Development of Zwitterionic Additives to Aqueous Foams to Enhance Suppression of Aromatic and Aliphatic Fuel Pool-Fires

WP22-3391

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14. ABSTRACT

The technical objective of this project is:
-Vary siloxane sulfobetaine zwitterionic surfactant structures to enhance gasoline fire suppression, by increasing synergism and suppressing surfactant extraction into gasoline.

15. SUBJECT TERMS

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Firefighting foams   Siloxane surfactants

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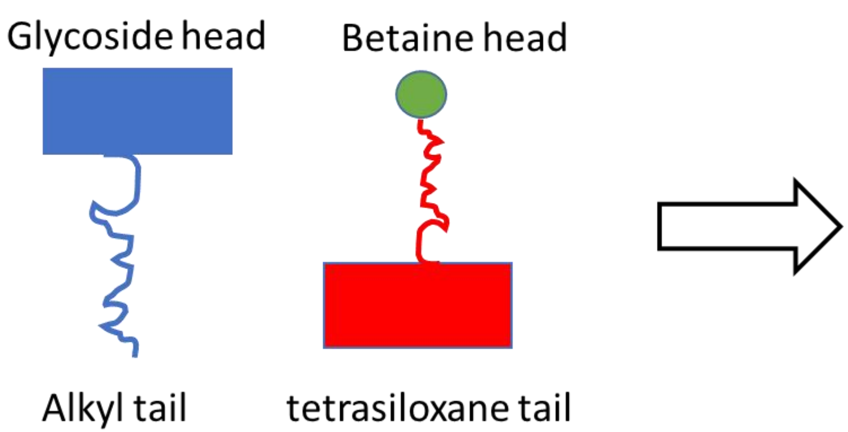
Background

This one-year project initiated in 2022 to address the following SON:

“Functional Additives and Foam Formation to Enhance PFAS-Free Fire Suppressants for Military Use”

Technical Objectives

- Vary siloxane-sulfobetaine zwitterionic surfactant structures to enhance gasoline-fire suppression, by increasing synergism and suppressing surfactant extraction into gasoline.
- Our hypothesis is:



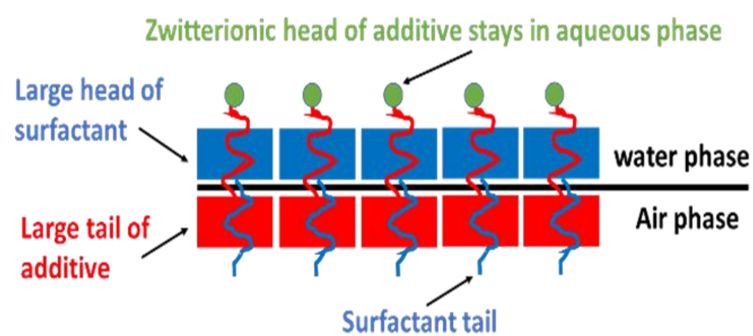
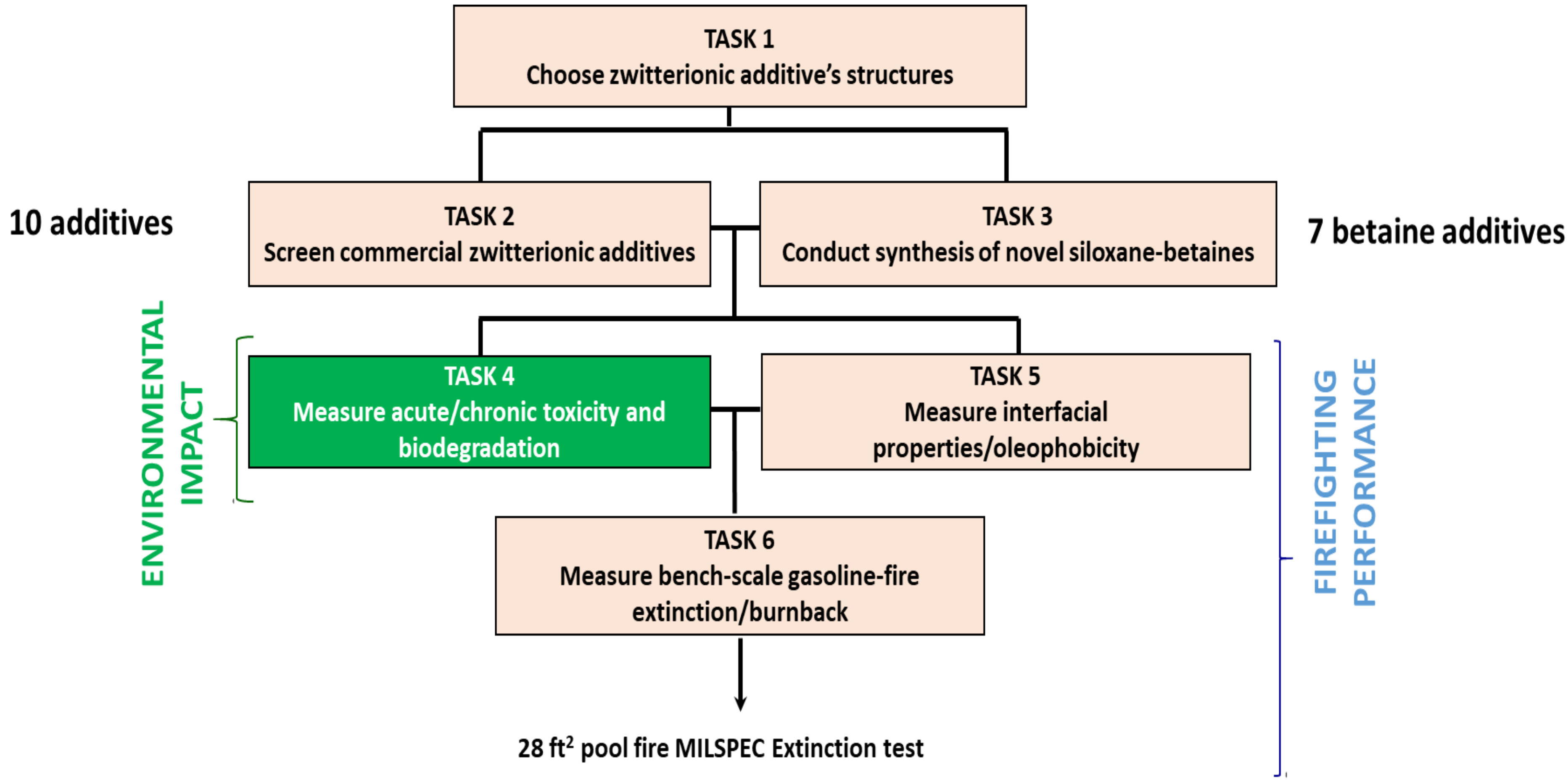


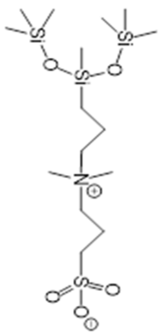
Fig. 1. Zwitterionic additive enables bilayer formation at bubble surfaces; the bilayers form additional barriers in foam to fuel feeding a fire.

Technical Approach

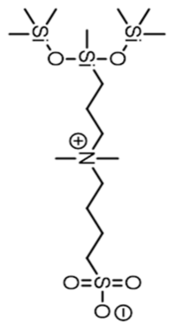


Results

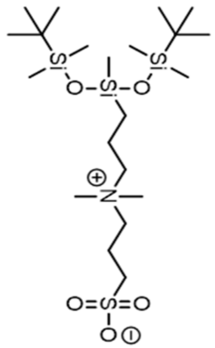
Vary siloxane-zwitterionic surfactant structure



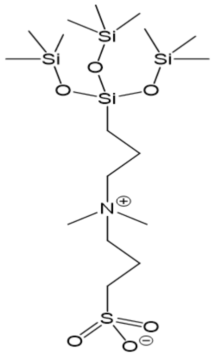
TrisiloxaneSB
MD2102-16/N10478-40



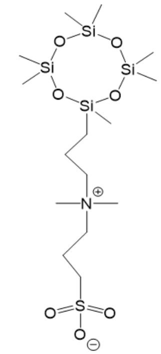
TrisiloxaneSbutylB
CB-1-123



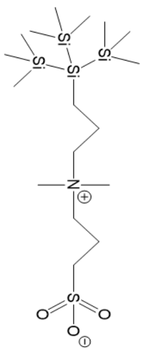
t-ButyltrisiloxaneSB
CB-DTBTS-SB



TetrasiloxaneSB
MD2062-54/N10478-198



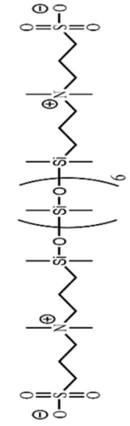
CyclictetrasiloxaneSB
N10477-81



TetrasilaneSB
N10477-189

t-ButyldisiloxaneSB
MD2102-99

DisilaneSB
MD2102-90

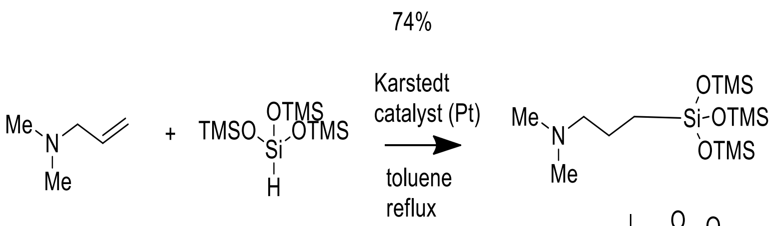


HexasiloxanediSB
CB-1-180B

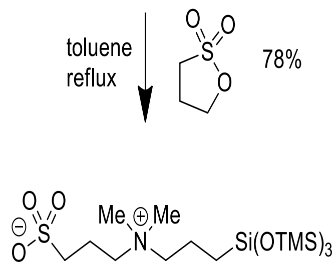
Gradual changes to head/tail conformities are made to enable hypotheses and interpretation of measurements

