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Bilgewater Emulsion Characterization: from Model Systems to Real World Samples

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Outline

- Overview of NSWCCD
- Introduction to Bilgewater
- Identification and Characterization of Cleaners
- Environmental Impacts on Simulated Bilgewater Emulsion Stability
- Role of Experimentally Determined Cleaner Properties on Emulsion Stability
- Extracted Bilgewater Characterization
- Conclusions and Future Work

NSWCCD Capability Overview

- Naval Surface Warfare Center Carderock Division Environmental Engineering, Science and Technology Branch (Code 633)
  - Knowledge base in environmental solutions for liquid waste treatment and management in oily, non-oily, and ballast water applications
  - Comprised of ~ 20 scientists and engineers and 2 postdocs
- Provide technical expertise primarily to the Navy, but also support U.S. defense and private organizations
- Outfitted with a unique combination of full and bench scale facilities

Introduction to Bilgewater

- Bilge – point of collection for water, oil and other substances used on-board
- Bilgewater composition is highly variable and dependent upon shipboard tasks
  - Fuels
  - Oils
  - Lubricants
  - Condensation
  - Cleaning Chemicals
  - Detergents
  - Solids (e.g. dirt, dust, fibers, etc.)
- Oil-in-water emulsions created from variable bilge influents compound challenges with consistent waste stream treatment

Bilgewater before (left) and after treatment (right)

Principal Challenges

Bilge Management Practices

- Settling time
- Contaminant oversight
- Tank soundings

Ease of Operability

- High crew turnover
- Operator demands
- System location

Oil-in-water Emulsions

- Behavior
- Composition
- Treatment

Hydrocarbon Measurement

- Interferences
- Accuracy

Emulsion Characterization Study for Improved Bilgewater Treatment and Management

Overview

Task 1: Scoping Study for Armed Forces Oil-in-Water Emulsions

- Literature, technical, and regulation review
- Shipboard personnel interviews

Review Article Publication

1. Documentation of common bilgewater contaminants
2. Provides comprehensive and consistent emulsion preparation and analysis techniques
3. Captures industry's "tools-of-the-trade" for emulsion characterization

Task 2: Prepared and extracted solution characterization

A. Neat Detergents:
- Chemical characterization (LC-MS/GC-MS)
- CMC (ST/IFT)
- Zeta potential
- Micelle size (DLS)

B. Prepared Emulsions:
- Surfactant type
- Surfactant Concentration
- Oil concentration
- Microprofiles
- Environmental factors

C. Extracted Bilgewater:
- Chemical characterization (LC-MS/GC-MS)
- Oil concentration
- Microprofiles

Test hypothesis

Task 3: Fundamental knowledge

1. Correlate data to specific trends
2. Develop mechanisms
3. Test hypotheses

Task 3: Multiparameter analysis

1. Fit collected data to an existing or developed analytical model
2. Test model

Task 3: Peer-Review Publications

1. Uncommon solution investigated for emulsion stability
2. Novel characterization methods investigated to determine emulsion stability
3. Unique data set applied to existing emulsion stability models

Task 3: Emulsion Stability Database

1. Decision map to identify stabilizing mechanisms
2. Translate stabilizing mechanisms to treatment issues and solutions
3. Inform decision makers of possible repercussions to changes in ship cleaners or treatment time

Identification and characterization of Navy cleaners

Environmental impacts on simulated bilgewater emulsion stability

Role of experimentally determined properties of cleaners on emulsion stability

Extracted bilgewater characterization

Impact of fuel additives on emulsion stability

Machine learning for predicting emulsion stability

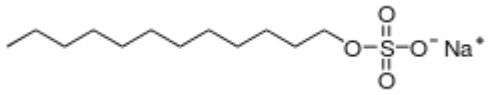
Identification and Characterization of Navy Cleaners

- Navy cleaners were identified by procurement volume→ Top 8 cleaners represented 70% by volume of all procured cleaners

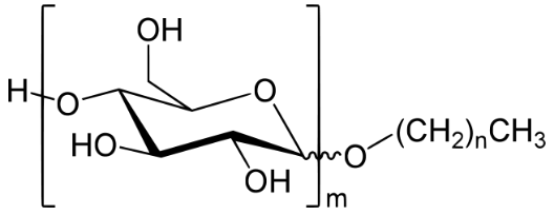
Cleaner	Primary surfactants	CMC (ppm)
AFFF 6% (Chem Guard)	• Flourosurfactant (e.g. Capstone 1157)	3,399
B&B™ 3100 (Vantage)	• Cocamide diethanolamine • 1-buoxyethanol (alcohol ethoxylate)	361
Super Blast Off (Elsco Inter. Inc.)	• Cocamide diethanolamine	934
Calla 855 (Zip-Chem Products)	• Alcohol ethoxylate (c10-c14) • Cocamide diethanolamine • Capriloamphorionate	328
Power Green (LHB Industries)	• Surfactant blend	3,824
PRC Deck Cleaner (Werth Sanitary Supply Co. Inc.)	• Alcohol ethoxylate	1,871
Ecolab Solid Surge Plus NP (Ecolab # 6117905)	• Alcohol ethoxylate (c12-16)	98
Type 1 Detergent (MILSPEC: MIL-D-16791)	• Alkyl aryl polyether alcohol	87

Characterization of Reference Surfactants

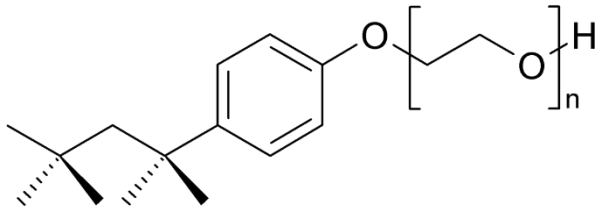
Cleaner	Primary surfactants	CMC (ppm)	Surface tension (mN/M)	IFT with NSBM#4 (mN/M)	Micelle size (nm)	Zeta Potential (mV)
SDS	• Ionic Standard	1,983	35.4 ± 0.8	10.1 ± 0.5	1.3 ± 0.2	-40 ± 6
Triton CG -110	• Nonionic Standard	1,748	26.9 ± 0.2	2.4 ± 0.4	6.5 ± 0.1	-10 ± 7
Triton X-100	• Nonionic Standard	102	29.6 ± 0.4	3.0 ± 0.1	9.1 ± 0.1	-16 ± 4



