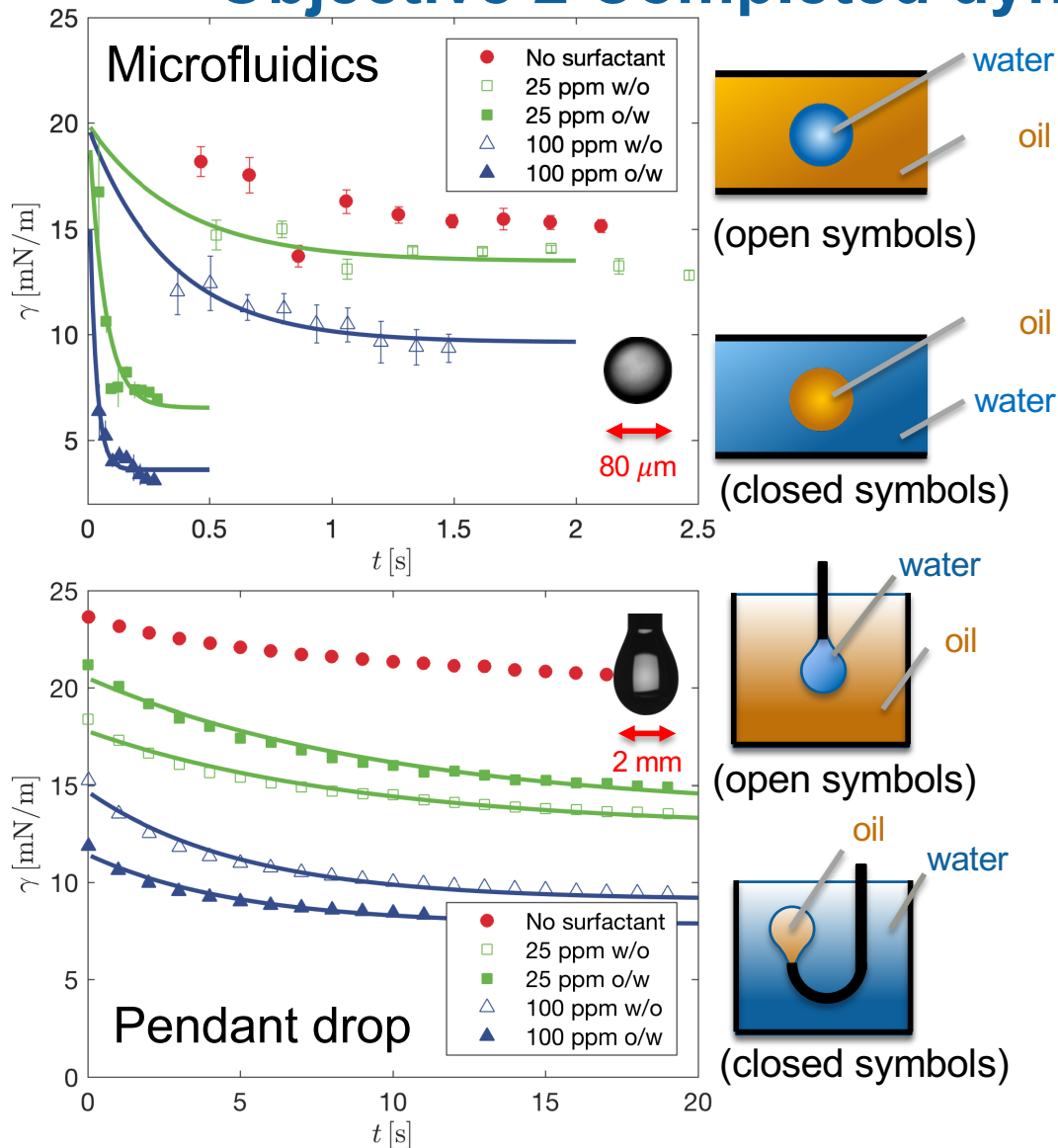
$$\alpha = \frac{(2\hat{\eta}+3)(19\hat{\eta}+16)}{40(\hat{\eta}+1)} \quad \hat{\eta} = \eta_d/\eta_c$$

η_d : viscosity of dispersive phase

η_c : viscosity of continuous phase

Task 1 Results

Objective 2 Completed dynamic IFT experiments



Key Results:

- Decay in IFT of microscale droplets much faster than macroscale droplets (i.e., microscale droplets are more stable)
- Phase does not matter for millimeter drops. Large drops area always diffusion-limited (~15 s for both phases).
- Phase does matter for microscale droplets. Both diffusion and adsorption timescales important (0.065 s for outer phase; 0.38 s for inner phase)

Results-Task 1

Objective 3 Characterization of Surfactant

Max surfactant surface coverage, Γ_∞

(Close to CMC)

$$\Gamma_\infty = -\frac{1}{nRT} \left(\frac{\partial \gamma}{\partial \ln C} \right)_T \quad (\text{Gibbs Equation})$$

Equilibrium constant, κ

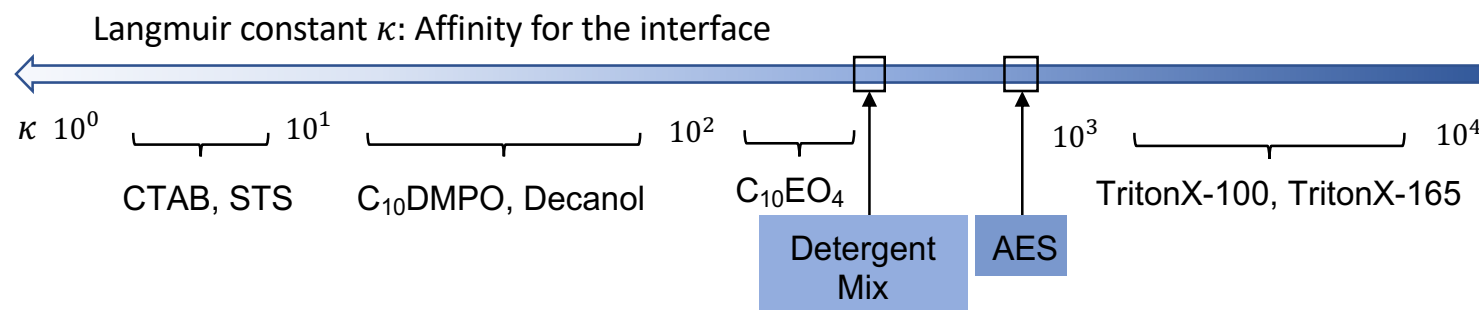
$$\frac{\Gamma_{eq}}{\Gamma_\infty} = \frac{\kappa C}{1 + \kappa C} \quad \gamma = \gamma_0 + nRT\Gamma_\infty \ln \left(1 - \frac{\kappa C}{\kappa C + 1} \right) \quad (\text{Langmuir Isotherm})$$

$$\frac{\Gamma_{eq}}{\Gamma_\infty} = \frac{\kappa C}{e^{K\Gamma_{eq}/\Gamma_\infty} + \kappa C} \quad (\text{Frumkin Isotherm, for surfactant interaction})$$

Surfactant	Detergent Mix	AES
M_w (g/mol)	300	420
Γ_∞ (mol/m ²)	1.52×10^{-6}	2.53×10^{-6}
κ (m ³ /mol)	380	904
CMC (mol/m ³)	1.77×10^{-1} (50 ppm)	6.25×10^{-2} (25 ppm)
$D_{C < CMC}$ (m ² /s)	3.2×10^{-11}	1.9×10^{-10}

Surfactant Diffusivity, D

$$\gamma - \gamma_{eq} \sim \frac{RT\Gamma_{eq}^2}{C} \sqrt{\frac{\pi}{4Dt}}$$



Results-Task 1

Objective 3 Characterization of Surfactant

Adsorption rate (k_{ads}) and **desorption rate** (k_{des}) from Langmuir's equation

$$\frac{\Gamma(t)}{\Gamma_{\infty}} = \frac{\Gamma_{eq}}{\Gamma_{\infty}} \left(1 - \exp\left(-\frac{t}{\tau}\right) \right)$$

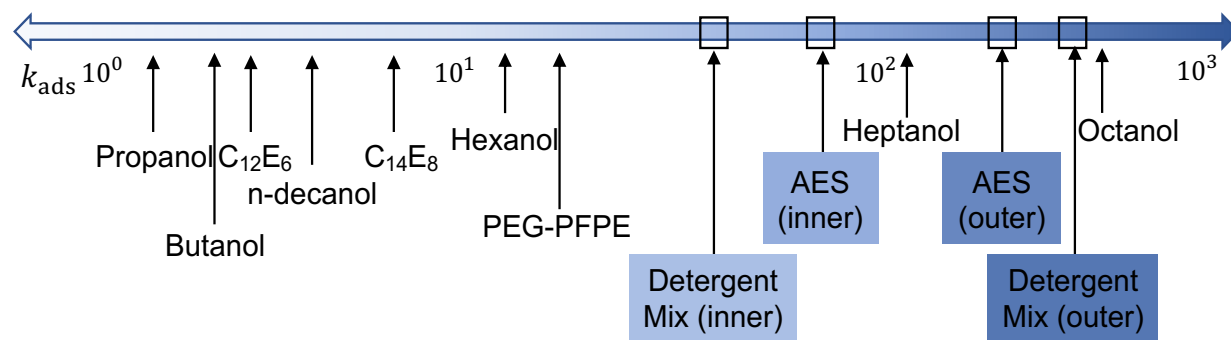
$$\tau = \frac{1}{k_{des}} \frac{1}{1 + \kappa C}$$

$$\kappa = k_{ads}/k_{des}$$

Key Results

- Phase matters: k_{ads} is smaller when the surfactant is inside the drop, suggesting larger energy barrier due to curvature.
- CMC matters: k_{ads} is larger for detergent mix when $C < CMC$.