Results

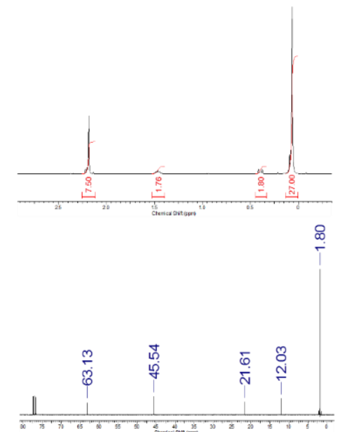
Typical synthesis of sulfobetaine surfactants



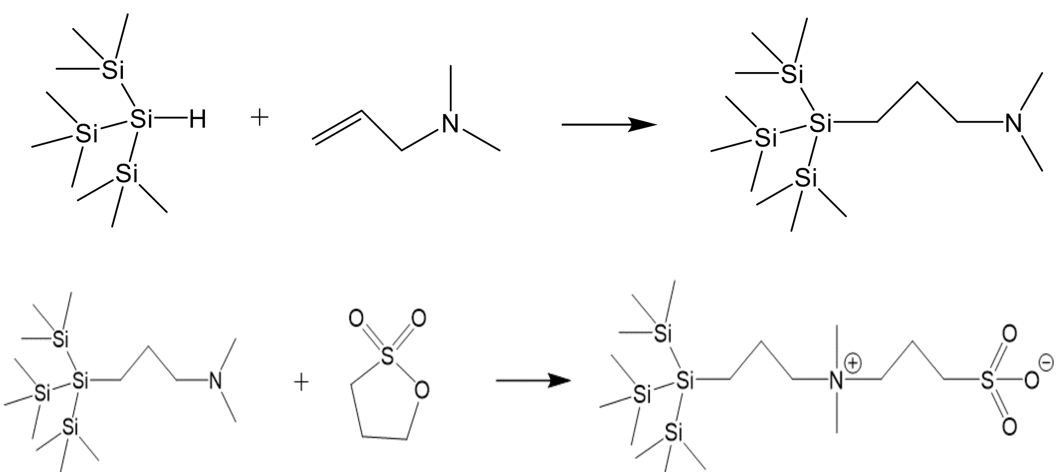
Tetrasiloxane-sulfobetaine

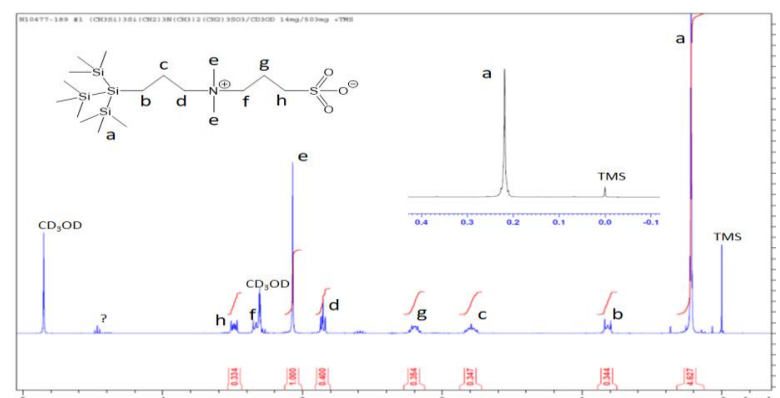


Characterization by ^{1}H ^{29}Si NMRs



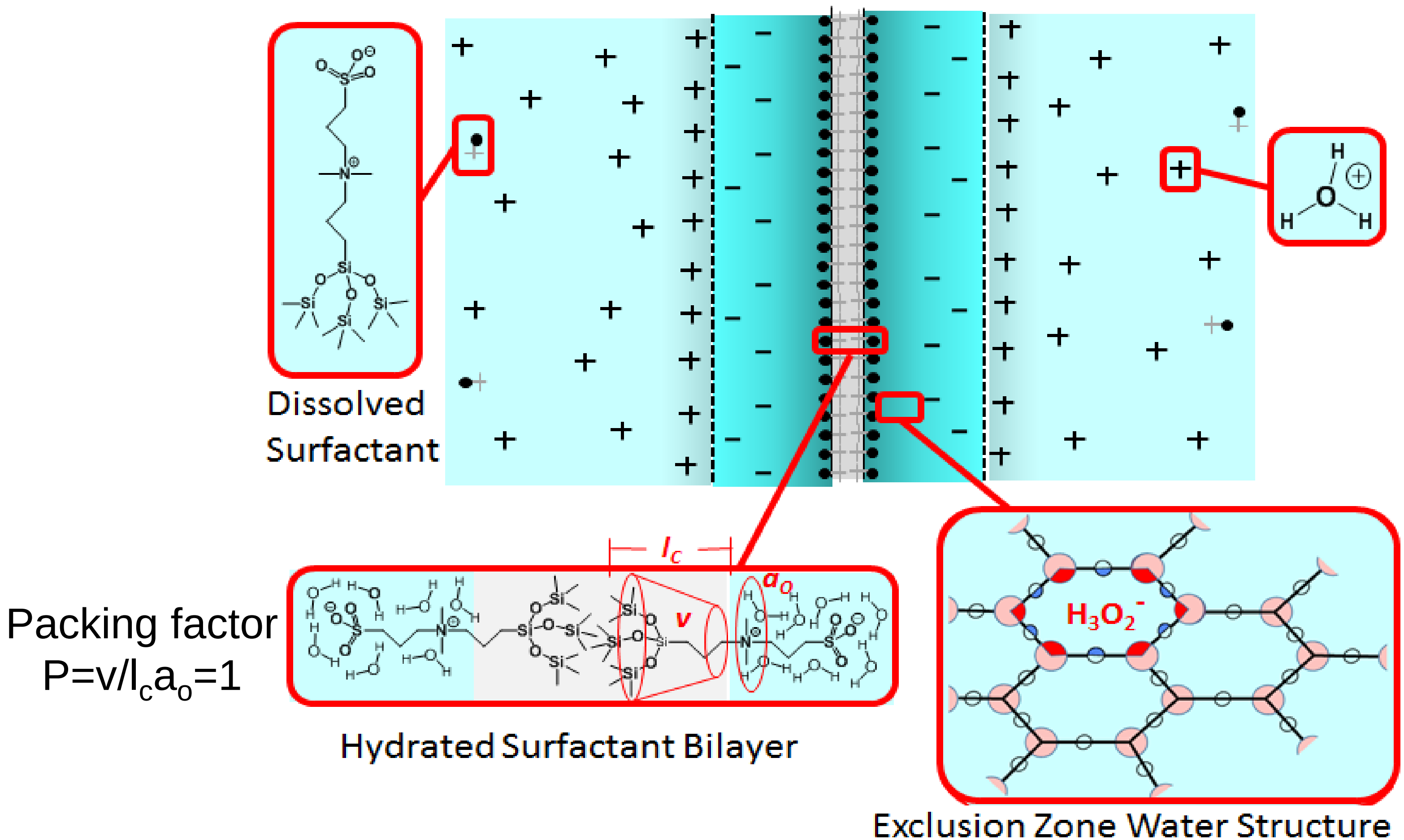
Tetrasilane-sulfobetaine





Results

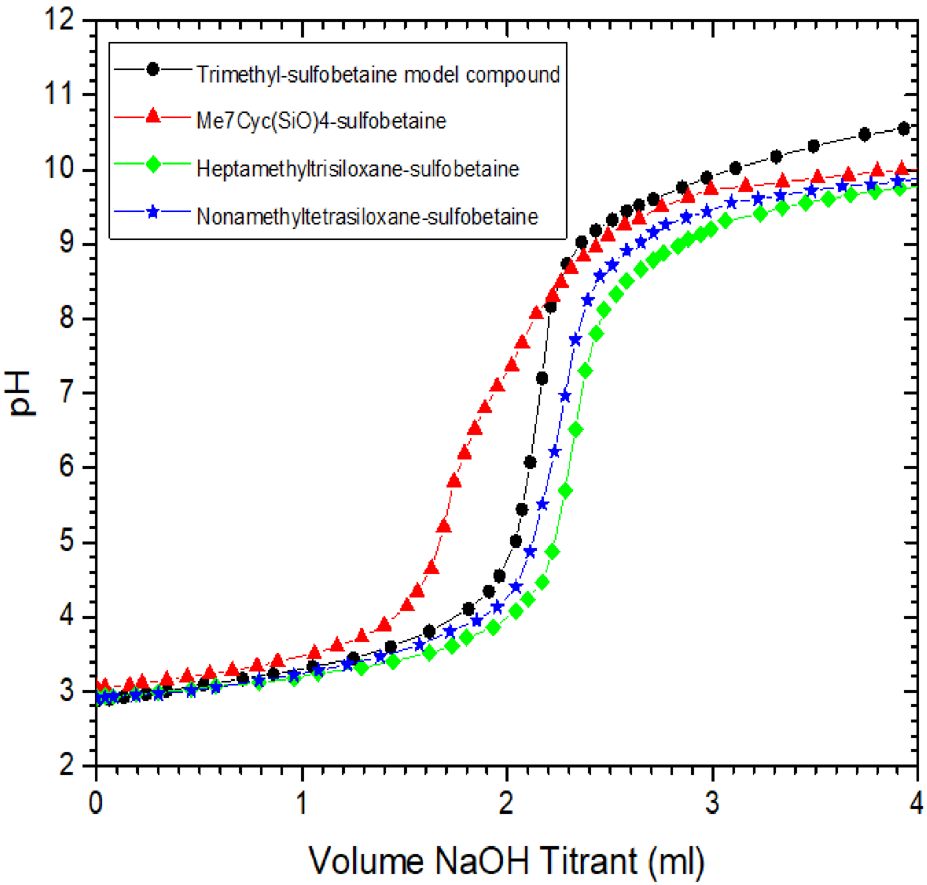
"Exclusion zone" formed at a bilayer micelle of sulfobetaine



The double layer can form a barrier to species like fuel, especially ions, across it

Results

About 4 to 8 water molecules are attached to one sulfobetaine as estimated by titration