Sodium dodecyl sulfate (SDS)



Triton CG - 110



Triton X-100

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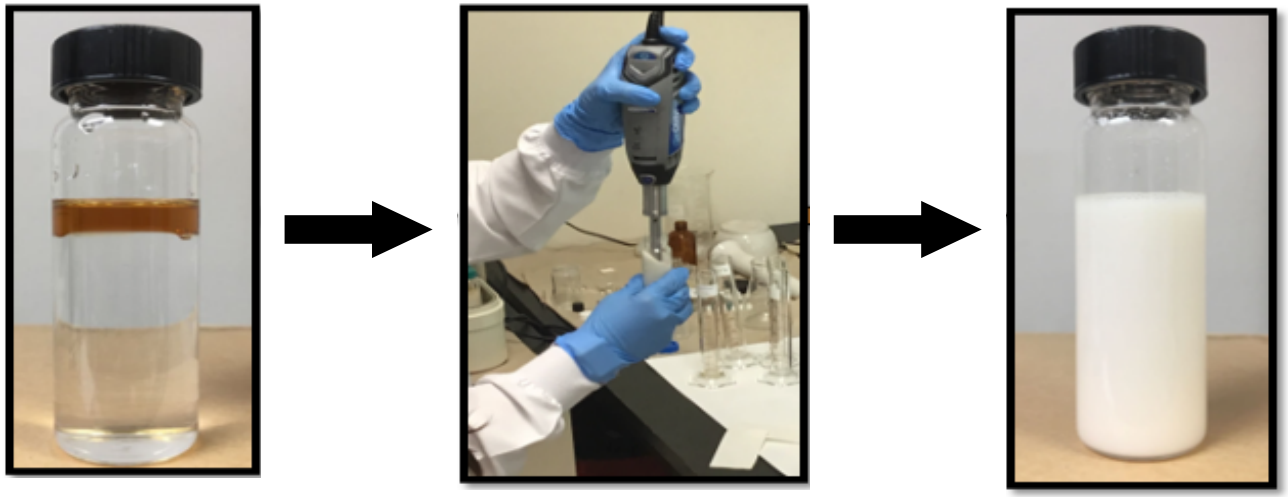
Emulsion Preparation

- Simulated bilgewater emulsions were prepared using a tissue homogenizer
  - 20,000 RPM
  - 2 minutes
- Emulsion components:
  - i) Aqueous phase
    - Cleaners/surfactants
    - Environmental additives
  - ii) Oil phase
    - Mineral Oil
    - Navy Standard Bilge Mix (NSBM) #4

Bilgewater model emulsion preparation



System Components → Homogenize (2 min) → Emulsion

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Environmental Impacts on Simulated Bilgewater Emulsion Stability

Motivation: To study the impacts of environmental factors on simulated bilgewater emulsion stability

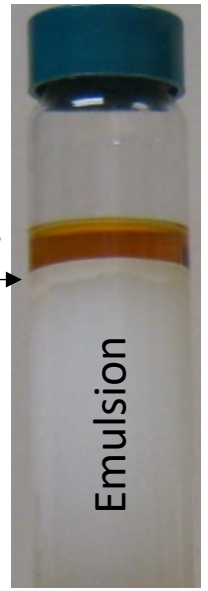
Approach: Prepared emulsions with 10% NSBM #4, Navy cleaners (7x CMC concentration) and various temperatures, pH, suspended solids, and salt concentrations. Visually observed samples after 5 days.

Environmental Factor	Tested Values
Temperature	5, 25, 35°C
pH	Unadjusted, 4, 10
Suspended Solids	0 and 1,000 ppm
Salt Concentration	0 and 35,000 ppm

Analysis: Determined emulsion stability based on

i. Turbidity: opacity of emulsion solution
ii. Oil and cream layer height

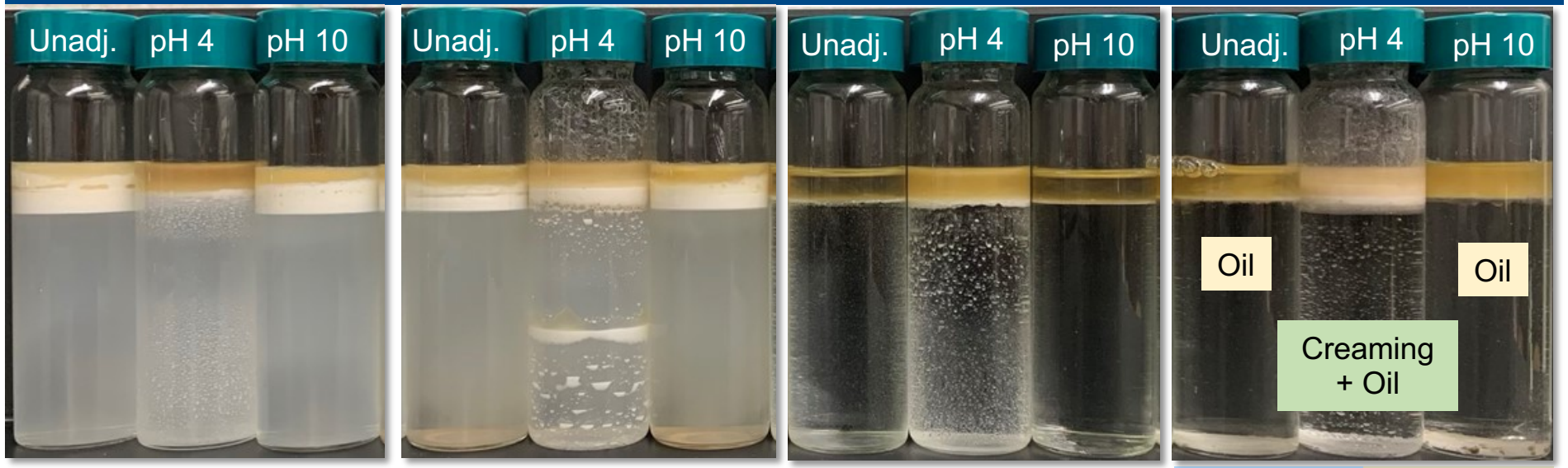
Anatomy of an Emulsion



Environmental Impacts on Simulated Bilgewater Emulsion Stability: Experimental Design

