

NRL/6180/MR—2023/4

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

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October 10, 2023

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REPORT DOCUMENTATION PAGE				Form Approved OMB No. 0704-0188	
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1. REPORT DATE (DD-MM-YYYY) 10-10-2023		2. REPORT TYPE NRL Memorandum Report		3. DATES COVERED (From - To) 6/6/22 – 6/5/23	
4. TITLE AND SUBTITLE Development of Zwitterionic Additives to Aqueous Foams to Enhance Suppression of Aromatic and Aliphatic Fuel Pool-Fires				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) R. Ananth (PI), K.M. Hinnant, A.W. Snow, Caleb M. Bunton, S. Karwoski, J.P. Farley, Dr. M.C. Davis*, and Dr. D.W. Moore**				5d. PROJECT NUMBER WP22-3391	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER 1P02	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Naval Research Laboratory, 4555 Overlook Avenue SW, Washington DC 20375-5320 NAWCWD, Chemistry Department, China Lake, CA 93555 US ARMY ERDC Environmental Lab, Vicksburg, MS 39180				8. PERFORMING ORGANIZATION REPORT NUMBER NRL/6180/MR--2023/4	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Office of the Deputy Assistant Secretary of Defense (Energy Resilience & Optimization) 3500 Defense Pentagon, RM 5C646 Washington, DC 20301-3500				10. SPONSOR / MONITOR'S ACRONYM(S) SERDP	
				11. SPONSOR / MONITOR'S REPORT NUMBER(S) WP22-3391	
12. DISTRIBUTION / AVAILABILITY STATEMENT DISTRIBUTION STATEMENT A: Approved for public release; distribution is unlimited.					
13. SUPPLEMENTARY NOTES *NAWCWD, Chemistry Department, China Lake, CA 93555 **US ARMY ERDC Environmental Lab, Vicksburg, MS 39180					
14. ABSTRACT Environmentally-friendly fluorine-free alternatives are being developed because fluorosurfactants belong to a class of per- and polyfluoroalkyl substances (PFAS), which can pose significant threats to environment and human health. . In the present work, changes to siloxane-sulfobetaine (siloxaneSB) surfactant's head and tail structures are made gradually, one step at a time, to vary hydrophilicity of the head and hydrophobicity of the tail. Several closely related surfactant structures are synthesized to affect the amphiphilic balance between the head and tail. The results suggest that the amphiphilic balance of the siloxane surfactant can have dramatic effects on CMC, interfacial tension, foam expansion ratio, foam degradation, heptane vapor permeation through a foam layer, and fire suppression.					
15. SUBJECT TERMS AFFF replacement Fluorine-free surfactants Firefighting foams Siloxane surfactants					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT UNCLASS	b. ABSTRACT UNCLASS	c. THIS PAGE UNCLASS			Ramagopal Ananth
			UNCLASS	125	19b. TELEPHONE NUMBER (include area code) (202) 404-3197

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Abstract

Objectives: Develop siloxane-betaine zwitterionic additives to enhance fire suppression and burnback resistance for gasoline, which contains aromatic and aliphatic components. Specifically, vary siloxane-betaine's molecular structure to promote bilayer formation at an interface for increased surfactant packing density, and to suppress extraction by fuel. To vary the structure, synthesize new zwitterionic silicones, and evaluate commercial zwitterionic hydrocarbons as functional additives to glycoside foams.

Technical Approach: We will vary size and configuration of the surface-active molecules to optimize the structure. We will systematically vary the siloxane-betaine additive's chemical structure by synthesis and by using commercial zwitterionic hydrocarbon surfactants as additives to the APG foams. We will characterize surfactant layers at air-water, air-fuel interfaces by quantifying composition and packing density. We will quantify the effects of oleophobicity through quantification of change in contact angles due to the presence of surfactant molecules adsorbed at interfaces, solubility in fuel and water or partition coefficients, and equilibrium phase separation (or emulsification). These are in addition to the measurements of foam dynamics and gasoline-fire suppression/burnback at bench scale. Varying molecular structure of the siloxane additive can affect the hydrolysis of the siloxane tails. We will measure acute lethality endpoints (LC₅₀) and chronic sublethal toxicity endpoints (EC₅₀, IC₅₀).