Surfactant		Detergent Mix		AES	
C (mol/m ³)		0.0887 (25 ppm)	0.354 (100 ppm)	0.025 (10 ppm)	0.25 (100 ppm)
k_{ads} (m ³ /mol · s)	Inner	55	5.6	95	88
k_{des} (1/s)		0.14	0.015	0.11	0.097
k_{ads} (m ³ /mol · s)	Outer	299	96	220	170
k_{des} (1/s)		0.78	0.25	0.24	0.19



Task 1 Results

Objective 3 Characterization of the surfactant cleaners

Surfactant	M_w (g/mol)	CMC (ppm)	Γ_∞ (mol/m ²)	κ (m ³ /mol)	K	D (m ² /s)	k_{ads} (m ³ /mol · s)	k_{des} (s ⁻¹)	Type
Detergent Mix	300	50	1.52×10^{-6}	380	-	3.19×10^{-11}	299.1	0.78	Anionic
AES	420	25	2.53×10^{-6}	904	-	1.9×10^{-10}	220.7	0.24	Anionic
TritonX-100	625	350	1.64×10^{-6}	1.41×10^5	1.152	6.28×10^{-11}	42.548	2.3×10^{-3}	Non-ionic
SDS	288	4500	2.81×10^{-6}	104.98	3.618	2.45×10^{-11}	53.8	2.7	Anionic
Type 1	617	110	1.88×10^{-6}	1.19×10^5	0.3947	1.04×10^{-10}	31.83	4.11×10^{-4}	Non-ionic
Solid Surge	214	420	1.04×10^{-6}	4.04×10^6	0.3587	3.40×10^{-12}	5.59	2.68×10^{-6}	Non-ionic
PRC	293	7300	1.005×10^{-6}	2.10×10^6	1.341	9.50×10^{-14}	1.73	2.80×10^{-6}	Non-ionic + Anionic

Commercial Surfactants



Type 1 Detergent
(MILSPEC: MIL-D-1691)



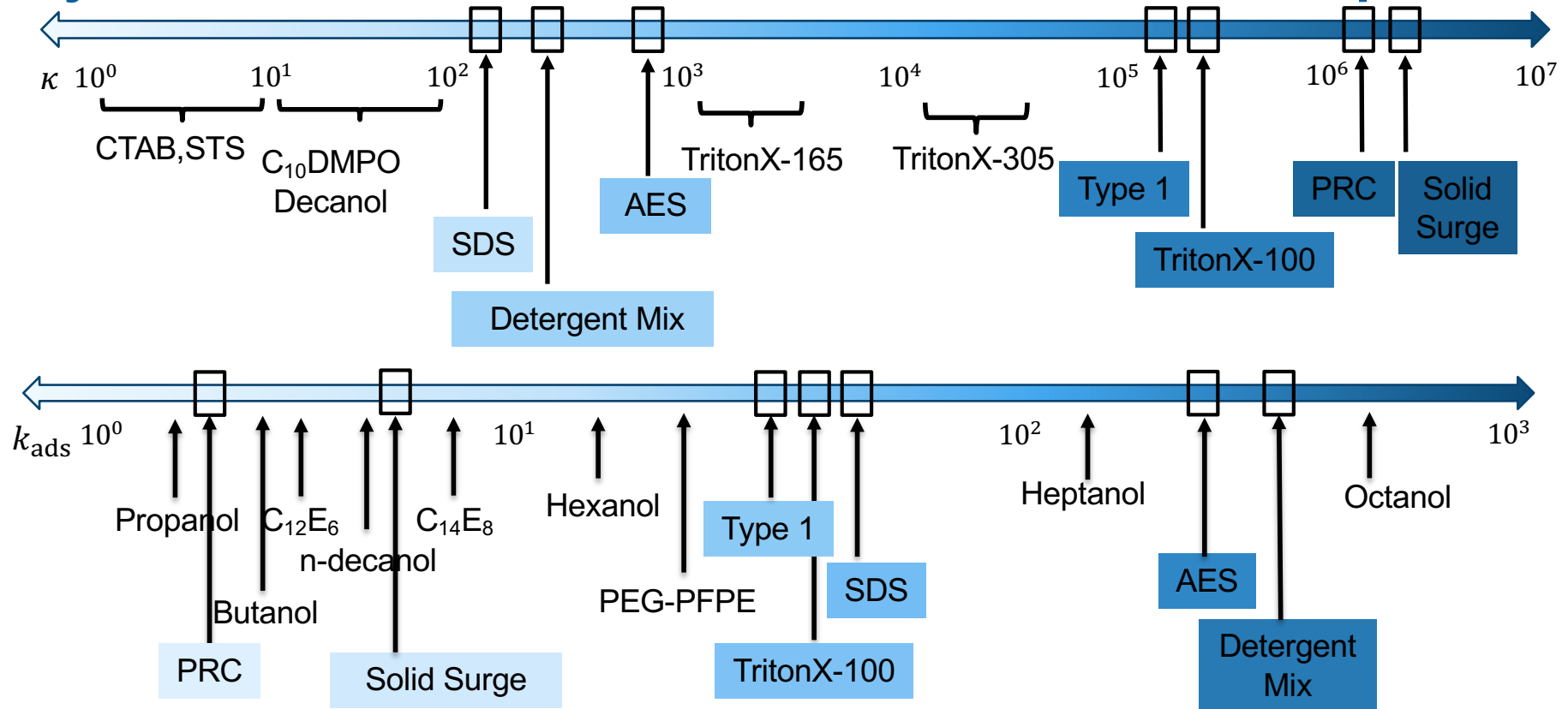
Solid Surge Plus
(Ecolab # 611905)



PRC Deck Cleaner
(Werth Sanitary Supply
1100868)

Task 1 Results

Objective 3 Surfactant characterization in cleaner products

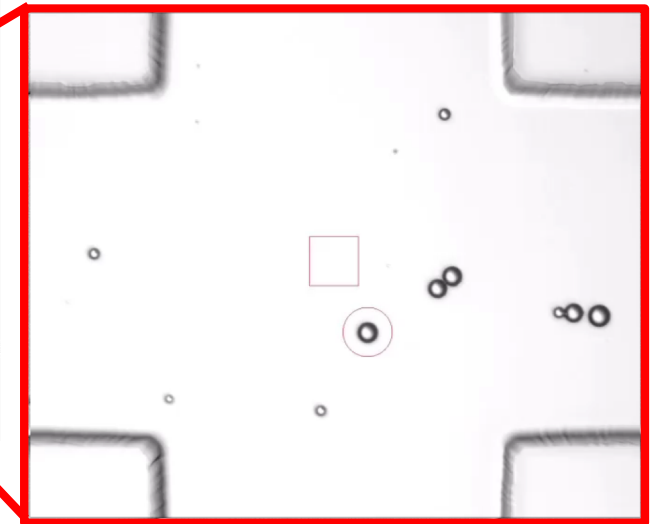
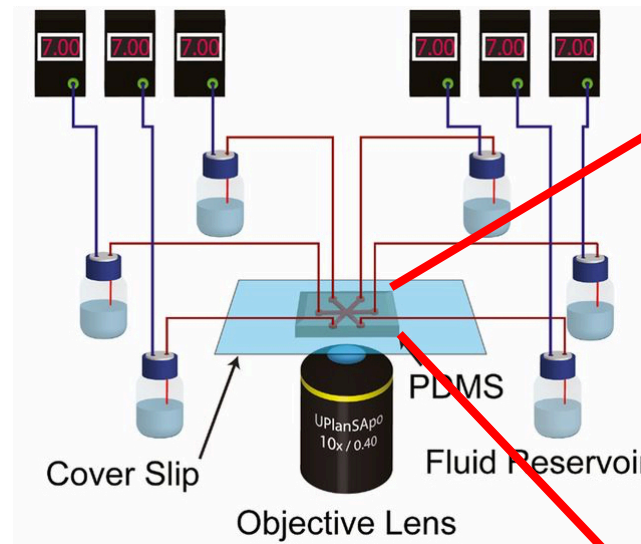
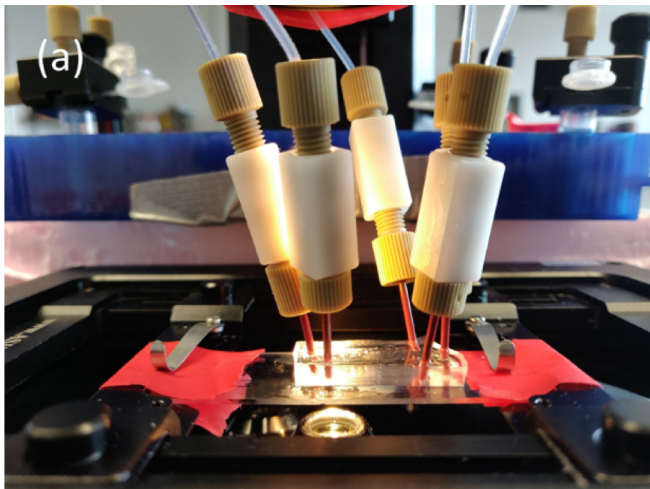


Key Results

- Microfluidic and pendant drop measurements for each systems at varied concentration (CMC and surface coverage), characterized diffusivity, surface affinity and adsorption rate.