Experimental Design: Sets of 12 emulsions were run simultaneously at each temperature and evaluated after 5 days

Blast Off - 25℃



No Additions	Suspended Solids (1,000 ppm)	Salt (NaCl) (35,000 ppm)	Salt + Solids

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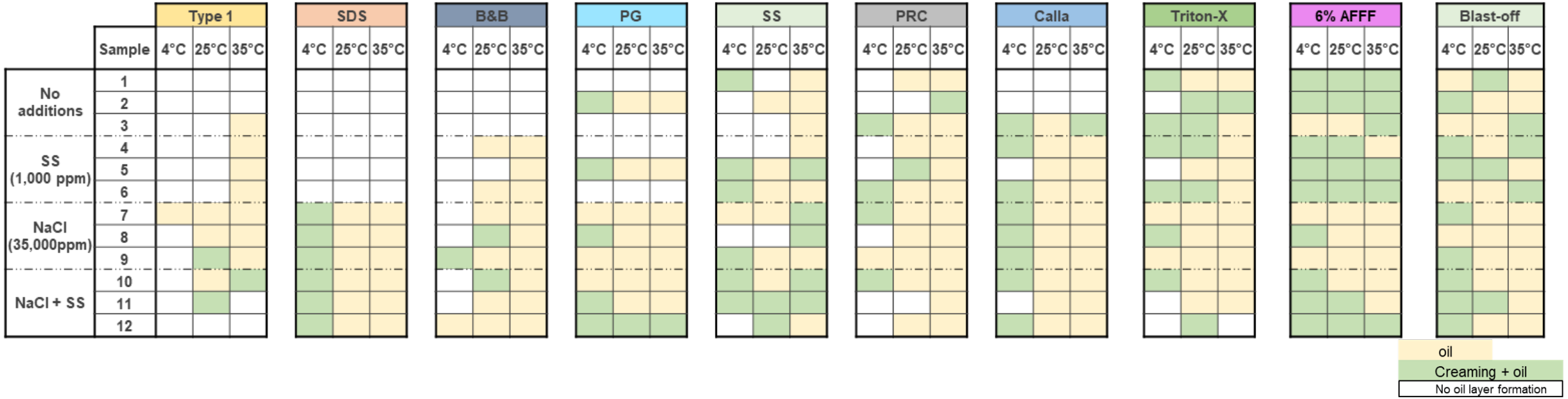
Environmental Impacts on Simulated Bilgewater Emulsion Stability: Results Summary

Summary of environmental stability data



Stability order: Type 1 (61%) > SDS (50%) > B&B (47%)> PG (33%) > [SS (25%) = PRC (25%)] > Calla (22%) > Triton-X (14%) > [6% AFFF (100%) = Blast-off (100%)]

Stability calculated by determining the percentage of emulsions that exhibited no coalescence

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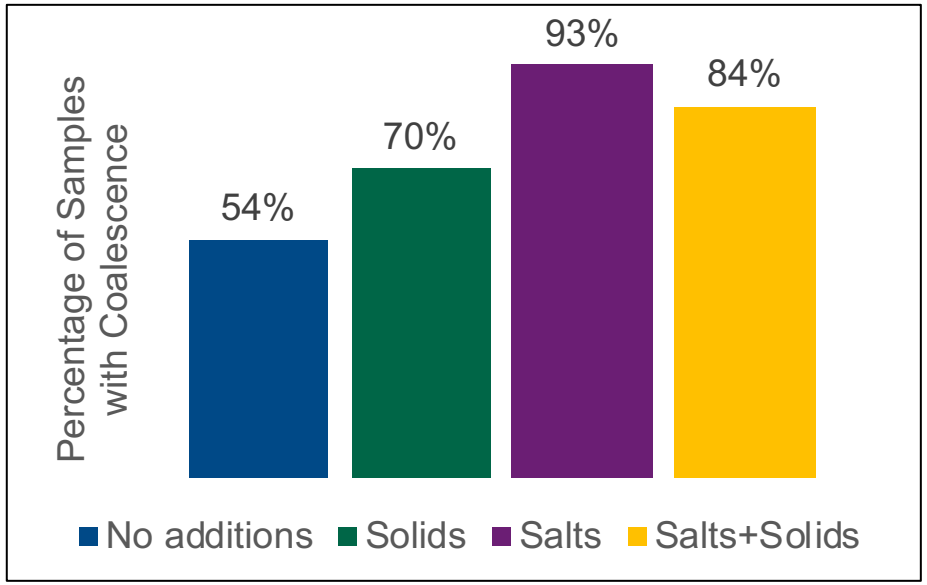
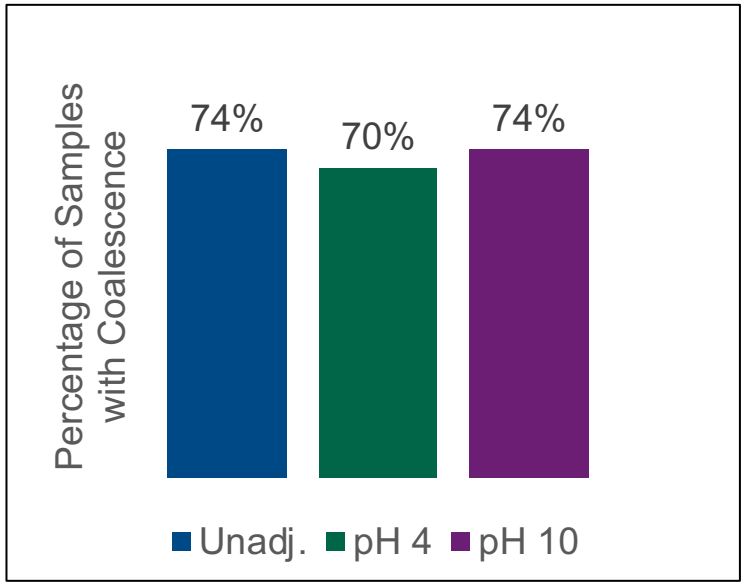
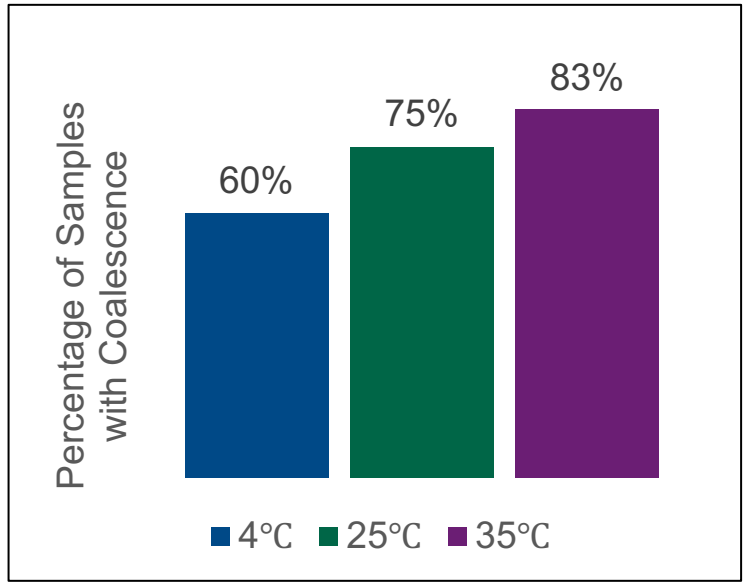
Environmental Impacts on Simulated Bilgewater Emulsion Stability: Results Summary