Results: The results presented show that surprisingly small changes to a surfactant molecular structure can result in dramatic changes in CMC, foam expansion ratio, foam degradation, fuel permeation through foam, and improvements in fire suppression. They appear to have only small effects on foam bubble size distributions and liquid drainage for foams generated by sparging method at bench scale but have significant effects for foams generated by a pressurized nozzle at large scale. Many of these changes could largely be explained by the changes to amphiphilic balance of the surfactants involved and we show that the effects of surfactant's amphiphilicity permeates from CMC and foam stability to fire suppression. But, the degree of improvement in fire suppression are fuel specific because fuels affect the degree synergism between the surfactants. Calculated packing parameter of 0.98 for the tetrasiloxaneSB suggests aggregation into bilayer or vesicle shaped micelles. In the micelles, the sulfobetaine head exhibits strong electrostatic interaction with water forming a hydration layer containing 4 to 9 units of water as determined by titration method. The hydration layer is acidic (pKa 3.3) and catalyzes hydrolysis of the siloxane tail with time. While this can help degrade the siloxane in aqueous environment, it can limit shelf life. We found that glucopon component in the formulation as well as adding a pH buffer can slow the hydrolysis.

We also quantified acute and chronic toxicities of individual siloxane, hydrocarbon, fluorocarbon surfactants and RefAFFF using *P. promelas* and *C. dubia* species following standard methods (in collaboration with Dr. David Moore, USACE, ERDC, Vicksburg, MS). Based on results to date with both species, the relative order of toxicity of the tested compounds from least toxic to most toxic is as follows: DGBE<, Capstone 1157<, 502W<, Glucopon 215UP<, Glucopon 225DK<, Silwet L-77,< HMTS-PEO-TMACl, <<RefAFFF.

Benefits: A fluorine-free alternative to the current AFFF will eliminate the bio-accumulative, environmentally persistent, and toxic perfluoro and polyfluoro alkyl surfactants (PFAS). The fluorine-free firefighting foam will lead to lower projected risks to the aquatic environment and human health. In addition, the fluorine-free formulation will meet MilSpec performance standards for gasoline, maintaining essential fire suppression performance of AFFF, critical to DOD applications. The fluorine-free formulation will be a *drop-in* replacement for AFFF, having low viscosity and be compatible with existing hardware.

Executive Summary

1. Introduction

Replacing fluorocarbon surfactant in AFFF with fluorine-free surfactant will significantly reduce the environmental impact because of the elimination of extremely stable C-F bonds, which persist in the environment. In addition, the fluorine-free alternatives must meet the fast pool-fire extinction requirement, which is part of the MILSPEC and is critical for DOD applications. Even though many fluorine-free surfactants are available commercially, a foam with fire-fighting effectiveness comparable to that of AFFF has not been found during the last few decades despite the fact that fluoro-surfactants are very expensive relative to hydrocarbon surfactants. Furthermore, because of high viscosity of the concentrate, the commercial fluorine-free foam-solutions available on the market today would require expensive hardware-upgrades to generate the foams in field application.