Results-Task 1

Objective 4 Droplet Coalescence and Film Drainage Time



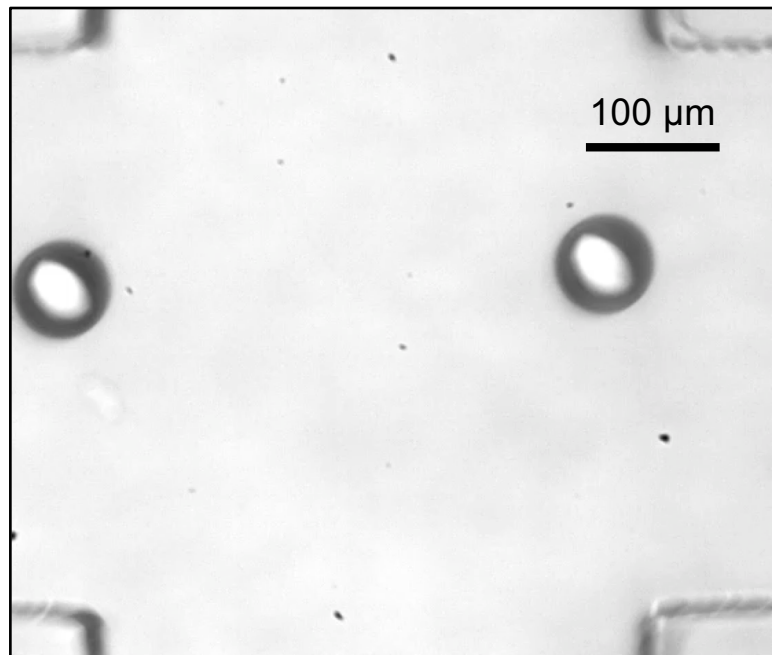
width 400 μm

Advantages

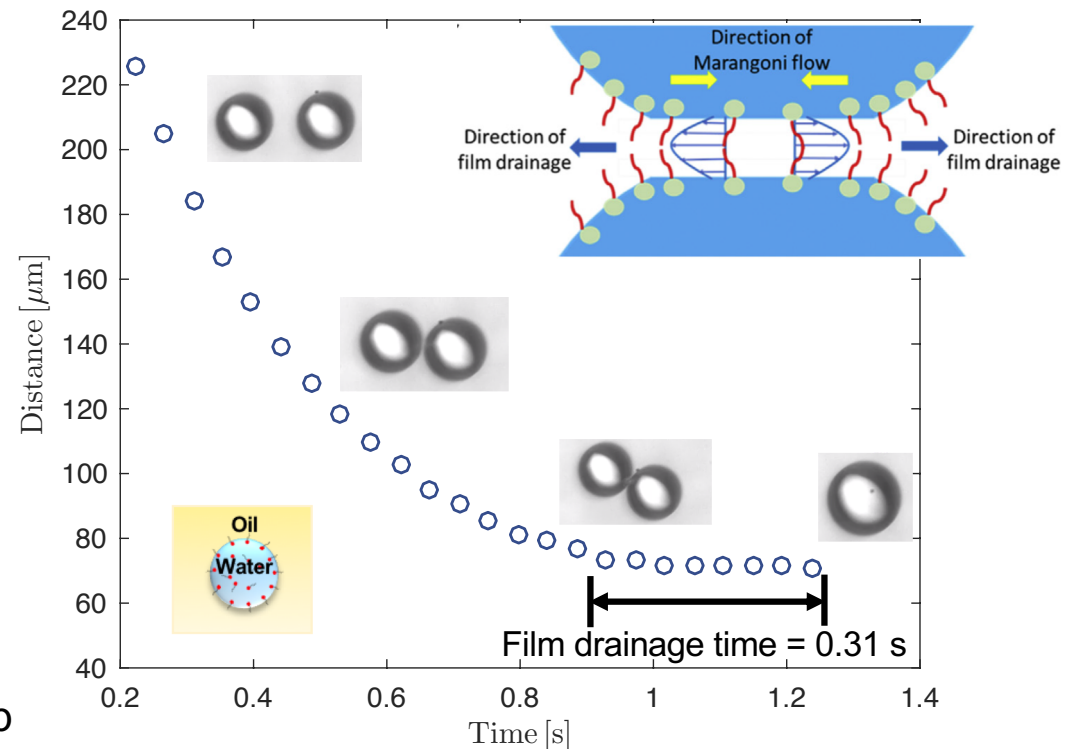
- Micrometer sized droplets can be trapped and manipulated to **directly visualize destabilization processes** such as coalescence and creaming.
- Stokes Trap uses optimization algorithm to automate trapping to desired position (based on Shenoy et al. PNAS 2016).

Results-Task 1

Objective 4 Droplet Coalescence and Film Drainage Time



Droplet coalescing in a 4-channel Stokes trap
(water in mineral oil with 1000 ppm SDS)



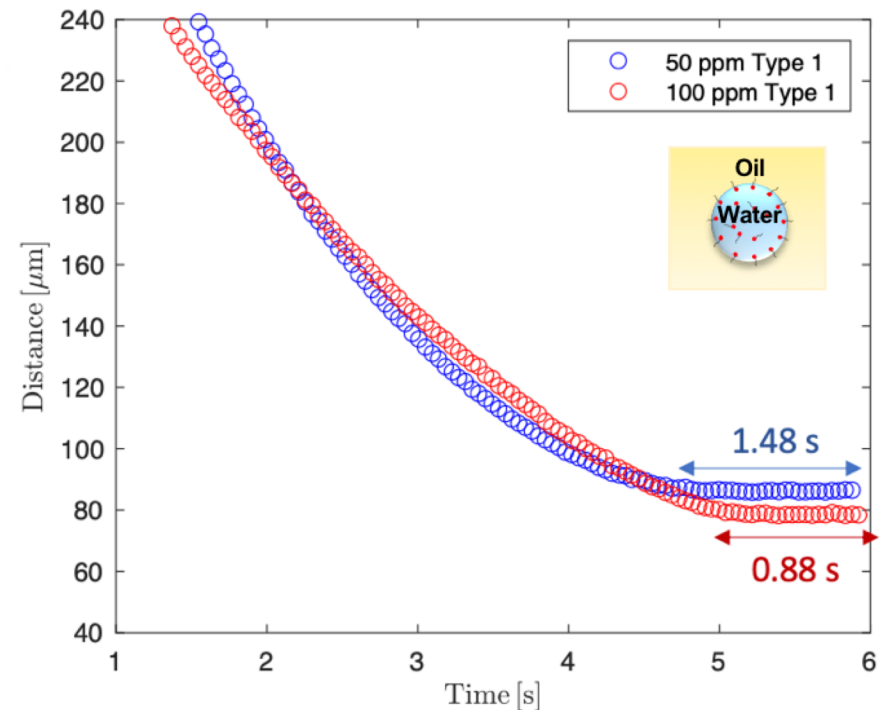
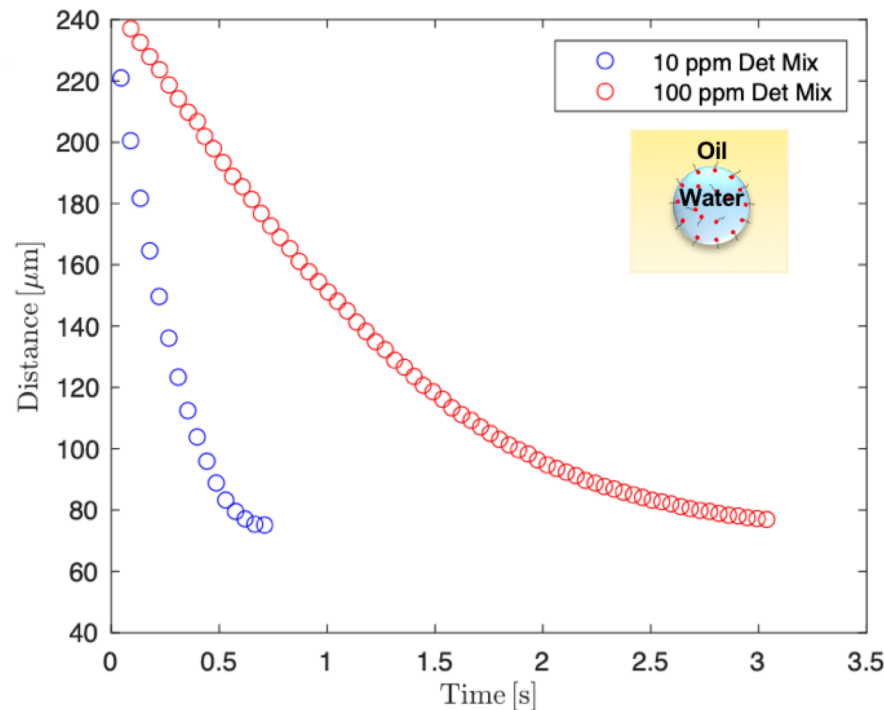
As dispersed phase viscosity ↑
the film drainage time ↑

Key Result

- Coalescence readily observed for water in oil systems, applicable for dry bilge systems.
- Chen, Narayan, Dutcher, Langmuir (2020); Narayan, et al, Current Opinion in Colloid & Interface Science (2020)

Results-Task 1

Objective 4 Droplet Coalescence and Film Drainage Time

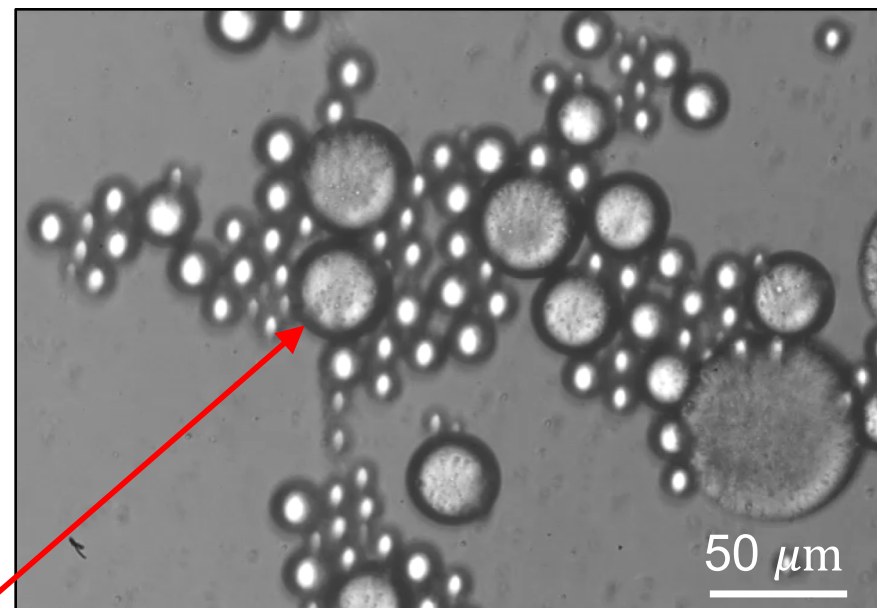
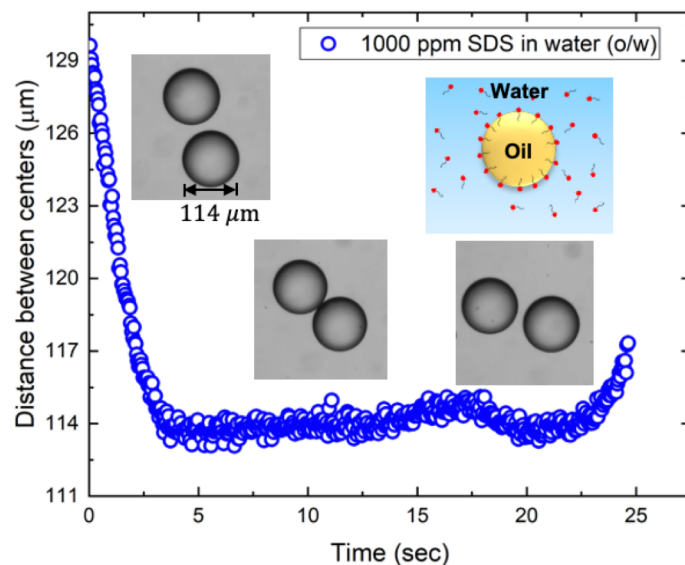


Key Results

- Both cases for distilled water in LMO with 10 ppm and 100 ppm detergent mix in water show immediate coalescence when the droplets are in contact with each other.
- Film drainage time of droplet coalescence for distilled water in LMO with 50 ppm and 100 ppm commercial surfactant Type 1 in water are 1.48 s and 0.88 s, respectively.

