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

WP18-1031

Cari Dutcher
University of Minnesota

December 11, 2020
## REPORT DOCUMENTATION PAGE

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

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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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Shipboard Oil/Water Emulsions, Macro- and Micro-scale Flows

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Project Team

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- 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

• 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.

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

Bilge water is a complex emulsion with oils, fuels, solids, soaps, and solvents
Task 1: Microscale Droplet using Microfluidics

- Single Droplet Measurements
  - Objective 1 – Device Treatment
- Single Droplet Measurements
  - Objective 2 – Dynamic IFT
  - Objective 3 – Characterization of Surfactants
- Droplet-Droplet Measurements
  - Objective 4 – Stokes Trap
- Follow-on WP19-1407

Task 2: Macroscale Taylor-Couette Flows

- Bulk Emulsion Stabilization Measurement
  - Objective 1 – Static Stability Test
  - Objective 2 – Steady-shear Viscosity
- Taylor-Couette Cell Emulsion Stabilization Test
  - Objective 3 – Pre-prepared
  - Objective 4 – In Situ
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.

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

\[ D(x) = \frac{d_{\text{major}}(x) - d_{\text{minor}}(x)}{d_{\text{major}}(x) + d_{\text{minor}}(x)} \]

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

\( a_0 \): equilibrium droplet radius
\( u \): velocity of droplet
\( \dot{\varepsilon} \): extension rate \((\dot{\varepsilon} = du/dx)\)

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

\( \gamma \): interfacial tension

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

Chen & Dutcher, Soft Matter (2020)
Results-Task 1
Objective 3 Characterization of Surfactant

Max surfactant surface coverage, \( \Gamma_\infty \)
(Close to CMC)

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

Equilibrium constant, \( \kappa \)

\[
\frac{\Gamma_{eq}}{\Gamma_\infty} = \frac{\kappa C}{1 + \kappa C} \gamma = \gamma_0 + nRT \Gamma_\infty \ln \left( 1 + \frac{\kappa C}{\kappa C + 1} \right)
\]
(Langmuir Isotherm)

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

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>Detergent Mix</th>
<th>AES</th>
</tr>
</thead>
<tbody>
<tr>
<td>( M_w ) (g/mol)</td>
<td>300</td>
<td>420</td>
</tr>
<tr>
<td>( \Gamma_\infty ) (mol/m²)</td>
<td>1.52×10⁻⁶</td>
<td>2.53×10⁻⁶</td>
</tr>
<tr>
<td>( \kappa ) (m³/mol)</td>
<td>380</td>
<td>904</td>
</tr>
<tr>
<td>CMC (mol/m³)</td>
<td>(50 ppm)</td>
<td>(25 ppm)</td>
</tr>
<tr>
<td>( D_{C&lt;CMC} ) (m²/s)</td>
<td>3.2×10⁻¹¹</td>
<td>1.9×10⁻¹⁰</td>
</tr>
</tbody>
</table>

Surfactant Diffusivity, \( D \)

\[
\gamma - \gamma_{eq} \approx \frac{RT\Gamma_{eq}^2}{C} \sqrt{\frac{\pi}{4Dt}}
\]

Langmuir constant \( \kappa \): Affinity for the interface

\( \kappa \) \( 10^0 \)  \( 10^1 \)  \( 10^2 \)  \( 10^3 \)  \( 10^4 \)

CTAB, STS  \( C_{10} \)DMPO, Decanol  \( C_{10} \)EO₄  TritonX-100, TritonX-165

Chen & Dutcher, Soft Matter (2020)
Results-Task 1
Objective 3 Characterization of Surfactant

Adsorption rate \( (k_{\text{ads}}) \) and desorption rate \( (k_{\text{des}}) \) from Langmuir’s equation

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

\[
\tau = \frac{1}{k_{\text{des}}} \frac{1}{1 + \kappa C}
\]

\[
\kappa = \frac{k_{\text{ads}}}{k_{\text{des}}}
\]