Titration results

Property	$(CH_3)_3N^+(CH_2)_3SO_3^-$	CycSi4SB	Si4SB	Si3SB
MW (g/mole)	181	490	504	430
Eq Wt (g/equivalent)	336	612	582	519
$(Eq\ Wt - MW)/MW_{H2O}$	8.6	6.8	4.3	5.0
pKa	3.4	3.4	3.3	3.3

Results

Quantified the effects of surfactant variation

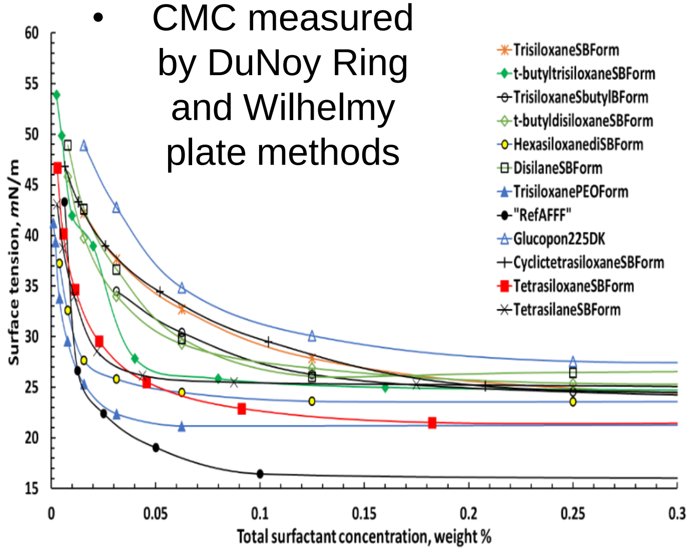
- Made gradual changes to head/tail conformities to enable hypotheses and interpretation of measurements.
    - Used weight % of surfactant in excess of Critical Micelle Concentration (CMC), up to 10xCMC.
    - Used identical foam generation (air sparged through solution).
    - Used identical measurement methods for solution properties, foam properties, and fire suppression.

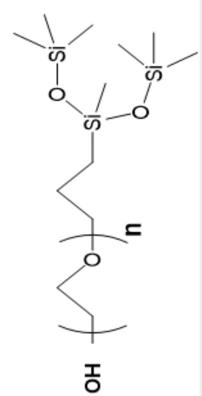
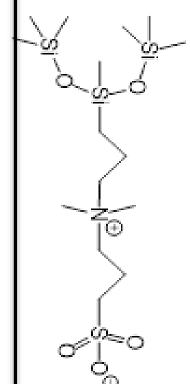
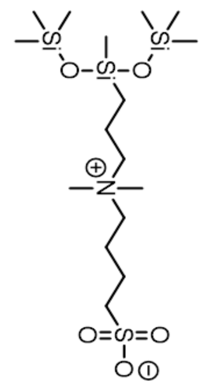
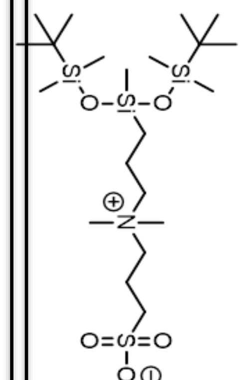
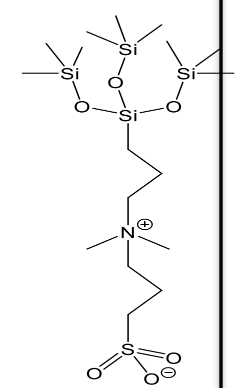
Results

Critical micelle concentration (CMC)

Surfactant Amphiphilicity : reduced → increased →

- CMC measured by DuNoy Ring and Wilhelmy plate methods



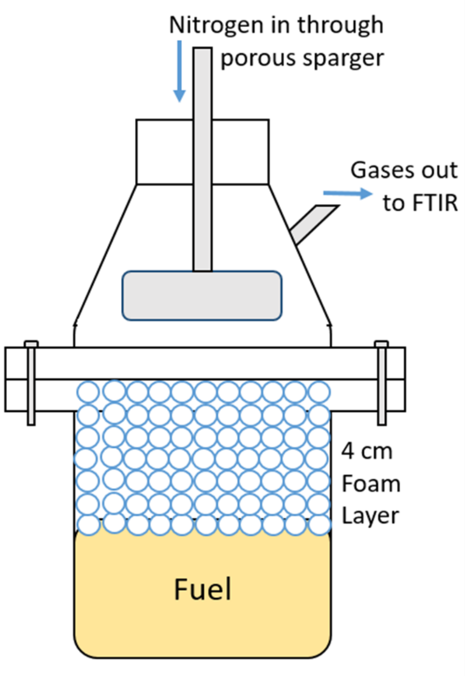
	Reference NRL 502W	Increase head hydrophilicity		Increase tail hydropobicity	
					
CMC mM	0.29	5.3	7.0	0.59	0.27
weight %	0.02	0.23	0.31	0.028	0.014

Smaller the number, better.

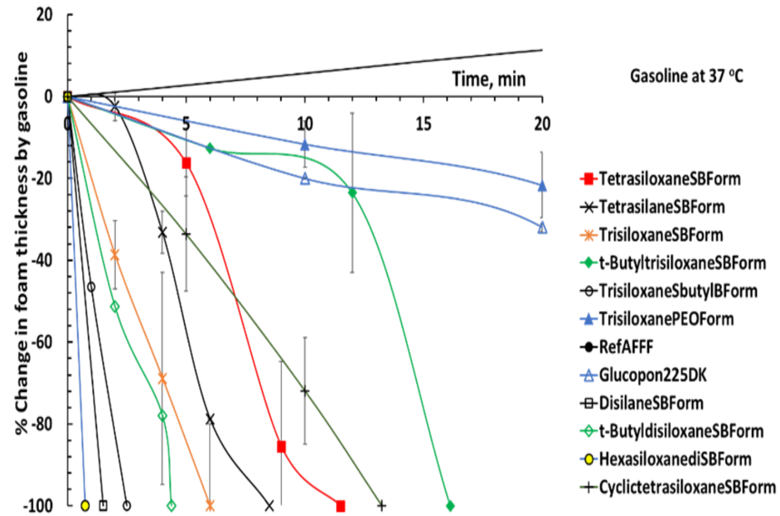
Amphiphilic balance between hydrophilic head and hydrophobic tail reduces CMC

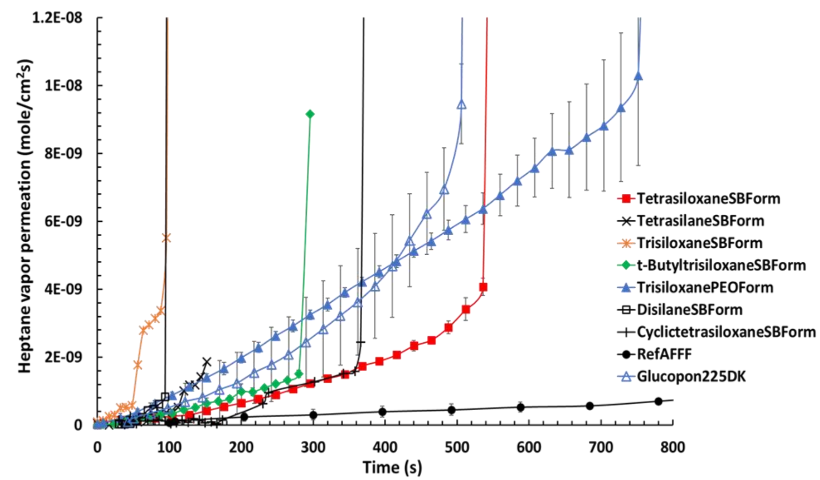
Results

Foam degradation by fuel vapors and vapor permeation



Heptane pool is heated to 60 ^oC

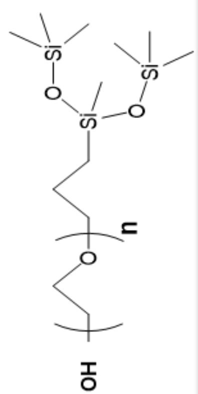
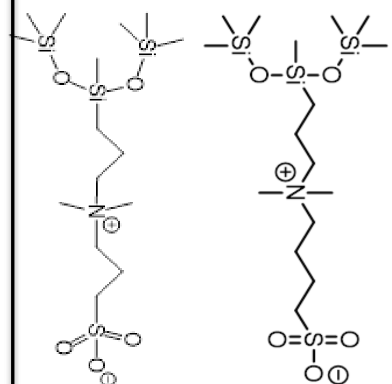
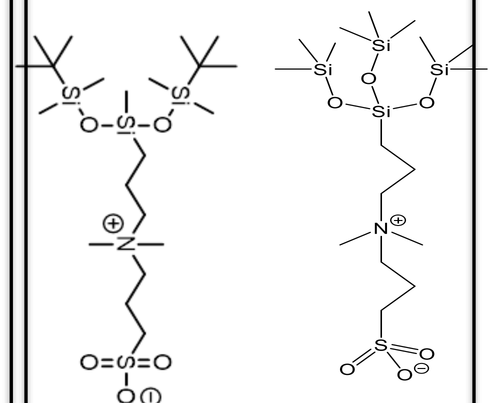




Results

Foam degradation by fuel vapors and vapor permeation

Surfactant Amphiphilicity : reduced → increased →

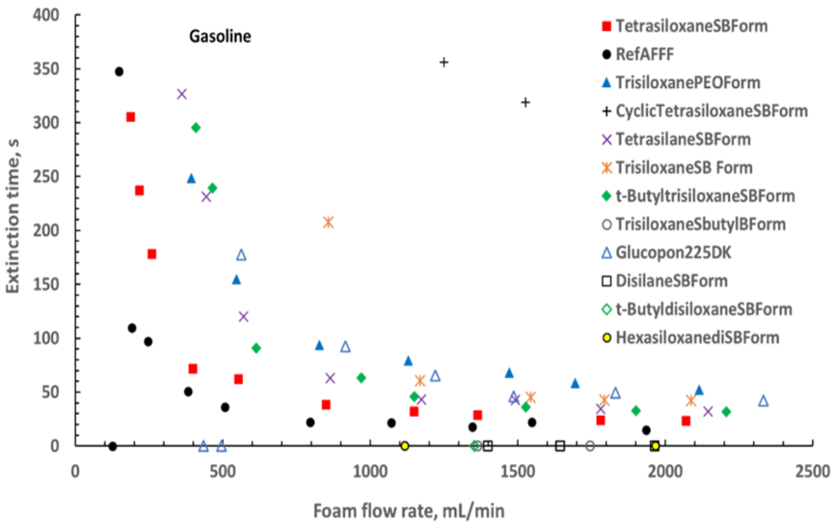
	Reference NRL 502W	Increase head hydrophilicity		Increase tail hydropobicity	
					
Foam life time, min	36	6	2.5	16	11.5
Fuel permeation time, s (for 5E-10 mole/cm²/s)	80	48	----	122	176

Larger the number, better.