Results-Task 1

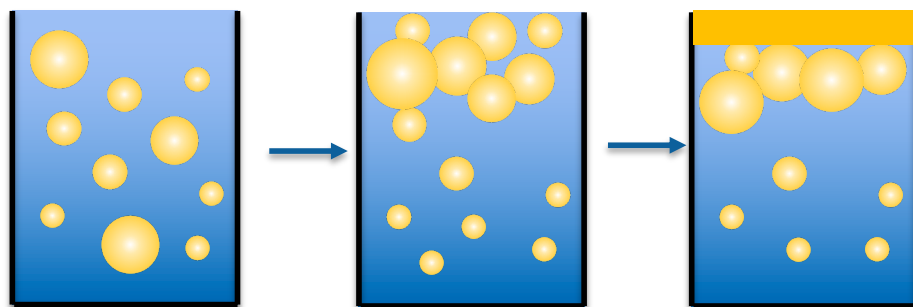
Controlled coalescence and creaming



Creaming of mineral oil droplet in water with 100 ppm detergent mix (5000 fps)

Key Results

- Coalescence of monodispersed droplets difficult for (o/w) systems.
- Creaming at interface more likely for wet bilge systems.

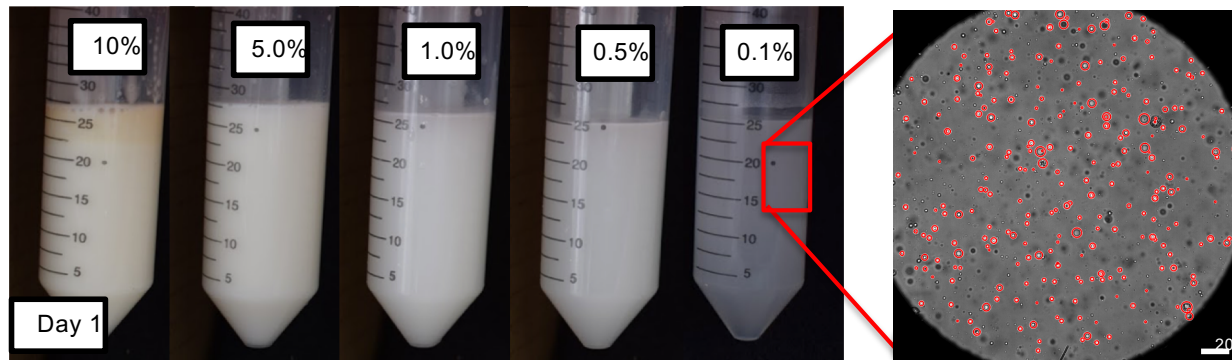


Chen, Narayan, Dutcher, Langmuir (2020)
Narayan, et al, Current Opinion in Colloid & Interface Science (2020)

Results-Task 2

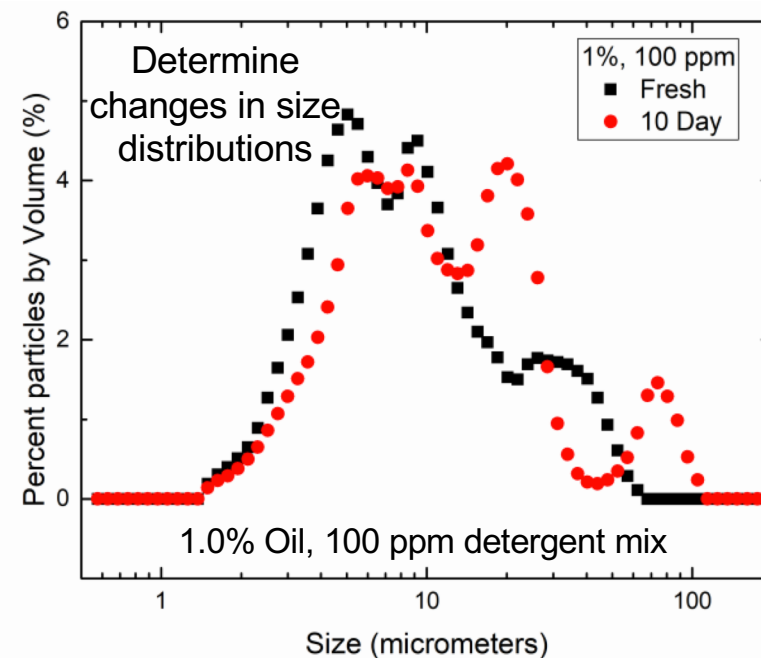
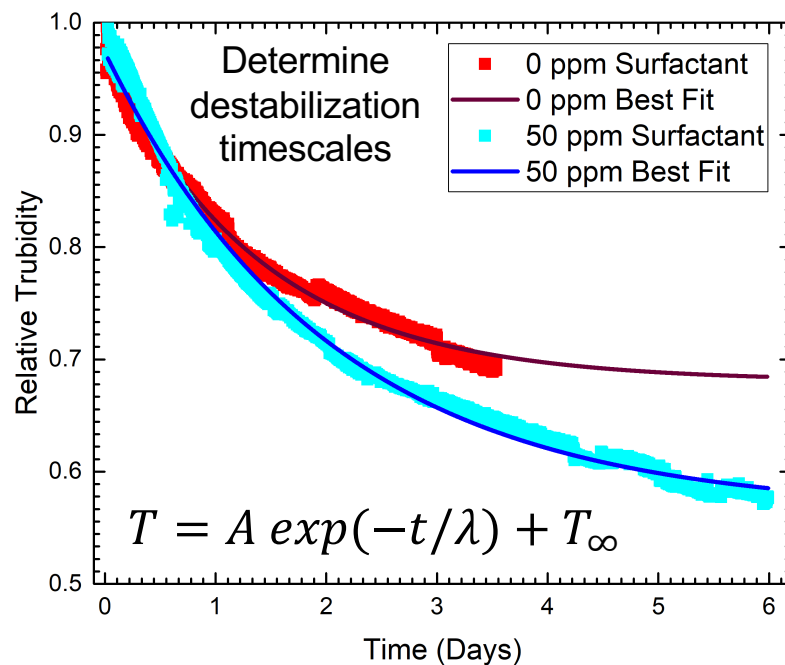
Objective 1 Static Emulsion Stability Test

Stability tests: Phase separation; Turbidity change



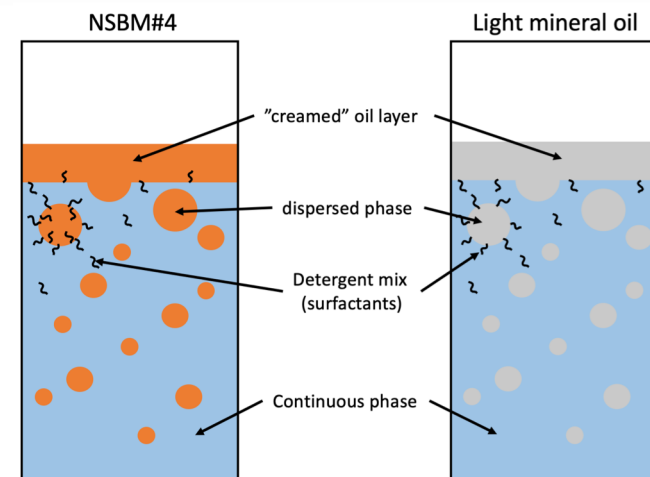
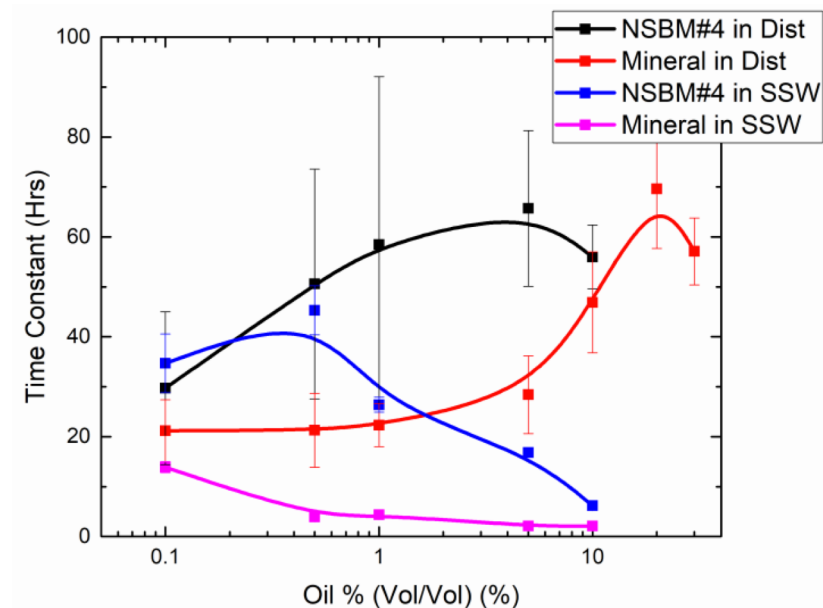
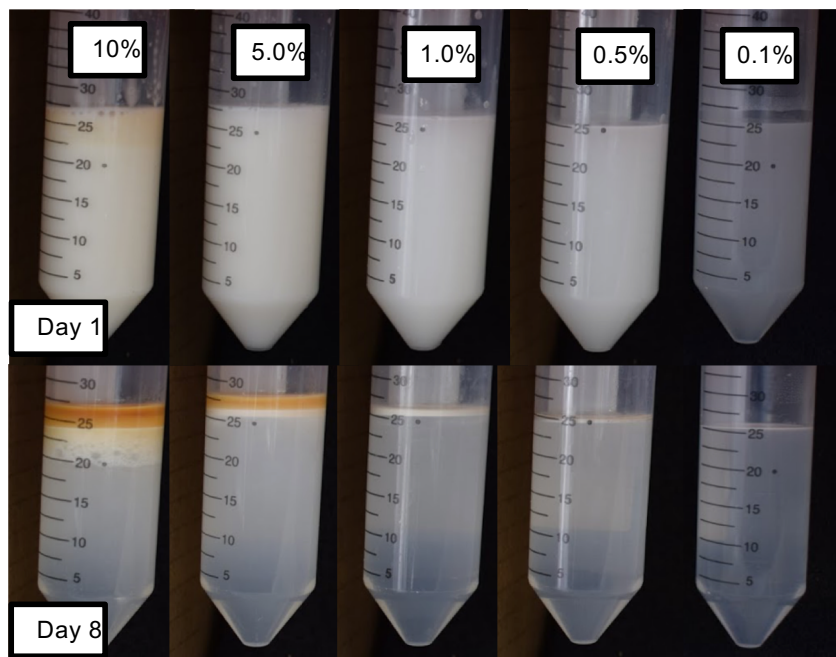
Method

- Observe phase separation and decrease in turbidity with time/shear.
- Characterize bulk stability with changes in turbidity and size distributions.