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>Detergent Mix</th>
<th>AES</th>
</tr>
</thead>
<tbody>
<tr>
<td>C (mol/m³)</td>
<td>0.0887 (25 ppm)</td>
<td>0.354 (100 ppm)</td>
</tr>
<tr>
<td>( k_{\text{ads}} ) (m³/mol · s)</td>
<td>Inner</td>
<td>55</td>
</tr>
<tr>
<td>( k_{\text{des}} ) (1/s)</td>
<td>Outer</td>
<td>0.14</td>
</tr>
<tr>
<td>( k_{\text{ads}} ) (m³/mol · s)</td>
<td>inner</td>
<td>299</td>
</tr>
<tr>
<td>( k_{\text{des}} ) (1/s)</td>
<td>outer</td>
<td>0.78</td>
</tr>
</tbody>
</table>

Key Results

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

Chen & Dutcher, Soft Matter (2020)
# Task 1 Results

## Objective 3 Characterization of the surfactant cleaners

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>$M_w$ (g/mol)</th>
<th>CMC (ppm)</th>
<th>$\Gamma_{\infty}$ (mol/m²)</th>
<th>$\kappa$ (m³/mol)</th>
<th>$K$</th>
<th>$D$ (m²/s)</th>
<th>$k_{ads}$ (m³/mol·s)</th>
<th>$k_{des}$ (s⁻¹)</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Detergent Mix</td>
<td>300</td>
<td>50</td>
<td>$1.52 \times 10^{-6}$</td>
<td>380</td>
<td>-</td>
<td>$3.19 \times 10^{-11}$</td>
<td>299.1</td>
<td>0.78</td>
<td>Anionic</td>
</tr>
<tr>
<td>AES</td>
<td>420</td>
<td>25</td>
<td>$2.53 \times 10^{-6}$</td>
<td>904</td>
<td>-</td>
<td>$1.9 \times 10^{-10}$</td>
<td>220.7</td>
<td>0.24</td>
<td>Anionic</td>
</tr>
<tr>
<td>TritonX-100</td>
<td>625</td>
<td>350</td>
<td>$1.64 \times 10^{-6}$</td>
<td>$1.41 \times 10^5$</td>
<td>1.152</td>
<td>$6.28 \times 10^{-11}$</td>
<td>42.548</td>
<td>$2.3 \times 10^{-3}$</td>
<td>Non-ionic</td>
</tr>
<tr>
<td>SDS</td>
<td>288</td>
<td>4500</td>
<td>$2.81 \times 10^{-6}$</td>
<td>104.98</td>
<td>3.618</td>
<td>$2.45 \times 10^{-11}$</td>
<td>53.8</td>
<td>2.7</td>
<td>Anionic</td>
</tr>
<tr>
<td>Type 1</td>
<td>617</td>
<td>110</td>
<td>$1.88 \times 10^{-6}$</td>
<td>$1.19 \times 10^5$</td>
<td>0.3947</td>
<td>$1.04 \times 10^{-10}$</td>
<td>31.83</td>
<td></td>
<td>Non-ionic</td>
</tr>
<tr>
<td>Solid Surge</td>
<td>214</td>
<td>420</td>
<td>$1.04 \times 10^{-6}$</td>
<td>$4.04 \times 10^6$</td>
<td>0.3587</td>
<td>$3.40 \times 10^{-12}$</td>
<td>5.59</td>
<td>2.68</td>
<td>Non-ionic</td>
</tr>
<tr>
<td>PRC</td>
<td>293</td>
<td>7300</td>
<td>$1.005 \times 10^{-6}$</td>
<td>$2.10 \times 10^6$</td>
<td>1.341</td>
<td>$9.50 \times 10^{-14}$</td>
<td>1.73</td>
<td>2.80</td>
<td>Non-ionic + Anionic</td>
</tr>
</tbody>
</table>

**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

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

Key Result
• Coalescence readily observed for water in oil systems, applicable for dry bilge systems.
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

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)
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.

\[ T = A \exp\left(-\frac{t}{\lambda}\right) + T_\infty \]
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

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

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.
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

Oil is injected into the water-surfactant solution in the TC cell though the injection ports.

The flow rate of the injection ports and time required for injection is determined by calibration curve.

Wilkinson & Dutcher, Rev. Sci. Instruments, 2017; Metaxas, Wilkinson, and Dutcher, Soft Matter, 2018; Wilkinson and Dutcher, J Fluid Mechanics, 2018
Results-Task 2
Objective 4 In-situ Emulsion Stability in TC Flows

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

Technology Transfer (Cont’d)

Presentations


- 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, $\kappa$, maximum surface coverage, $\Gamma_\infty$, 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).