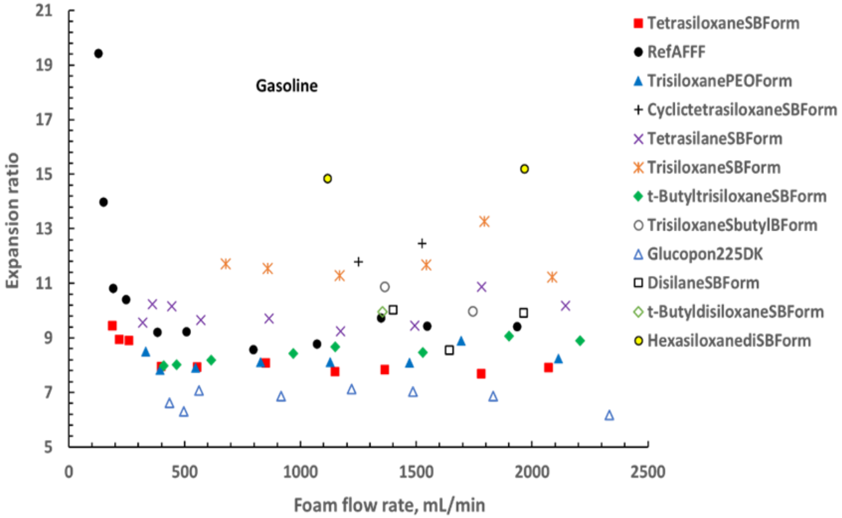
Fuel permeation and foam degradation trend with amphiphilic balance

Results

19 cm diameter gasoline pool fire extinction

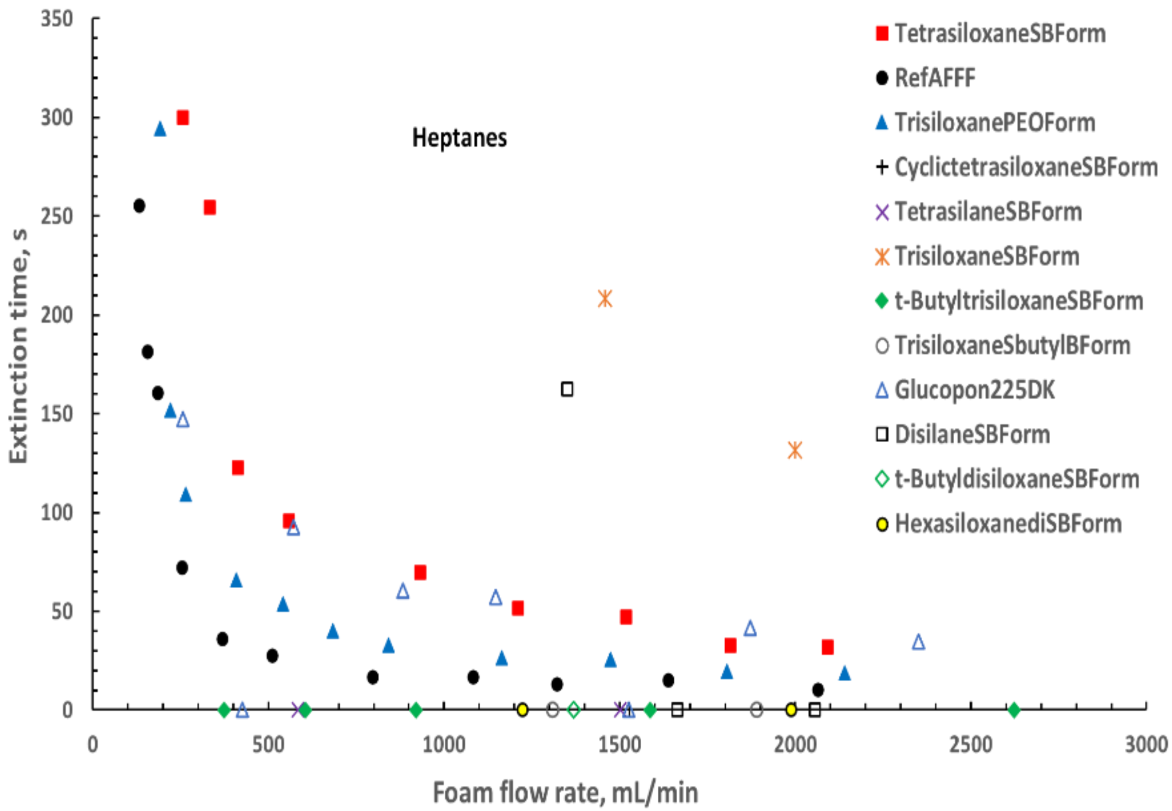


Foam is deposited at a constant rate at the edge of the pool and allowed to spread



Results

Heptane pool fire extinction

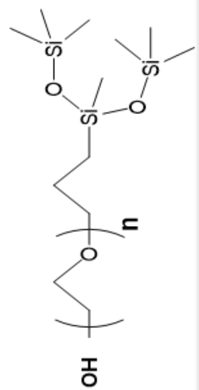
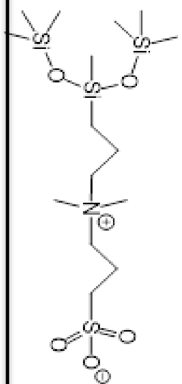
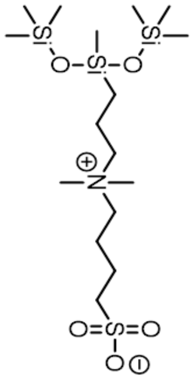
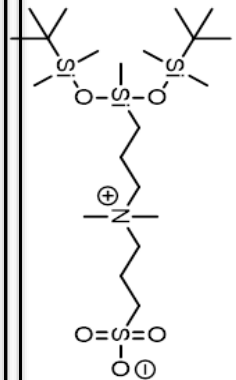
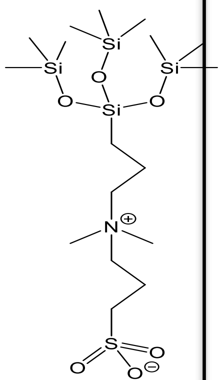


Results

Fire extinction with 19 cm pool

Surfactant Amphiphilicity : reduced → increased →

(600 mL/min foam = roughly 2 gpm/ft^2 for 28ft^2 pool)

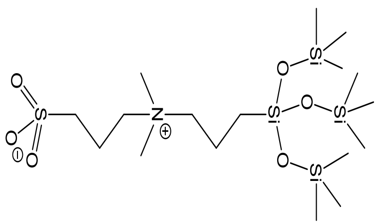
	Reference NRL 502W	Increase head hydrophilicity		Increase tail hydropobicity	
					
Fire extinction time at 600 mL/min foam, sec					
Gasoline	140	>210	>300	91	47
Heptane	43	>300	>300	>300	80

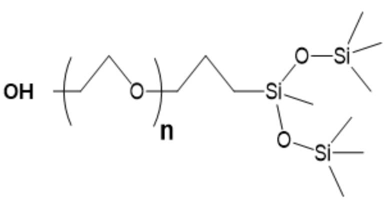
Smaller the number, better.