Results-Task 2

Objective 1 Static Emulsion Stability Test



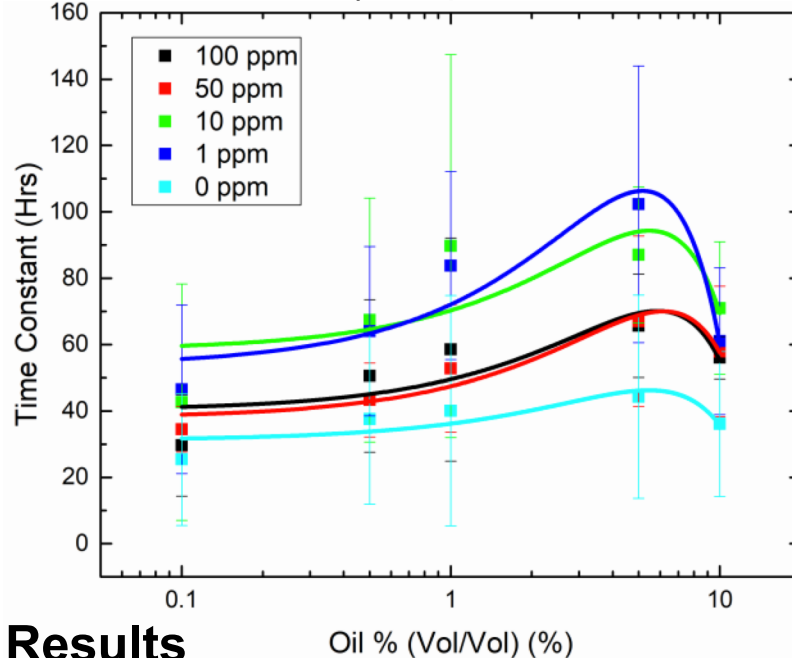
Key Results:

- Performed measurements with varied compositions of SERDP and mineral oils, AES and detergent mixes, and distilled (DI) and salt water.
- Found salt rapidly destabilized the systems, especially with mineral oil.

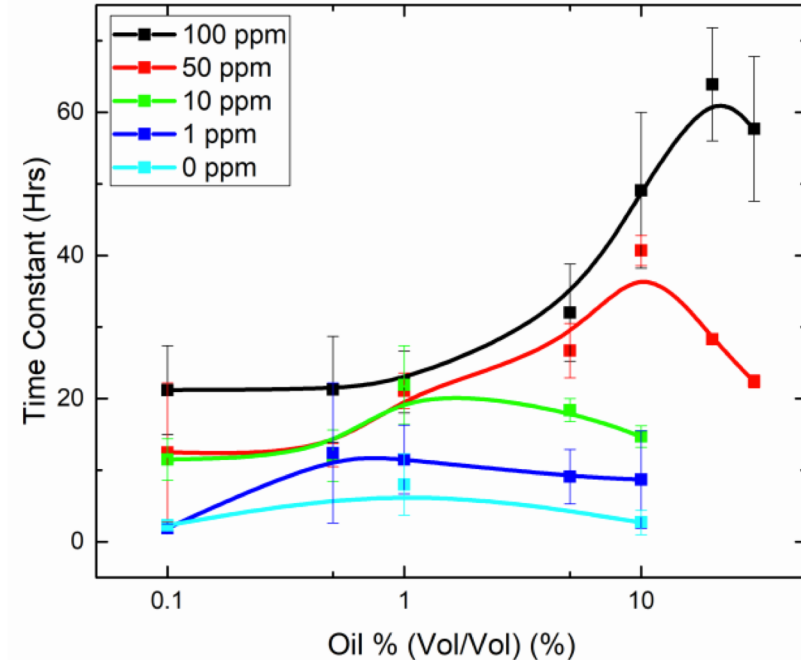
Results-Task 2

Objective 1 Static Emulsion Stability: varied oil content

SERDP oil mix (complex mix w/ surfactant)

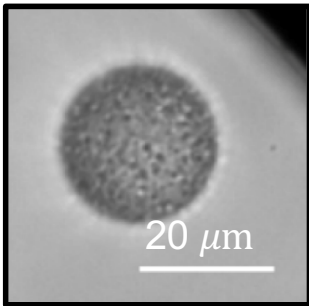


Mineral oil (simple model oil)



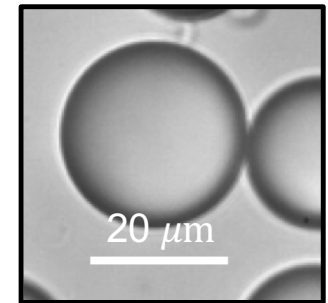
Key Results

- Non-monotonic relationship for both: increase, followed by decrease, in stability.
- “Turnover” point when collision and/or surface-coverage effects dominate.
- “Turnover” point shifts to higher surfactant concentration for mineral oil, indicating surfactant surface coverage plays an especially important role for simple systems.

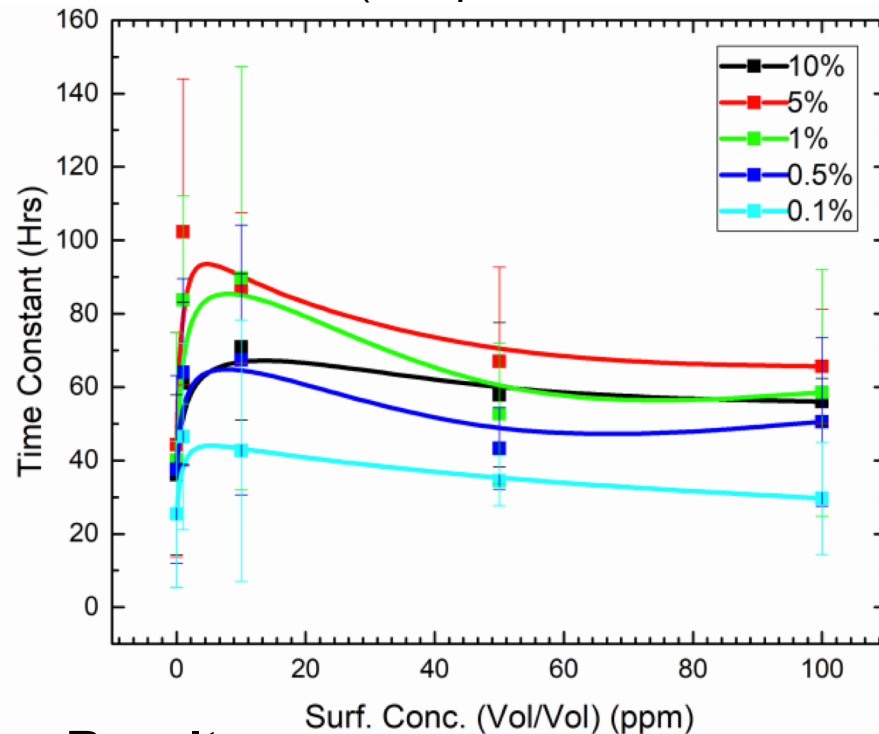


Results-Task 2

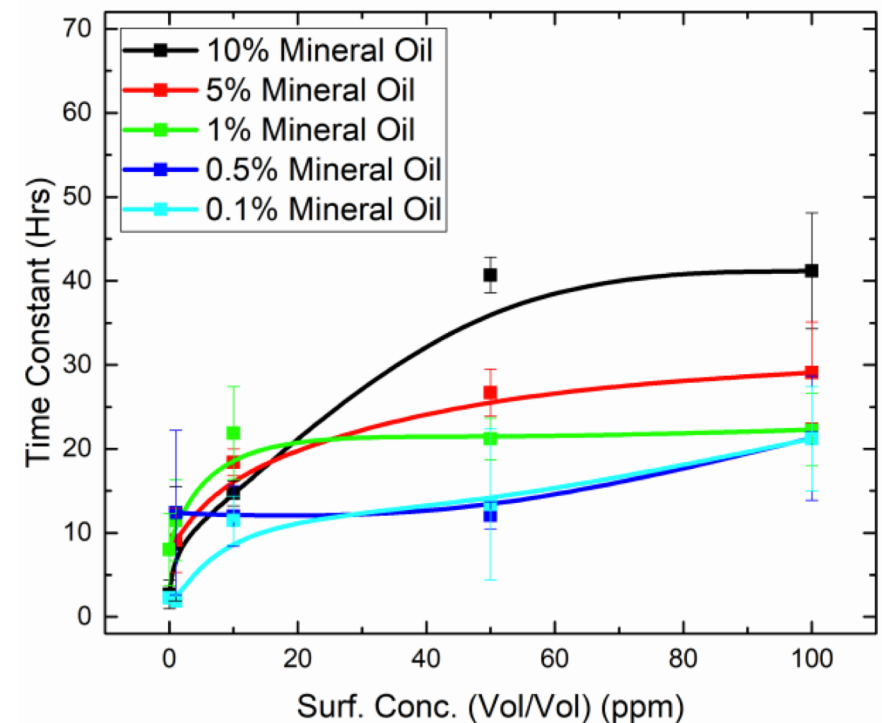
Objective 1 Static Emulsion Stability: varied surfactant content



SERDP oil mix (complex mix w/ surfactant)



Mineral oil (simple model oil)

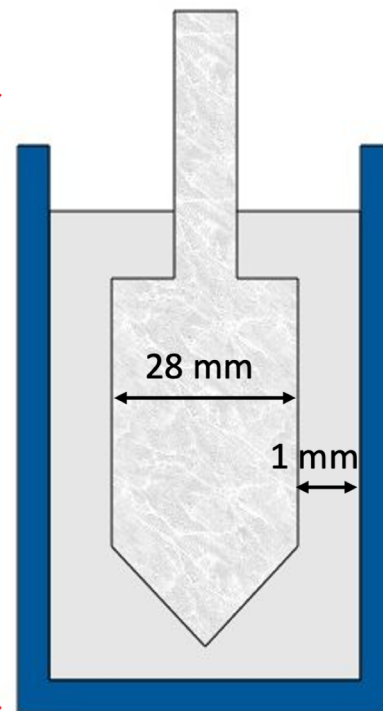
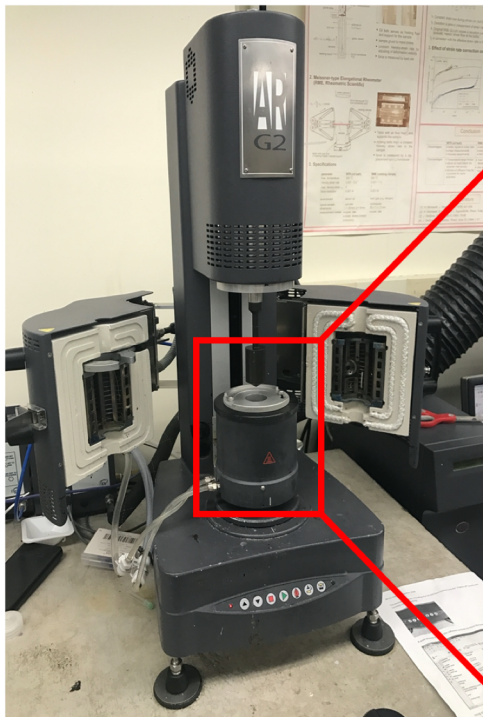