Zwitterionic hydrocarbons (Alkyl betaines, alkylamid betaines, and alkylamine oxides) are well-known additives to foams as foam boosters, which help generate more foam per liter of solution. These amphoteric hydrocarbon surfactants consist of both the cationic (amine salt, quaternary ammonium) and anionic (carboxylate, sulfonate, phosphate) moieties within the same molecule (zwitterionic). The zwitterionic additives substantially improve the foamability, foam stability, and rheological behavior of foams especially in the presence of hydrocarbon and silicone oils, which are known to degrade foams [1]. High foam stability is critical when a foam is applied onto a burning fuel pool because the foam forms a barrier to fuel vapors feeding a fire and the fire is extinguished due to the lack of fuel vapor [2,3]. However, while the hydrocarbon tails of zwitterionic additives are hydrophobic, many lack the oleophobic property of a siloxane tail, which is both hydrophobic and oleophobic. The oleophobic siloxane moiety can be crucial to increasing the foam's ability to repel hydrocarbon-fuel vapors and the siloxane's hydrophobicity is crucial for surface activity (amphiphilicity) needed for foam stability [3]. Most commonly available siloxane-polyoxyethylene or polyoxypropylene surfactants consist of permethylated siloxane tail coupled to non-ionic head group. These siloxanes are relatively less toxic than their hydrocarbon equivalents, and exhibit some unusual properties (high thermal stability, low surface tension, low surface viscosity, super-wetting, and UV resistance) due to the dual nature of the siloxane moiety [4]. They also form aggregates featuring surfactant bilayers, plate like micelles, and vesicles due to the conformational flexibility of the O-Si-O bonds [5] and can be important for synergistic fire suppression. The polar nature of the O-Si-O bonds shielded by the methyl groups allows for varying degrees of hydrophobic and oleophobic balance by varying the molecular structure of the silicone surfactants. Increasing the steric shielding can also increase the hydrolytic stability of the O-Si-O bonds, which are susceptible to hydrolysis in very dilute aqueous solutions. The dual nature (hydrophobic/oleophobic) of the permethylated siloxane tail is similar to that of a fluorocarbon surfactant, albeit to a significantly less degree, which could be altered by varying the siloxane molecular structure.

By coupling the siloxane tail to a zwitterion (instead of the non-ionic head), one can form amphoteric silicone additives, which are less common among commercial sources. The zwitterion can impart high foam quality and the siloxane can impart both hydrophobicity and oleophobicity in a single molecule. In addition, the zwitterionic moiety can suppress siloxane extraction into aromatic fuels, which is crucial for suppressing gasoline fires; gasoline contains various aromatic hydrocarbon components that extract silicones from the foams causing considerable foam degradation and poor fire suppression [6].

The zwitterionic siloxane-betaines could be used as additives to foams generated from carbohydrate surfactants to enhance their fire suppression. Carbohydrate foams such as *N*-alkyl glucosamides (NAGA) and alkylpolyglycosides (APG) are known to be less toxic, biodegradable, and are partially based on renewable resources [4]. Carbohydrate surfactants like commercial Glucocon-APGs make high quality aqueous foams but still suffer from foam degradation when exposed to aromatic fuels [6]. Addition of the siloxane-betaine can enhance their stability and suppress foam degradation against aromatic hydrocarbon fuels contained in gasoline.

2. Objectives

Develop siloxane-betaine zwitterionic additives to enhance fire suppression and burnback resistance for gasoline, which contains aromatic and aliphatic components. Develop a new understanding of the synergistic intermolecular mechanisms at an interface controlling suppression. Specifically, vary siloxane-betaine's molecular structure to promote bilayer formation at an interface for increased surfactant packing density, and to suppress extraction by fuel. To vary the structure, synthesize new zwitterionic silicones, and evaluate commercial zwitterionic hydrocarbons as functional additives to glycoside foams.

3. Technical Approach

We have two prong approach; (1) synthesize and evaluate zwitterionic siloxane surfactants in collaboration with Dr. Matthew Davis, NAWCWD, China Lake, CA), (2) evaluation of environmental impact in collaboration with Dr. David Moore (EL-ERDC, Vicksburg, MS). The approach is divided into several tasks as depicted in Figure 1. We varied size and configuration of the surface-active molecules to optimize the structure. We systematically varied the siloxane-betaine additive's chemical structure by synthesis and by using commercial zwitterionic hydrocarbon surfactants as additives to the APG foams. We characterized surfactant layers at air-water, air- fuel interfaces by quantifying composition and packing density. We quantify the effects of oleophobicity through quantification of change in contact angles due to the presence of surfactant molecules adsorbed at interfaces, solubility in fuel and water or partition coefficients, and equilibrium phase separation (or emulsification). These are in addition to the measurements of foam dynamics and gasoline-fire suppression/burnback at bench scale. Varying molecular structure of the siloxane additive can affect the hydrolysis of the siloxane tails. We measure acute lethality endpoints (LC_{50}), chronic sublethal toxicity endpoints (EC_{50} , IC_{50}).