Fire extinction time trends with amphiphilic balance

Results

28 ft^2 pool fire extinguishment and burnback



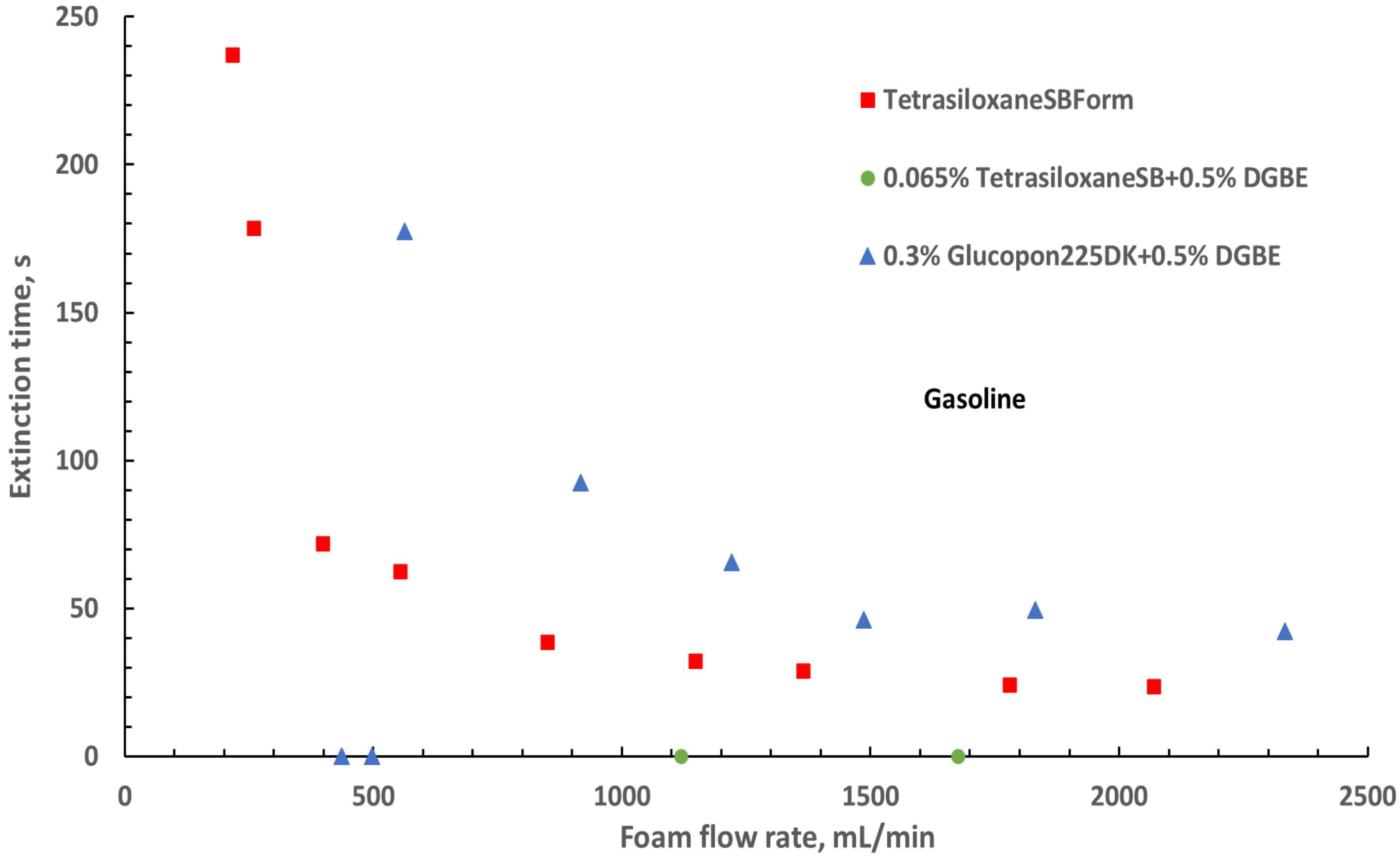


Formulation	Gasoline Extinction, s	Jet-A Extinction, s	Cold Burnback Gasoline, s	Regular Burnback Gasoline, s
TetrasiloxaneSB Form	62	22	360	205
Trisiloxane-PEOForm	No extinct.	39	144	N/A
RefAFFF	26	N/A	433	562

Large scale results are consistent with bench scale qualitatively.

Results

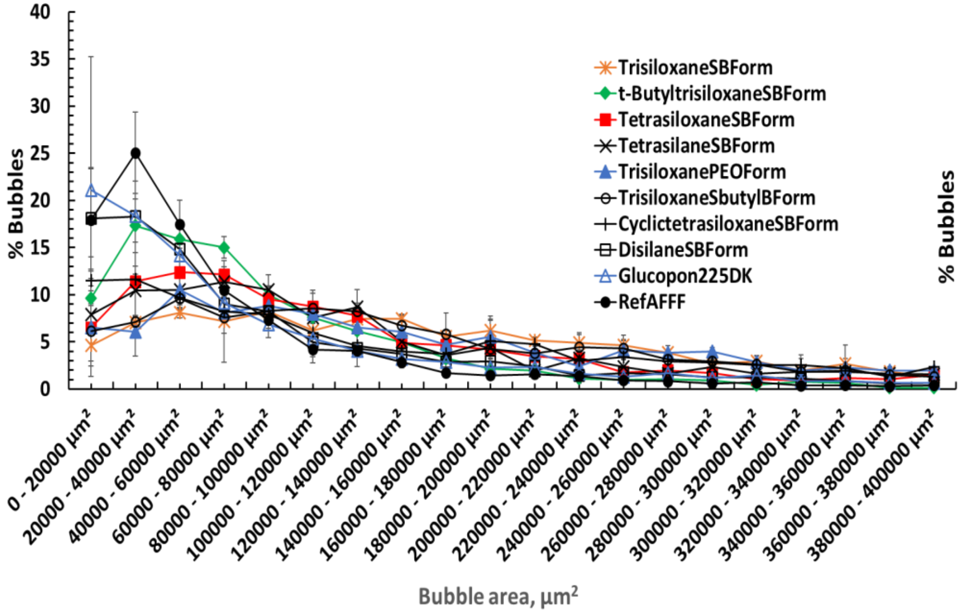
Synergistic effects for gasoline

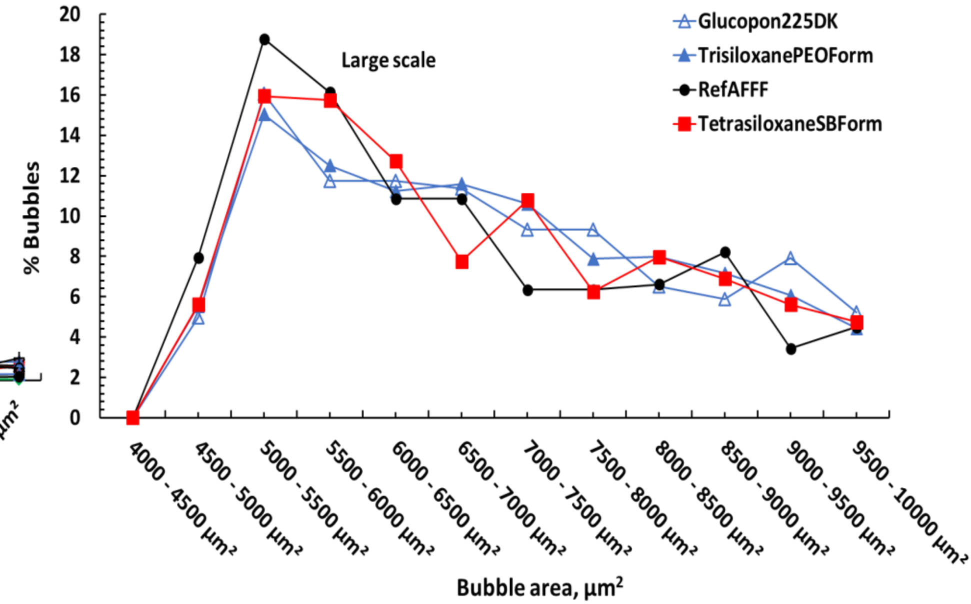


Tetrasiloxane-sulfobetaine shows synergism for gasoline, while Trisiloxane-polyoxyethylene showed for heptane. Need further understanding of surfactant-fuel interactions and oleophobicity.