- Salt concentration is a critical factor in controlling the coalescence stability of emulsions
- Initial pH has a minimal impact on stability because of the buffering capacity of the cleaners
- Emulsions at 4°C are more stable, however, exhibit higher tendency to form a creaming layer
- Data is matrixed and would be better expressed using a model

Role of Experimentally Determined Properties of Cleaners on Emulsion Stability

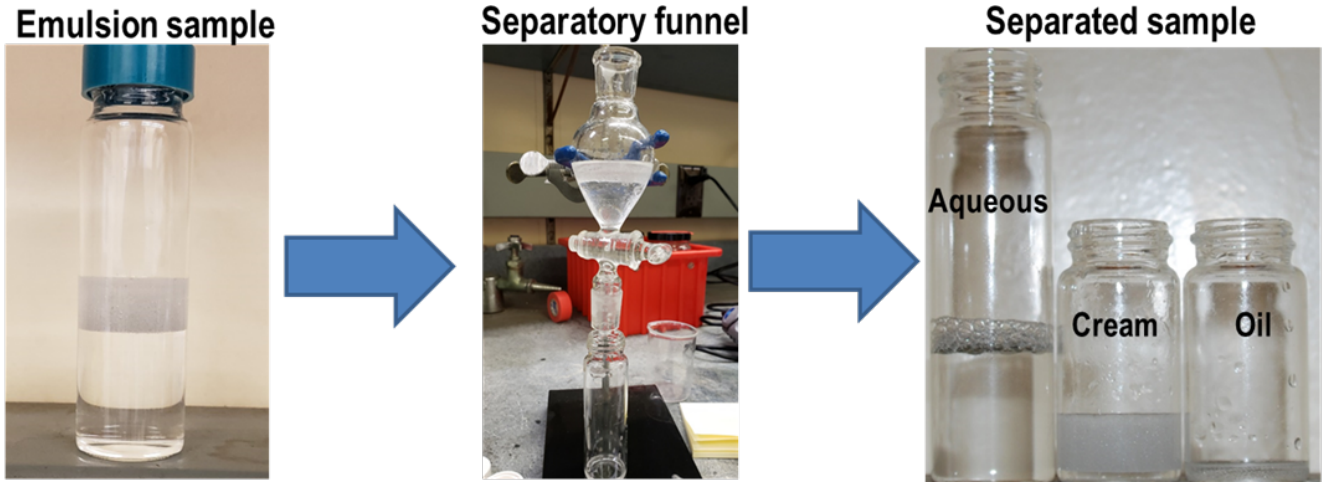
Motivation: To understand the effect of IFT and CMC on the stability and formation of macroemulsion

Approach: Prepared emulsion systems with varying IFTs and concentrations at the standard homogenization speed (20,000 rpm) and at low homogenization (10 shakes) for both the reference surfactants and Navy Cleaners

- 10 concentrations of cleaner tested 0 ppm – 10,000 ppm
- IFT measured at each concentration