Key Results

- Non-monotonic for the SERDP oil mix, but not for the simple mineral oil systems.
- SERDP oil mix forms spontaneous microemulsions, resulting in oil drops too small to be seen with turbidity measures; collaborating with Purdue University ongoing.
- Narayan et al. Current Opinion Colloidal Interface Science (2020)

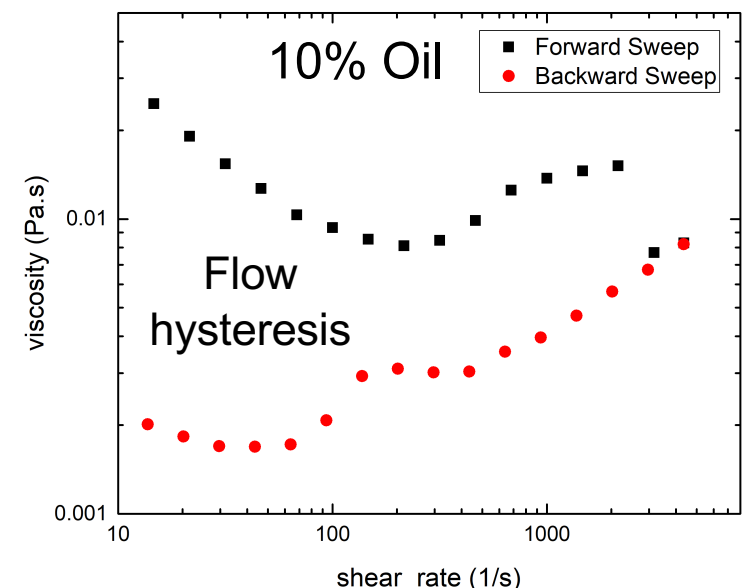
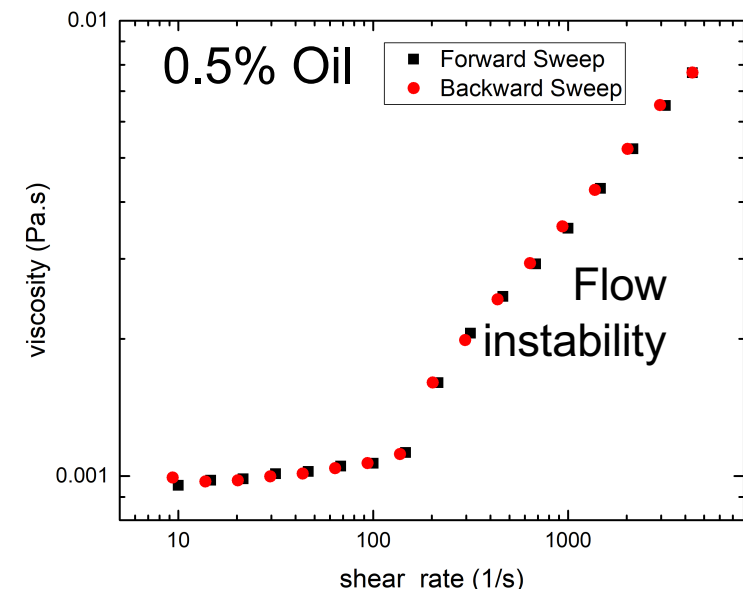
Results-Task 2

Objective 2 Steady-shear Emulsion Viscosity Measurement



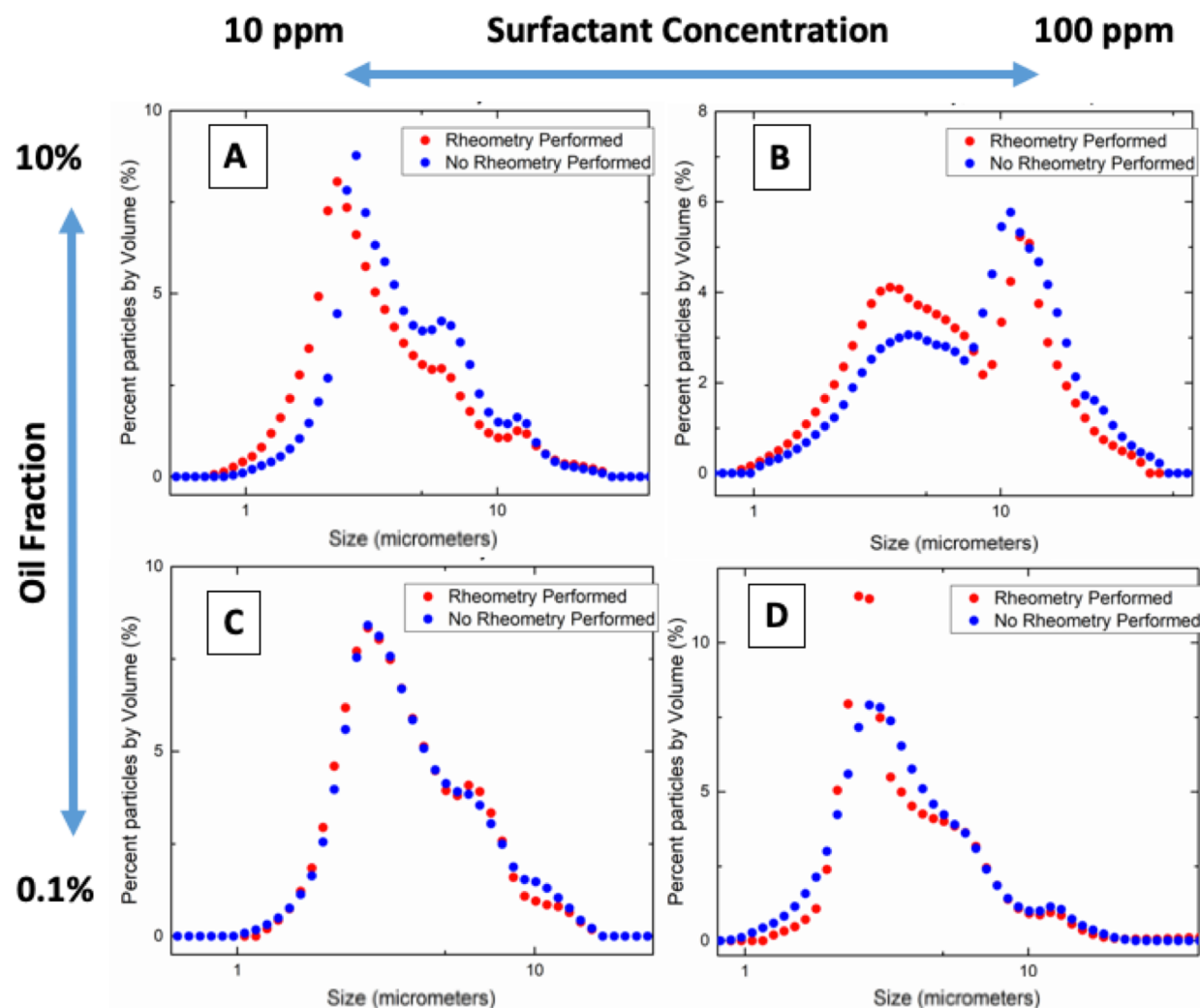
Key Results

- Determined viscosity of the emulsions.
- Regions of constant viscosity are observed for low to moderate shear rates.
- The appearance of shear thickening at high shear rates is due to flow instabilities.



Results-Task 2

Objective 2 Steady-shear Emulsion Viscosity Measurement

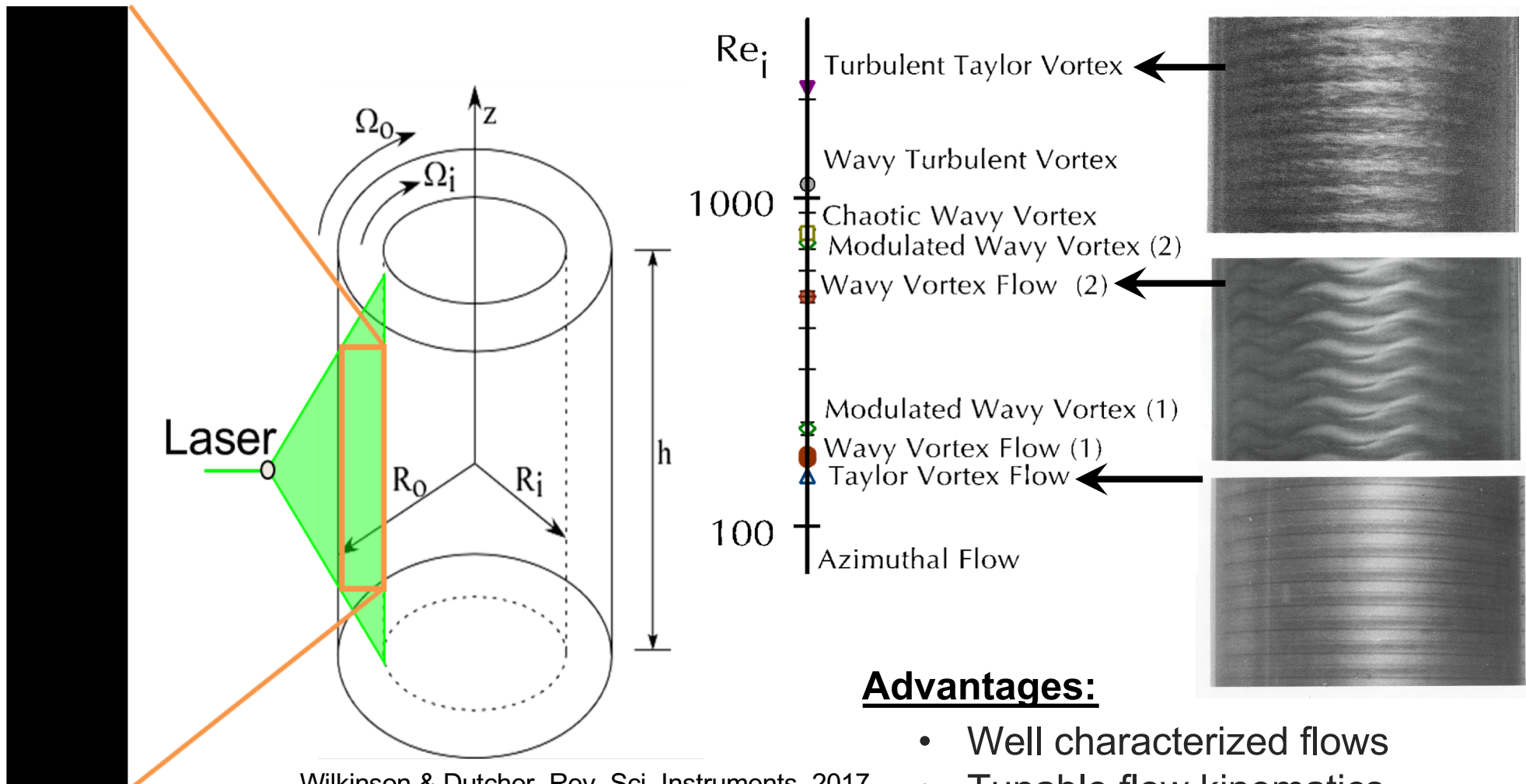


Key Results

- Ran emulsions with SERDP oil mix (from 0.1% to 20%) and mineral oil, with both distilled and salt water
- Shear effect strong at 10% oil, weak below 5%.
- Larger droplets appear to coalesce/cream into oil phase, leaving higher % of small droplets in the system.