Results

Choose siloxane-zwitterionic surfactant structures

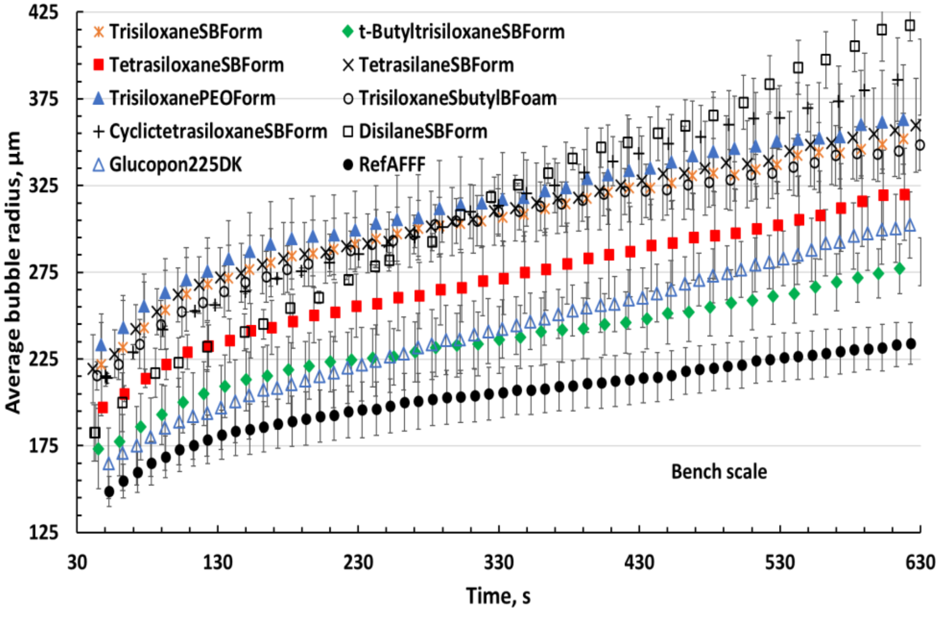


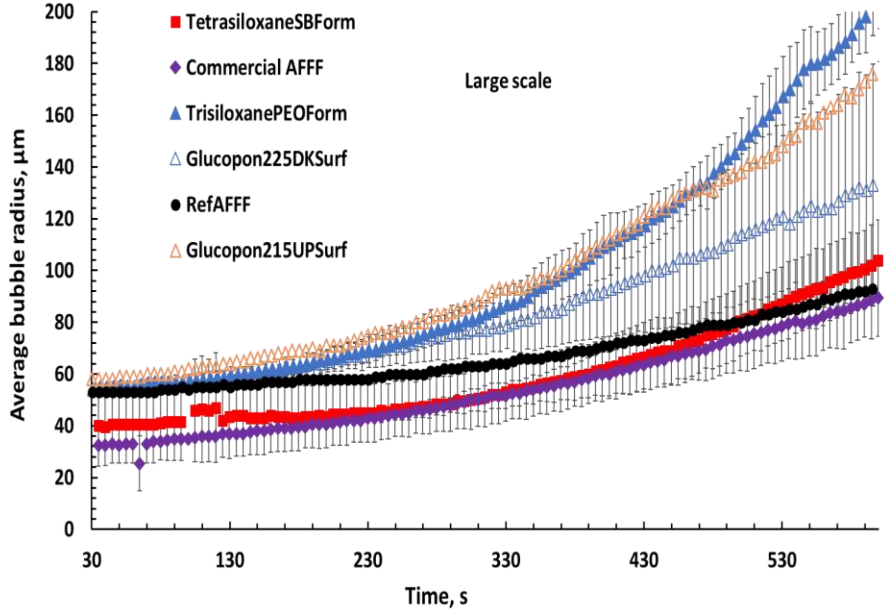


Bubble areas are 10 times smaller at large scale than at bench scale

Results

Choose siloxane-zwitterionic surfactant structures

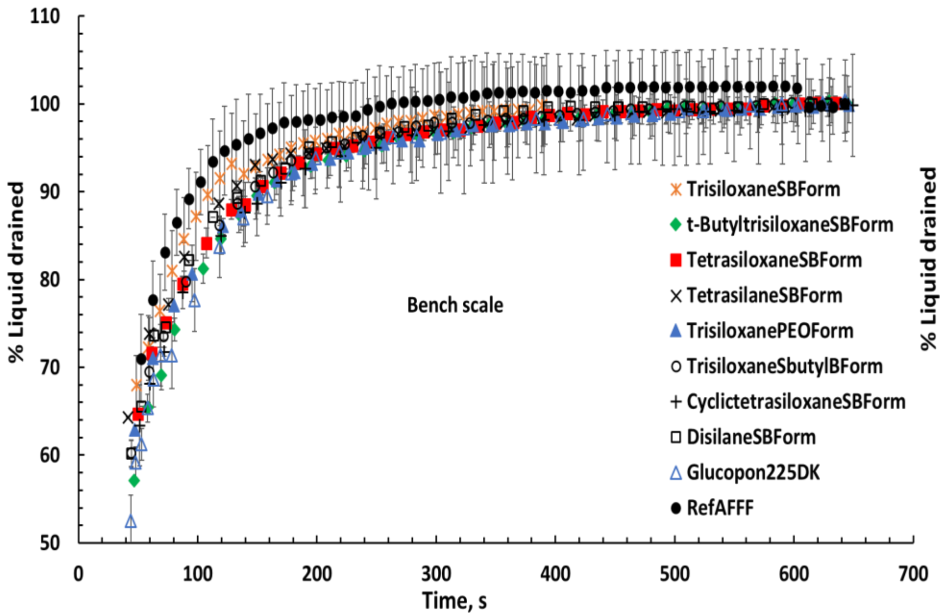


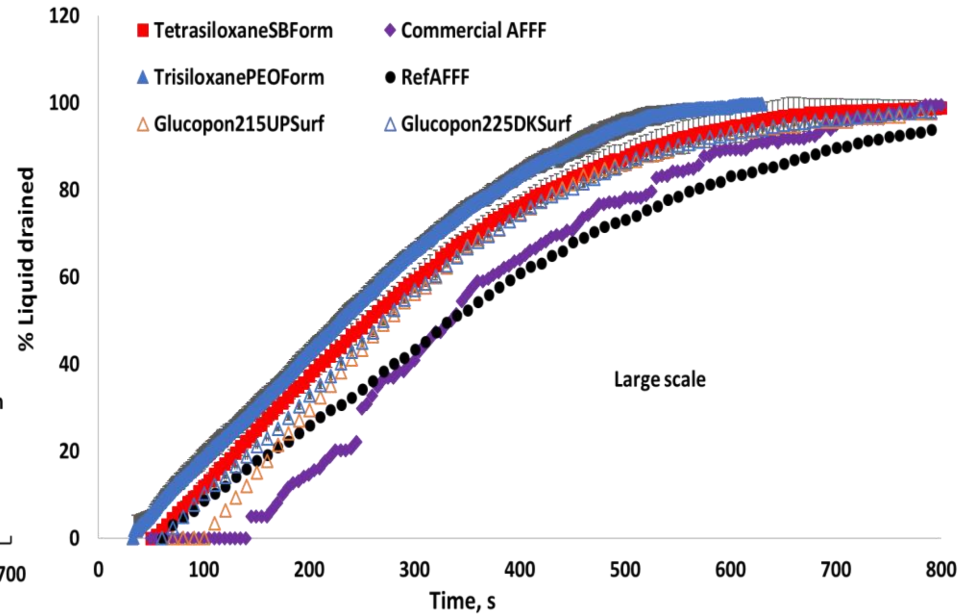


Bubbles coarsen faster at large scale because they are smaller than at bench scale.

Results

Choose siloxane-zwitterionic surfactant structures



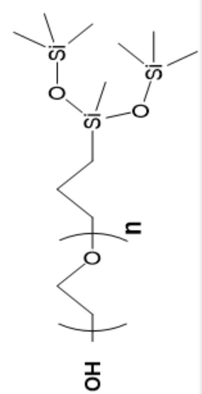
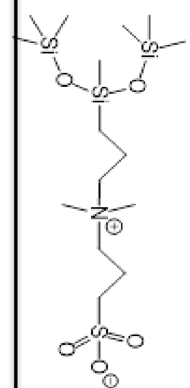
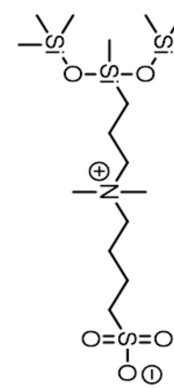
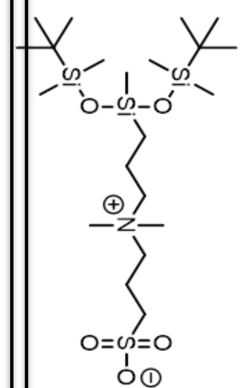
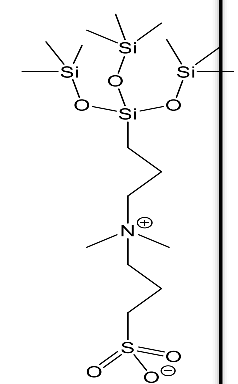


Liquid drainage is much slower at large scale than at bench scale.

Results

Foam characteristics are unchanged by surfactant structure

Surfactant Amphiphilicity : reduced → increased →

	Reference NRL 502W	Increase head hydrophilicity		Increase tail hydropobicity	
					
Initial bubble radius. µm	233	222	215	173	197
Coarsening rate, µm/min	12.4	12.4	12.7	9.9	11.7
% Liquid drained in 2 min	85	91	86	85	89

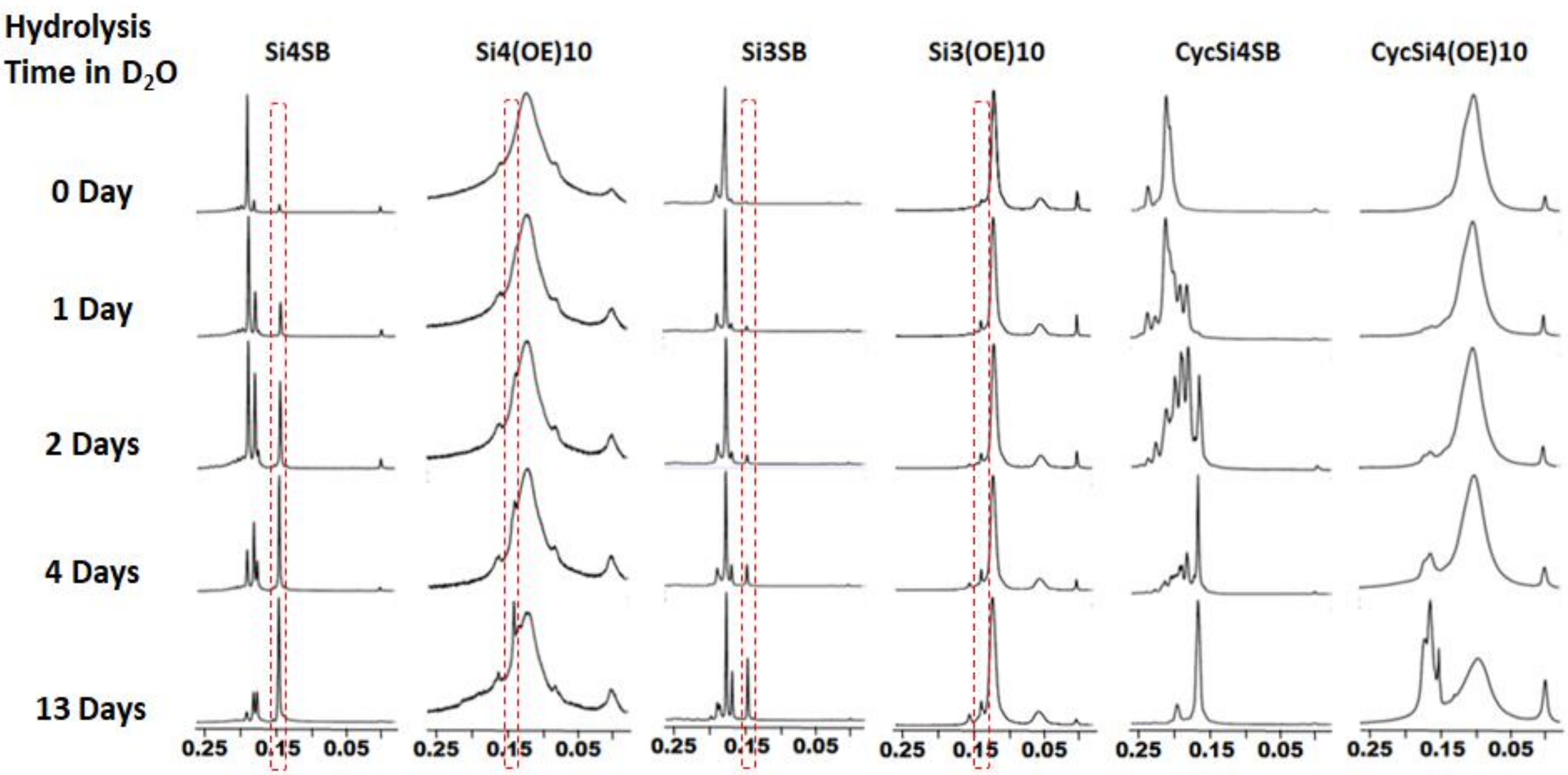
Smaller the number, better.