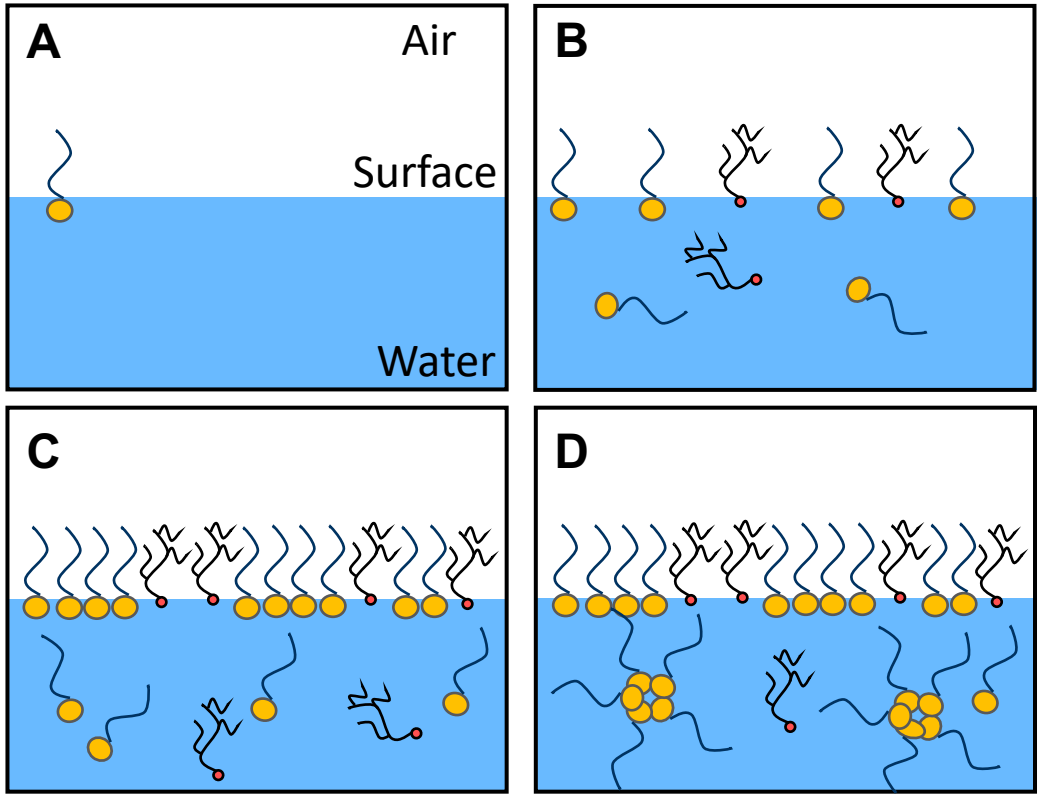
Analysis:

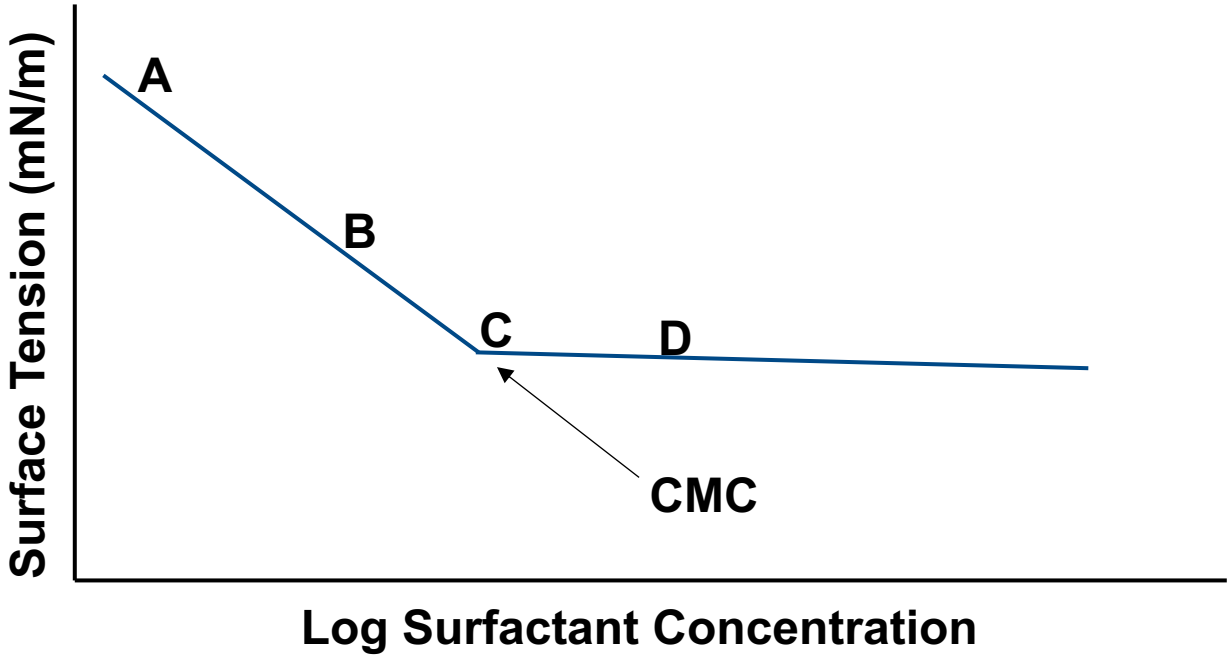
- Bulk emulsion stability→ Visual observations and macrophase separation
- Droplet size analysis→ microscopy and laser diffraction



Critical Micelle Concentration

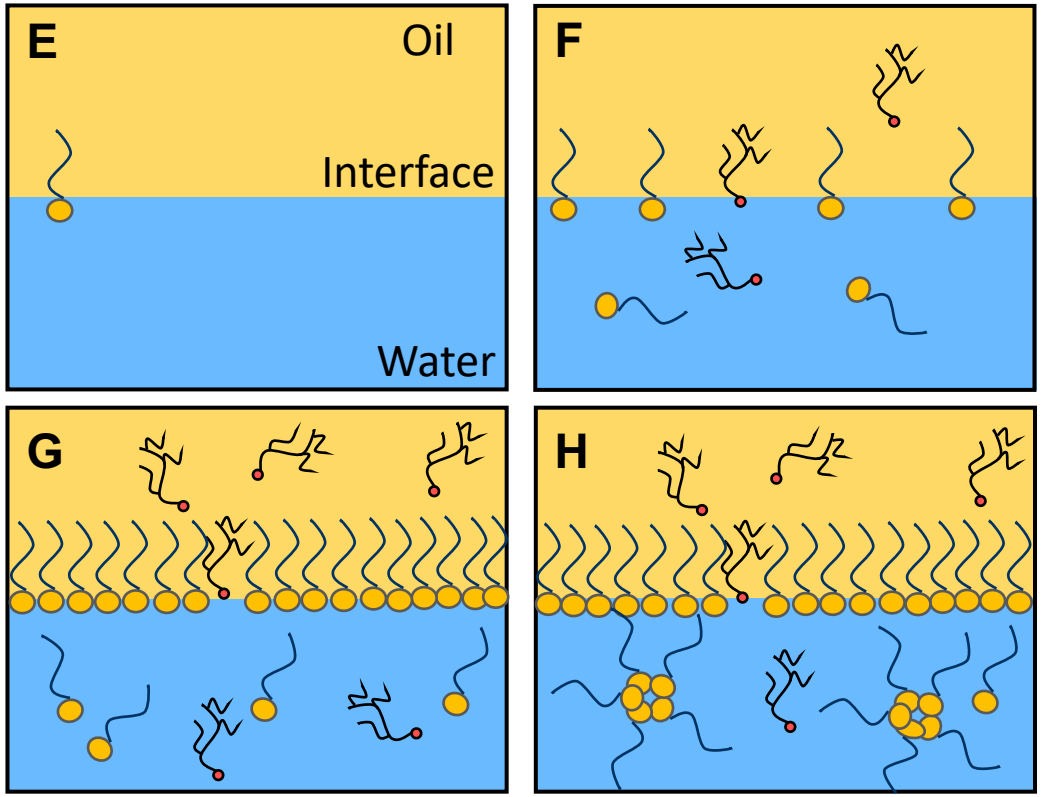
- Critical Micelle Concentration is defined as the concentration at which a surfactant forms micelles and is calculated from surface tension measurements