Results-Task 2

Objective 3 Pre-prepared Emulsion Stability in TC Flows



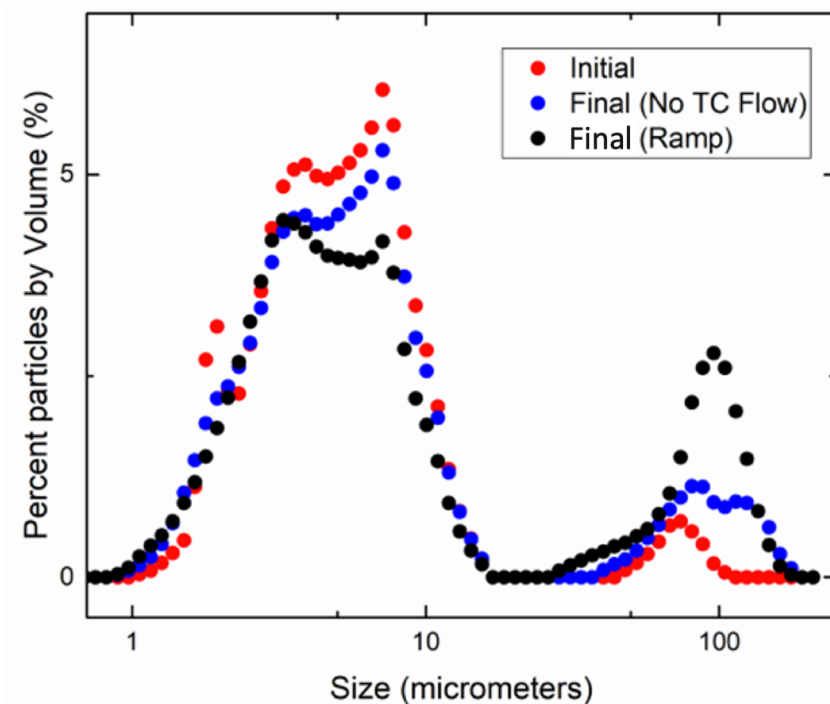
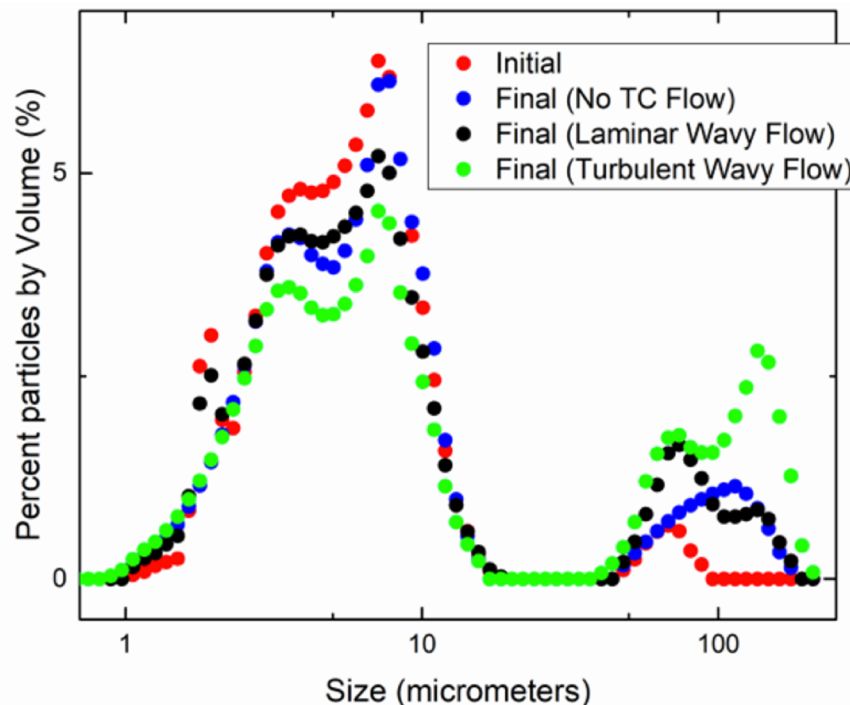
Advantages:

- Well characterized flows
- Tunable flow kinematics
- Direct visualization

Wilkinson & Dutcher, Rev. Sci. Instruments, 2017
 Metaxas, Wilkinson, and Dutcher, Soft Matter, 2018
 Wilkinson and Dutcher, JFM, 2018

Results-Task 2

Objective 3 Pre-prepared Emulsion Stability in TC Flows

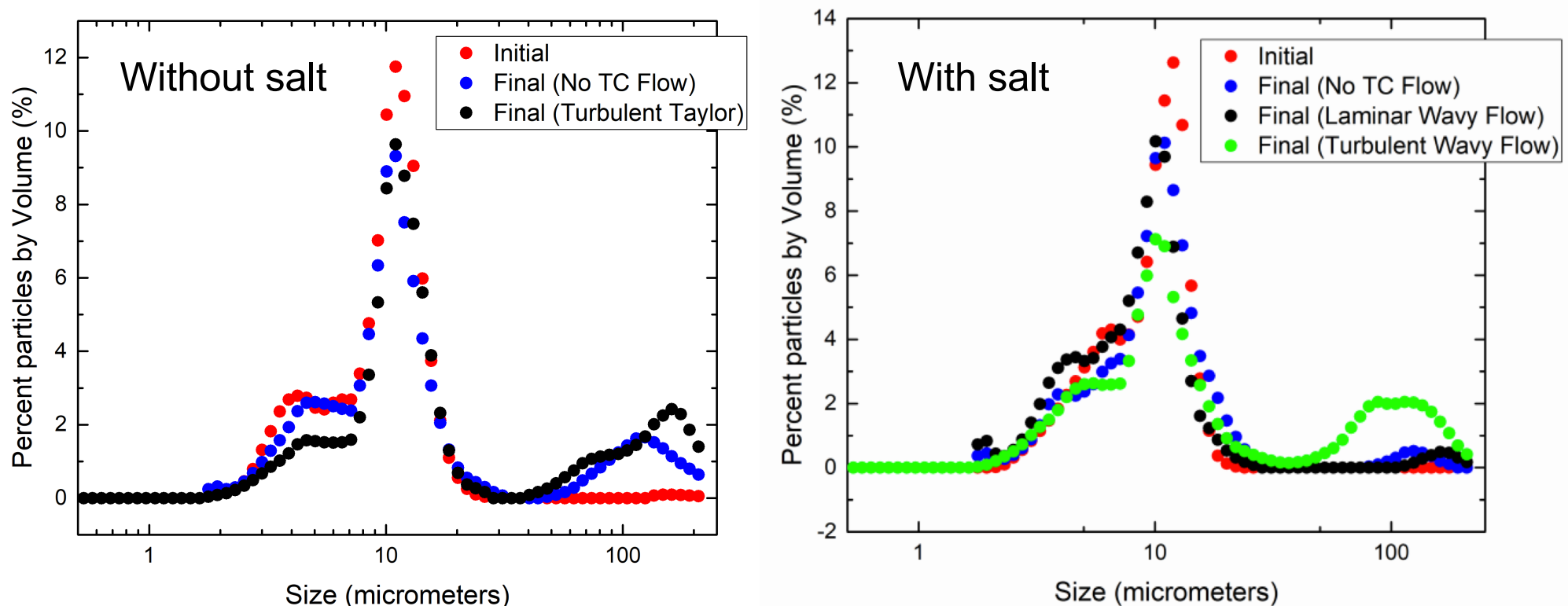


Key Results

- Taylor-Couette flows **destabilized the low-oil emulsions**, shown by the decrease in droplets of size less than 10 micrometers and increase in droplets of size on the order of 100 micrometers.
- In contrast, traditional rheology did *not* destabilize the low-oil emulsions.

Results-Task 2

Objective 3 Pre-prepared Emulsion Stability in TC Flows



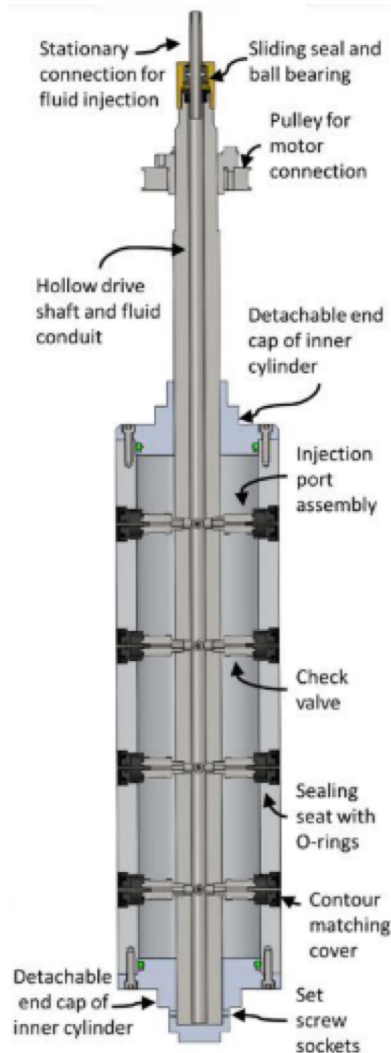
Key Results

- Ran SERDP oil mix and mineral oil, DI and salt water
- Destabilization at turbulent flow states, no observed with rotational rheometry up to 2000 1/s.
- Increase in larger droplets, and decrease in smaller drops.