No trends in bubble size, bubble coarsening rate, and liquid drainage rate

Results

Acidic bilayer of sulfobetaine micelle enhances hydrolysis of siloxane tail in water

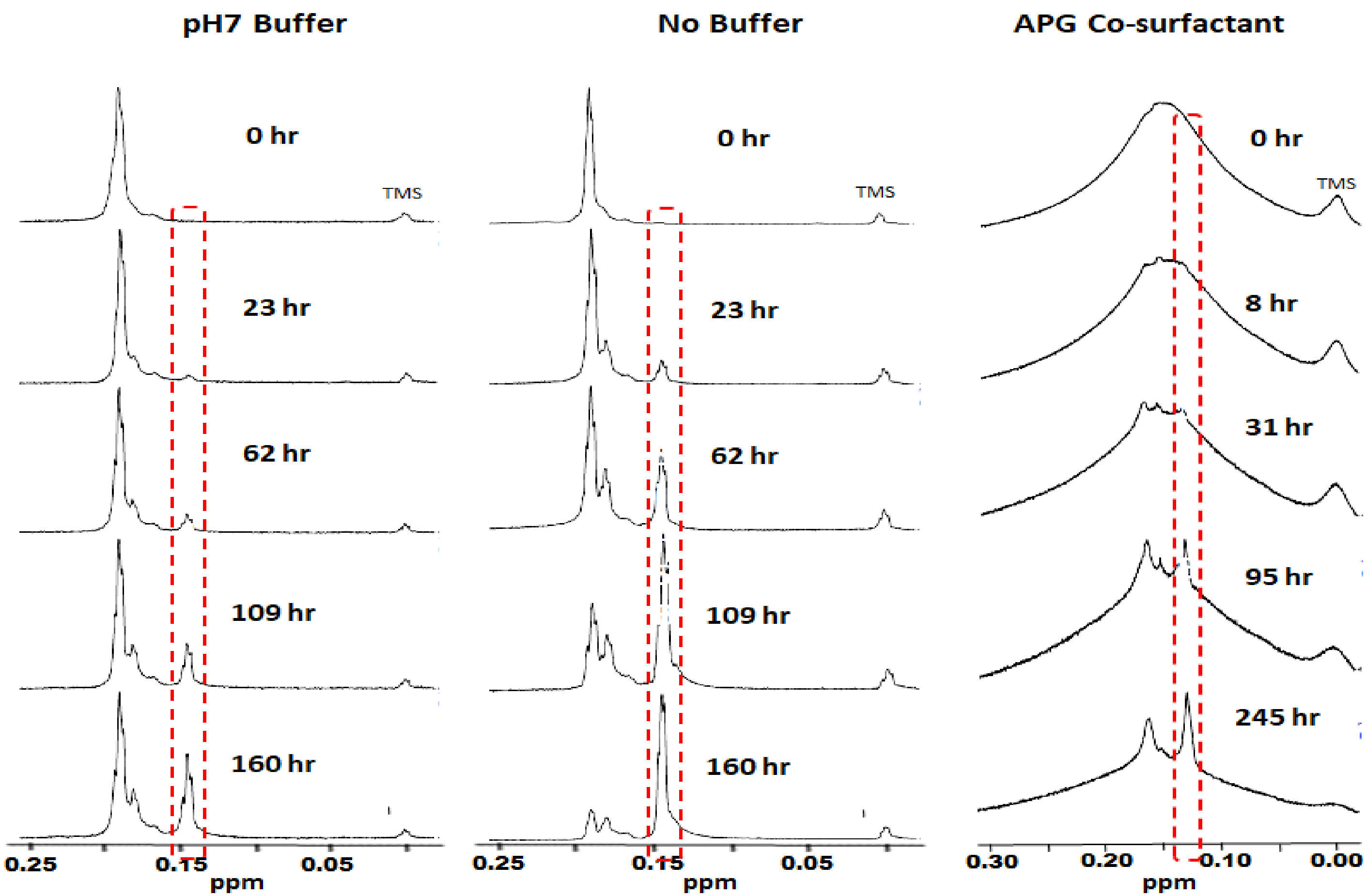
Hydrolysis of surfactant in solution studied by NMR



Hydrolysis is more rapid with sulfobetaine head than with polyoxyethylene

Results

Effects of adding pH7 buffer and alkylpolyglucoside (APG)

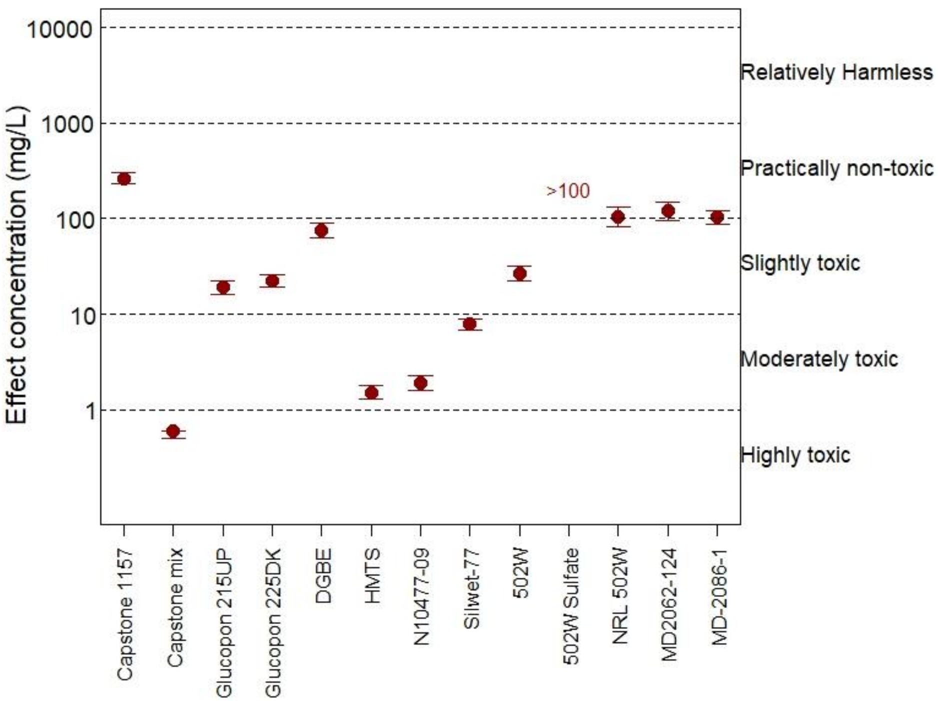


Alkyl polyglucoside co-surfactant in the sulfobetaine formulation slows hydrolysis

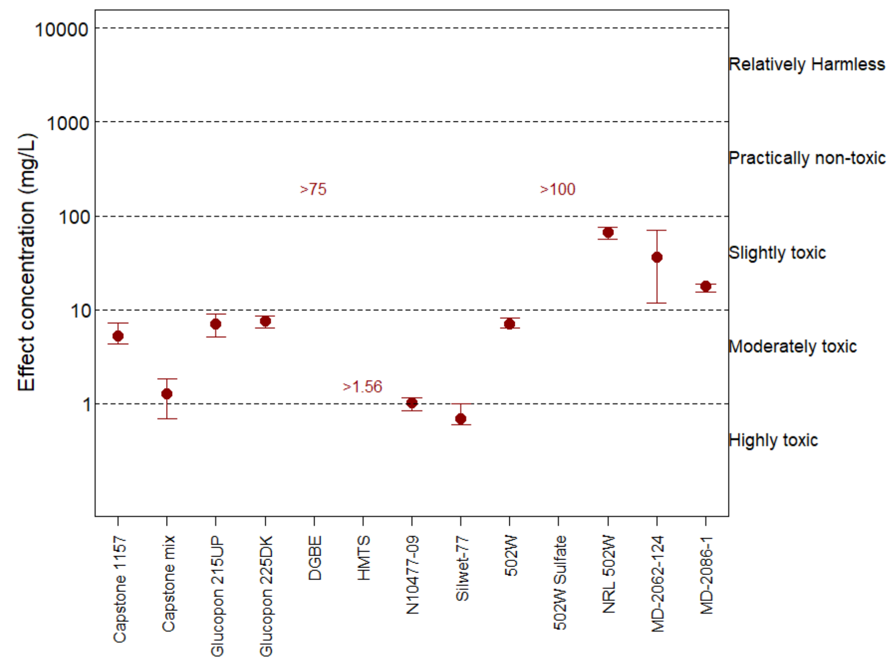
Results

C. dubia acute and chronic survival values (mg/L)

Acute LC_{50}



Chronic IC_{50}

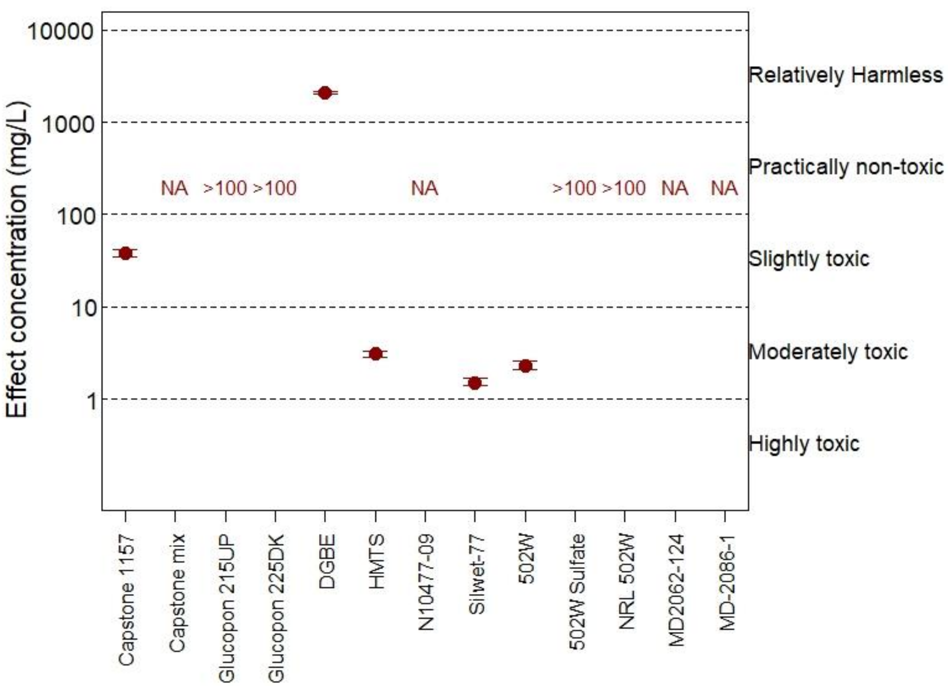


NRL's siloxane-polyoxyethylene and tetrasiloxane-sulfobetaine formulations are slightly to non-toxic to *C. dubia*