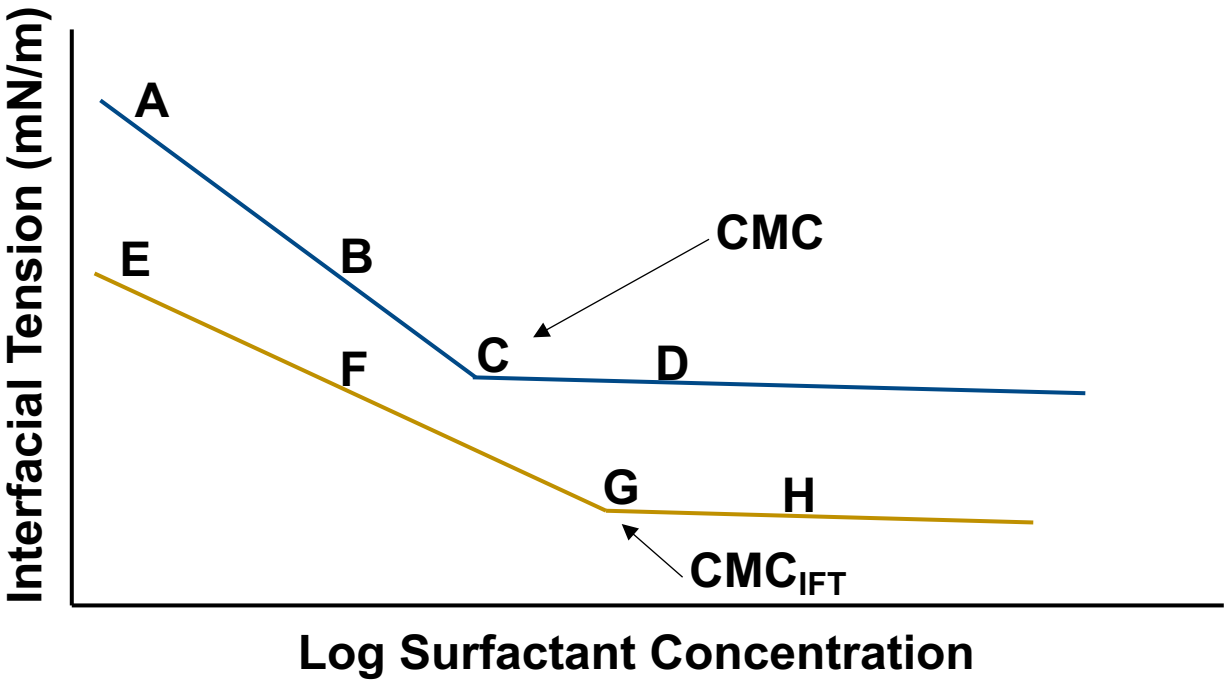




Critical Micelle Concentration

- In the context of bilgewater emulsions, CMC calculated based on IFT may be more representative in predicting stability.