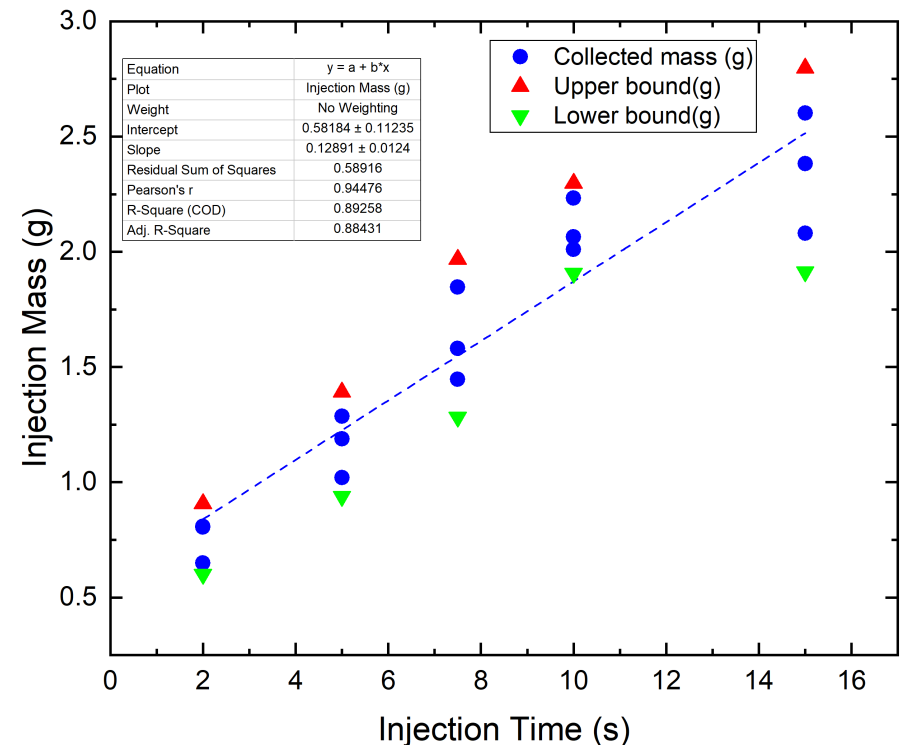
Both systems:
 0.1% SERDP oil mix;
 100 ppm detergent mix

Results-Task 2

Objective 4 In-situ Emulsion Stability in TC Flows



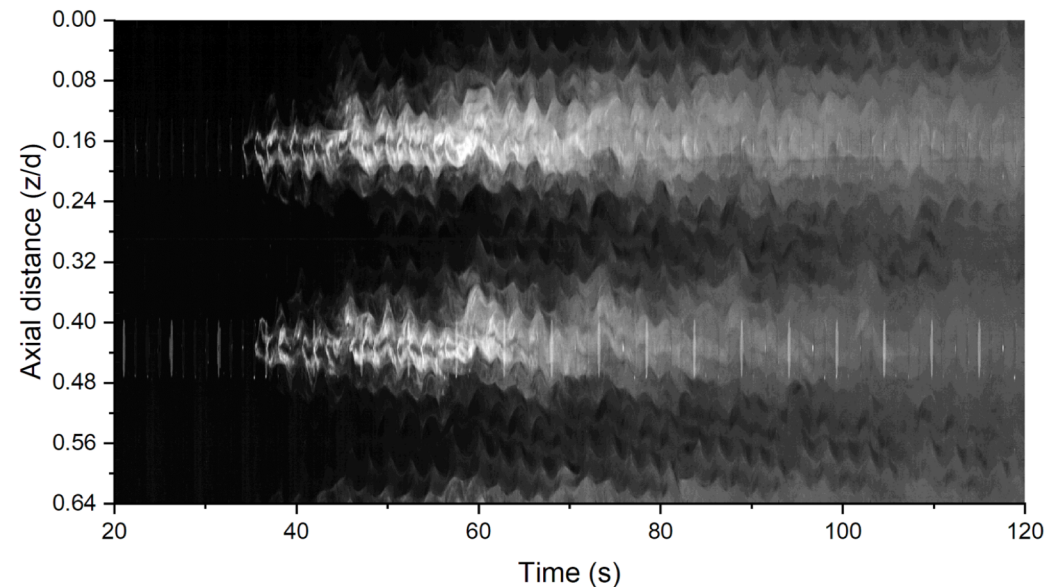
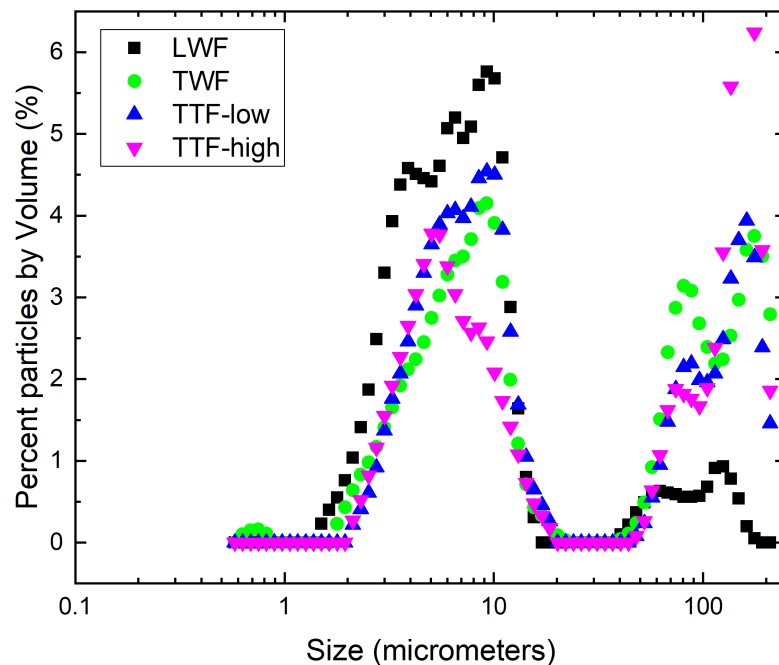
Wilkinson & Dutcher, *Rev. Sci. Instruments*, 2017;
 Metaxas, Wilkinson, and Dutcher, *Soft Matter*, 2018;
 Wilkinson and Dutcher, *J Fluid Mechanics*, 2018



- Oil is injected into the water-surfactant solution in the TC cell through the injection ports.
- The flow rate of the injection ports and time required for injection is determined by calibration curve.

Results-Task 2

Objective 4 In-situ Emulsion Stability in TC Flows



Space-time plot for in-situ injected concentrated emulsion into the Taylor wavy vortices in the TC experiments

Key Results

- Peak formed at the smaller droplet size in the solution and reduces with increasing mixing speed.
- A second peak at larger droplet size increases with higher mixing speeds.
- The formation of a peak at higher mixing speed shows the effects of droplet coalescence due to shear in the flow.

Next Steps

- The results of this work has laid the foundation of systematic studies of surfactant transport for both bilgewater and fire-fighting foam systems, in follow up grant SERDP WP19-1407.

Technology Transfer

Publications and Reports

- Y. Chen, S. Narayan, C.S. Dutcher, *Phase-dependent surfactant transport on the microscale: Interfacial tension and droplet coalescence*, Langmuir, 2020 (*selected for ACS Editors Choice)
- J. Church, M.R. Willner, B.R. Renfro, Y. Chen, D. Diaz, W.H. Lee, C.S. Dutcher, J.G. Lundin, D.M. Paynter, *Impact of Interfacial Tension and Critical Micelle Concentration on Bilgewater Oil Separation*, Journal of Water Process Engineering, 2020 (*Collaborative effort)
- S. Narayan, A.E. Metaxas, R. Bachnak, T. Neumiller, and C.S. Dutcher, *Zooming in on the role of surfactants in droplet coalescence at the macro- and microscale*, Current Opinion in Colloid & Interface Science, 2020
- Y. Chen, C. S. Dutcher, *Size dependent droplet interfacial tension and surfactant transport in liquid-liquid systems, with applications in shipboard oily bilgewater emulsions*, Soft Matter, 2020

Technology Transfer (Cont'd)

Presentations

- Prof. Cari Dutcher gave an invited lecture *Understanding Shipboard Oil/Water Emulsions Using Macro- and Micro-scale Flows* for the Advancing Emulsion Science Session, SERDP/ESTCP Symposium 2019, Washington DC, Dec 2019.
- Dr. Yun Chen presented *Size dependent droplet interfacial tension and surfactant transport in oily bilgewater systems* at the American Physical Society - Division of Fluid Dynamics (APS – DFD) 72nd Annual Meeting, Seattle, WA, Nov 2019.
- Prof. Cari Dutcher gave an invited talk *Understanding Shipboard Oil/Water Emulsions Using Macro- and Micro-scale Flows* at Naval Research Laboratory, Chemistry Division, Washington DC, July 2019.
- Prof. Cari Dutcher gave an invited lecture *Droplet microfluidics for studying surfactant-rich interfaces: From atmospheric aerosols to bilgewater emulsions* for the ACS Colloids and Surface Science Symposium, Atlanta, GA, June 2019.

Technology Transfer (Cont'd)

Presentations (cont'd)

- Dr. Yun Chen presented poster *Size dependent droplet interfacial tension and surfactant transport in liquid-liquid system* at the Mathematical Fluids, Materials, and Biology Conference 2019 at the University of Michigan, Ann Arbor, MI.
- Dr. Yun Chen presented poster *Understanding Shipboard Oil/Water Emulsions Using Macro- and Micro-scale Flows* at the SERDP & ESTCP Symposium 2018, Washington, District of Columbia, USA.

Webinar and Training Short Course

- Prof. Cari Dutcher presented a webinar for the SERDP & ESTCP Webinar Series on waste reduction and treatment in Armed Forces vessels, June 2020.
- Prof. Cari Dutcher presented short course lectures on *Interfacial Rheology* and *Microfluidic Rheology* for the Rheological Measurements: Applications to Polymers, Suspensions, Processing, Minneapolis, MN, Aug 2018 and Aug 2020.

Key Points

- IFT was found to decay much faster when surfactant and water is in the outer phase and oil in the inner phase for *micro-scale* droplets, while the rate does not change significantly for *milli-scale* droplets.
- Equilibrium constant, κ , maximum surface coverage, Γ_{∞} , surfactant diffusivity, D , and adsorption/desorption rate constants of the surfactants were calculated and compared to other typical surfactants. Results provided to NSWCCD SERDP team collaborators.
- Non-monotonic relationships found for emulsion destabilization times with both *o:w ratio* and *surfactant concentration*, showing stabilization of emulsion depending on the amount of oil and surfactant due to competing factors.
- Emulsion destabilization was observed after the pre-prepared emulsion underwent the Taylor-Couette flow test. Changes in droplet size distributions and emulsion destabilization were observed for low oil content samples (0.1% oil).