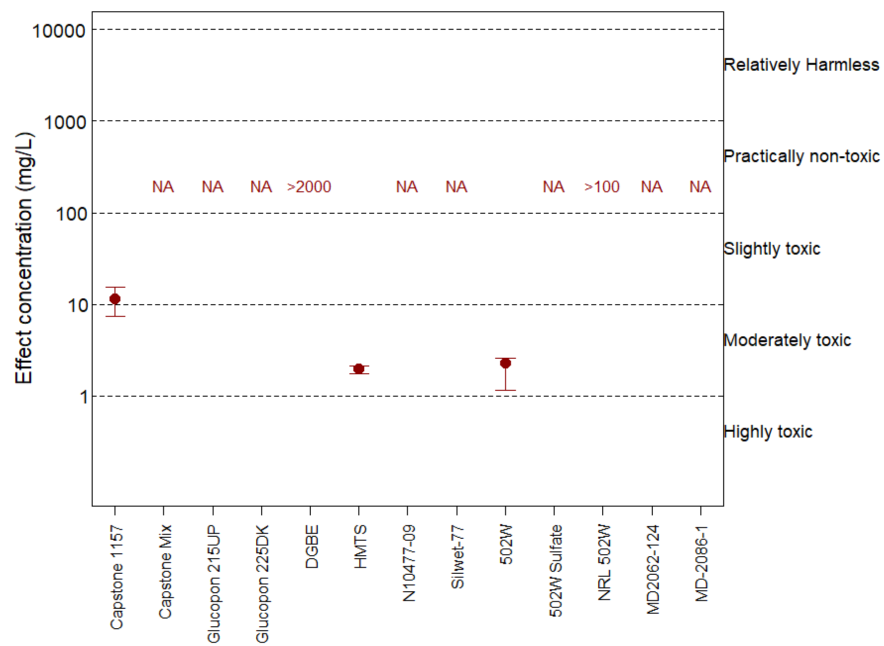
Results

P. promelas acute and chronic survival values (mg/L)

Acute LC_{50}



Chronic IC_{50}



NRL's siloxane-polyoxyethylene formulation is practically non-toxic to *P. promelas and C. dubia*

Next Steps

- This one year project has been completed.

Technology Transfer

- 1 U.S. patent issued
- 2 refereed journal articles submitted
- Presented a poster at SERDP Symposium 2023
- Presented a poster at IAFSS conference in Japan, 2023
- Interest in a database of our siloxane surfactants from toxicologists
  - Currently a journal article on the database is under preparation.

Key Points

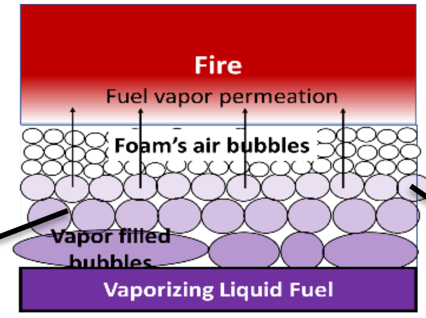
- A small change to surfactant structure has a large effect on fire suppression due to amphiphilicity, synergism, and oleophobicity. Improved gasoline fire suppression.
- Sulfobetaine head attaches to several water molecules to form a water layer suppressing diffusion of fuel vapors.
- CMC, foam degradation, vapor diffusion in foam, and fire extinction trend with surfactant amphiphilic balance.
- Sulfobetaine head exhibits synergism with alkylpolyglucoside for gasoline and polyoxyethylene head for heptane.
- Sulfobetaine and polyoxyethylene have slight to no ecotoxicities for certain species of fish tested to date.
- Sulfobetaine's acidic water layer enhances hydrolysis of siloxane over that of polyoxyethylene.

Future Research

- Fire suppression is determined by the permeation of fuel vapors through a foam layer and surfactant structure has significant effect.
- Bubble lamellae pose the most resistance to permeation of vapors through foams.
- Fundamental studies of vapor diffusion in a single bubble-lamella are essential to isolate and understand surfactant effects more clearly.

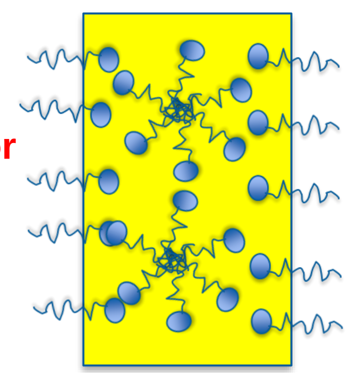
Future Research

Mechanisms of fuel vapor diffusion in a single bubble-lamella and surfactant structure effects



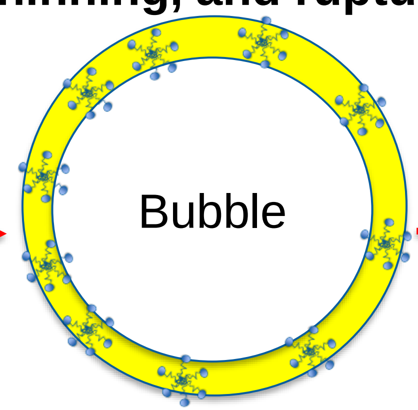
Single layer of surfactant solution with micelles

Fuel vapor



Single bubble, lamella thinning, and rupture

Fuel vapor



- Quantify micelles' effect on vapor diffusion. Vary surfactant concentration, structure, and oleophobicity - quantify the effect on fuel vapor diffusion in a solution layer.
- Quantify bubble growth and lamella thinning effects on vapor diffusion. Vary surfactant structure and H-bonding - quantify effects on bubble rupture.

BACKUP SLIDES

Publications

- NRL patent invention award 2023
- R. Ananth, A.W. Snow, S.L. Giles, M. Davis, K.M. Hinnant 2022 Zwitterionic and glucoside surfactant formulations for firefighting foam applications, Patent US 11, 420, 083 B2, 2022
- K.M. Hinnant, C. Qu, R. Ananth 2023 Stability of an aqueous foam lamella at simulated fire conditions containing surfactants relevant to firefighting foams, 14th International Symposium on Fire Safety Science (IAFSS 2023), Poster presentation, Tsukuba, Japan, October 22-27, 2023
- K.M. Hinnant et al, SERDP/ESTCP Symposium 2023
- R. Ananth, K.M. Hinnant, M.C. Davis, A.W. Snow, C.M. Bunton, S. Karwoski, J.P. Farley 2024 Systematically varying zwitterionic-siloxane surfactant structure to affect interfacial properties, foam stability, and fire suppression, Fire Technology Journal, Submitted.
- A.W. Snow, R. Ananth 2024 Sulfobetaine-siloxanes: A class of self-destructive surfactants, Langmuir, Submitted.

WP22-3391: Development of Zwitterionic Additives to Aqueous Foams to Enhance Suppression of Aromatic and Aliphatic Fuel Pool- Fires

Performers: NRL, NAWCD, USACE-ERDC

Technology Focus

- *Environmentally-friendly firefighting foams*

Research Objective

- *Vary siloxane-sulfobetaine surfactant's head and tail chemical structure to optimize synergism and reduce extraction into gasoline.*

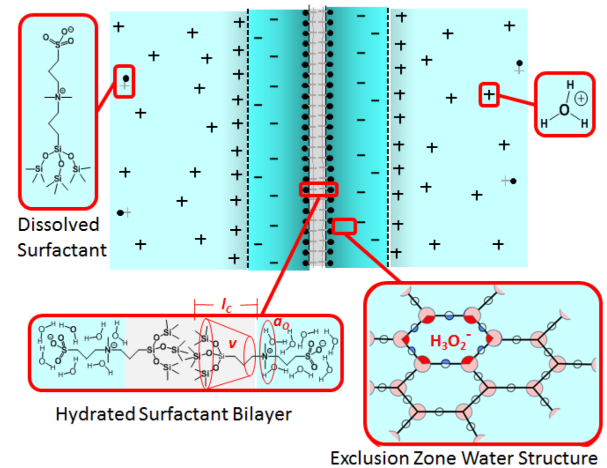
Project Progress and Results

- Developed structure-property-fire suppression trends by gradual and systematic variations of surfactant conformation.
- Small changes in conformation improve gasoline suppression by a lot.
- Amphiphilic balance between hydrophilic vs hydrophobic head and tail groups is increased by varying the structure resulting in improvement..
- Sulfobetaine head tightly attaches to 7 water molecules (Figure) in a bilayer micelle that could suppress fuel vapor diffusion in foams.
- Siloxane-sulfobetaine exhibits synergism with alkyl polyglucoside for gasoline, while polyoxyethylene exhibits it for heptane
- LC_{50}/IC_{50} measurements with *C. dubia show* sulfobetaine formulation has practically no acute toxicity and slight chronic toxicity..

Technology Transition

- *After further research to improve gasoline fire extinction/burnback times/shelf-life, transition to industry (Dow/Colonial Chemical/) for scale-up and MilSpec testing to qualify for shipboard firefighting.*

Formation of electrical double layer attaches water layer attached to sulfobetaine head reducing fuel diffusion into a bilayer micelle



28 ft^2 pool fire extinction and burnback times for gasoline and Jet A.

Formulation	Gasoline Extinction, s	Jet-A Extinction, s	Cold Burnback Gasoline, s	Regular Burnback Gasoline, s
TetrasiloxaneSB Form	62	22	360	205
Trisiloxane-PEOForm	No extinct.	39	144	N/A
RefAFFF	26	N/A	433	562