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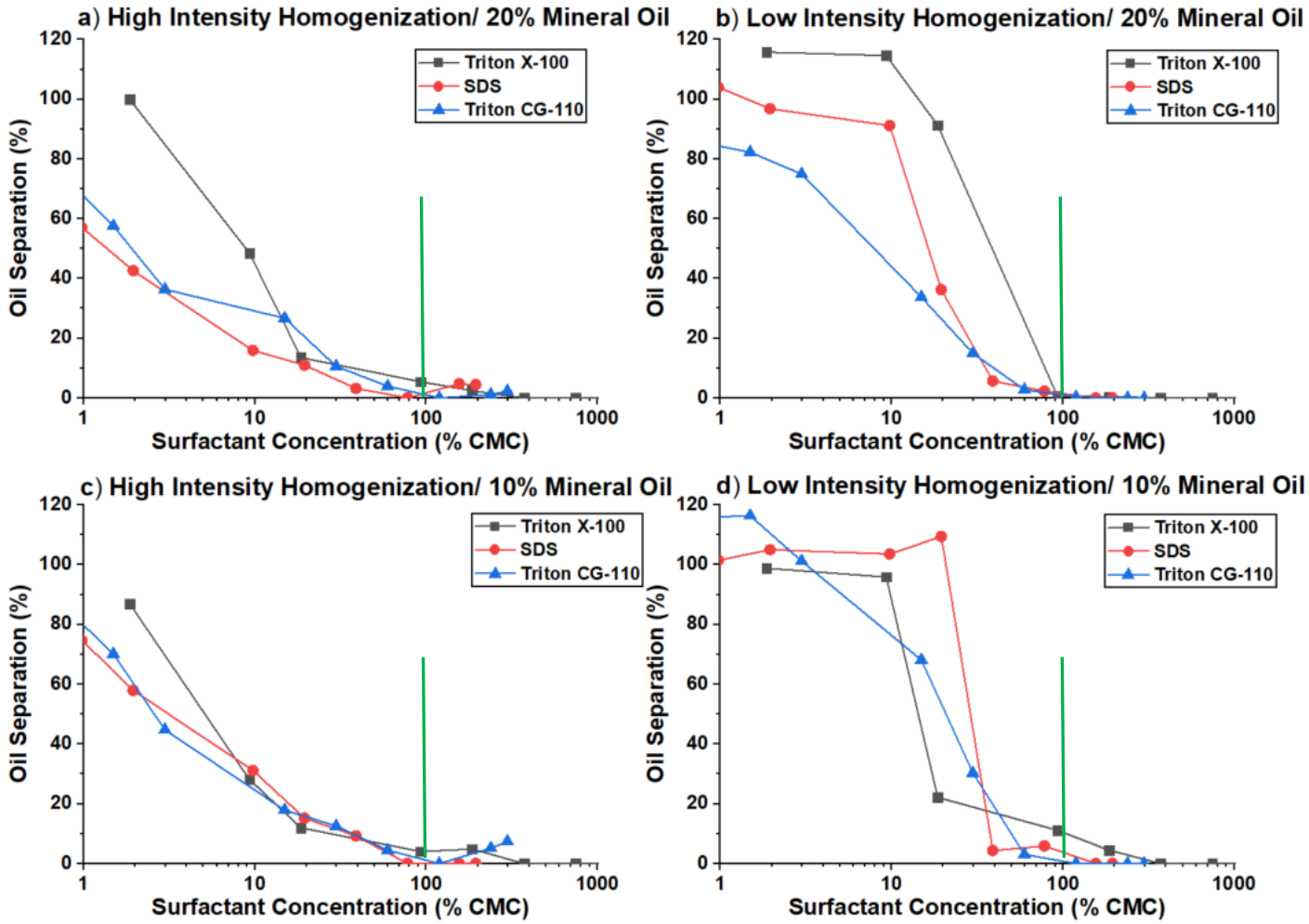
Experimental Properties of Model Surfactants and Bilge Cleaners

- Critical Micelle Concentrations (CMC) of surfactants and cleaner can vary based on surface tension or interfacial tension measurements.

Surfactant/Cleaner	ST CMC (ppm)	IFT CMC (ppm)	Equilibrium ST (mN/m)	Equilibrium IFT (mN/m)
Triton X-100	102	324	29.6 ± 0.4	3.02 ± 0.1
Triton CG-110	1,748	3,352	26.9 ± 0.2	2.15 ± 0.4
Sodium Dodecyl Sulfate (SDS)	1,983	5,130	35.4 ± 0.8	9.83 ± 0.5
Super Blast Off (Elsco Inter. Inc.)	934	5,381	27.7± 0.5	3.44 ±0.1
PRC Deck Cleaner (Werth Sanitary Supply Co. Inc.)	1,871	6,832	30.5 ± 0.1	7.68 ±0.3
Ecolab Solid Surge Plus NP (Ecolab # 6117905)	98	396	27.4 ± 0.3	4.08 ±0.1
Type 1 Detergent (MILSPEC: MIL-D-16791)	87	105	30.2 ± 0.4	3.10 ±0.1

Role of Experimentally Determined Properties of Cleaners on Emulsion Stability

- CMC was an inflection point between partially coalesced and fully emulsified systems
- Relationship was seen for all surfactant types and cleaners, oil concentrations, and homogenization intensities
- The importance of CMC was accentuated in the low homogenization samples



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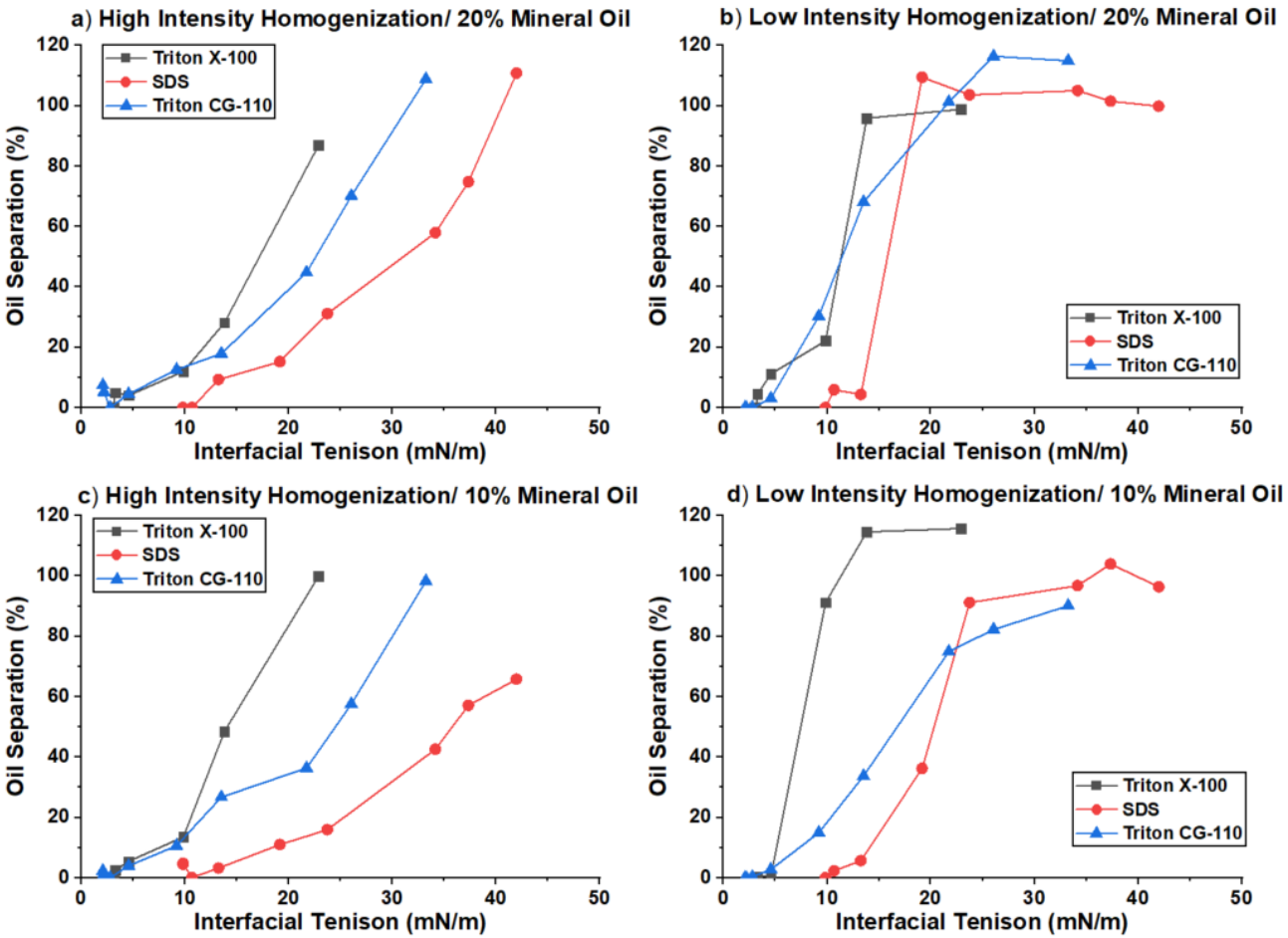
Role of Experimentally Determined Properties of Cleaners on Emulsion Stability

- IFT was evaluated as tool to predict emulsion stability but the results varied between surfactant types for high intensity homogenization
- Emulsions prepared using low intensity homogenization demonstrated similar profiles between the surfactants but the IFT at which coalescence occurs is unclear
- Overall CMC seems to be a better predictor of emulsions stability



Extracted Bilgewater Characterization

- Extracted bilgewater samples were collected from 3 U.S. Navy Vessels
- Observed variability - conductivity ranged from potable to sea water supporting our investigation into environmental factors

Extracted bilgewater samples

Parameter	Bilgewater #1	Bilgewater #2	Bilgewater #3
pH	7.0 - 7.2	5.1	7.8 - 8.4
Conductivity (mS/cm)	16.3 ± 0.1	1.74 ± 0.05	24.0 ± 0.4
Turbidity (NTU)	1,104 ± 104	10,402 ± 20	52 ± 2.3
COD (mg/L)	1279 ± 87	42,800 ± 1,500	547 ± 11
TS (mg/L)	13,793 ± 146	3,043 ± 502	20,320 ± 500
TSS (mg/L)	4,248 ± 212	1,848 ± 58	256 ± 16
UV_{254} (cm^{-1})	0.22 ± 0.02	0.381 ± 0.00	0.08 ± 0.01
Alkalinity (mg/L $CaCO_3$)	230 ± 4.1	5 ± 0.0	92 ± 2.4
TN (mg/L N)	12 ± 3.6	18 ± 13.7	12 ± 1.3
TP (mg/L PO_4^{3-})	3.8 ± 0.1	12.6 ± 0.5	0.3 ± 0.1
HEM (ppm)	50,000	50,000	3,000

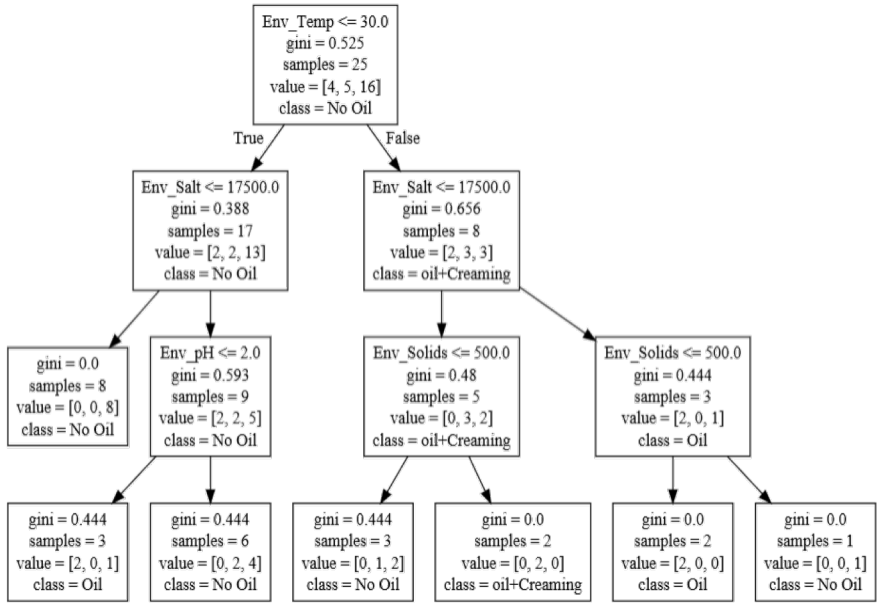
Conclusions

- Task 1: Scoping Study for Armed Forces Oil-in-Water Emulsions
  - Identified the top 8 cleaners procured by Armed Forces vessels which represented 70% by volume of all cleaners found on ship
  - Determined that the primary surfactant of the top 8 cleaners were nonionic
- Task 2: Prepared and Extracted Emulsion Characterization
  - Found that builders found in cleaners can impact the performance of a cleaner's surfactant
  - Demonstrated that salt concentration and temperature have a large impact on emulsion stability
  - Demonstrated CMC_{IFT} as an experimental property that can be used to predict bilgewater emulsion stability
  - Determined though extracted bilgewater composition is highly variable, the hydrocarbon phase composition may be more predictable.

Future Work

- Impacts of fuel additives on emulsion stability
  - Control experiments without surfactants exhibited stable emulsions suggesting the mass transport of compounds from the fuel into the aqueous phase

- Development of an emulsion stability model
  - A key question is how and which properties of an emulsion system determine stability
  - Machine learning methods are being used to develop the model



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