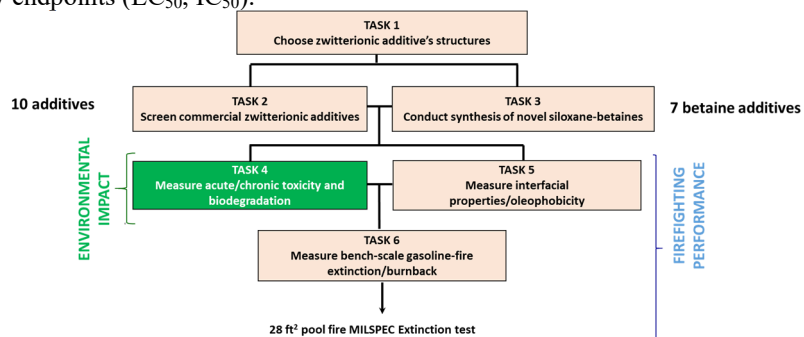


Figure 1. Approach consisting of different tasks.

4. Results and Discussion

The methods are described in detail in our previous paper on siloxane-polyoxyethylene surfactant formulation [9]. Interfacial and static surface tensions were measured using a Du Nouy ring and Wilhelmy plate methods. Surface tension was measured at different concentrations of the total surfactant. CMC values were determined from the log plot of surface tension against volume % of the sum of siloxane and glucopon surfactant concentrates supplied by the manufacturers. Foams were generated by air sparging method and foams are characterized by expansion ratio, liquid drainage, foam degradation when placed on fuel pool, and fuel vapor permeation rate through a foam layer using methods developed in our laboratory [2, 3]. Fire extinction experiments were conducted on a 19-cm diameter pool as described in detail elsewhere [9, 26, 27]. In this method, foams are generated by sparging air continuously at a constant rate through a porous disc while feeding solution continuously to maintain a constant liquid column height (3-cm) above the porous disc (25-50 μm pores, 1.9-cm diameter) by using a leveling system. Foam collects to form 5.5-cm thick layer above the solution surface while flowing out from a 2.5-cm diameter outlet tube connected to the cap of a 0.7-liter plastic bottle (7.6-cm diameter, 15.9-cm height). Foam flow rate is maintained constant during fire extinction and are measured by recording time taken to collect 500 mL volume before and after fire extinction. Foam expansion ratio (volume of foam/weight of foam) is also measured before and after each fire extinction experiment in order to calculate liquid flow rate (foam flow rate/expansion ratio). To apply the foam continuously on to burning fuel pool, the outlet tube from the foam generating plastic bottle is placed about 1-inch above the pool surface. The foam is applied directly at the near-edge of a burning gasoline (alcohol-free) or heptane or Jet fuel pool (circular shape) and allowed to spread across the pool to cover it and until fire extinction, or a maximum time of 5 minutes if there is no extinction. Extinction experiments are conducted at different values of foam flow rates. The jet fuel pool is ignited by pouring about 10 mL of heptane just before lighting. The fuel pool is allowed to burn for 60 s (preburn time) prior to the foam application. The pool consisted of 1-cm thick fuel layer above a 5-cm thick water layer. The fuel level is maintained at 1-cm below the rim of the 19-cm diameter crystallizing dish to accommodate the foam and prevent overflow of the fuel by using a leveling system. The apparatus used for generating the foams and conducting fire extinction were developed previously by us [27]. Large scale 28 ft^2 pool fire testing followed MilSpec methods described elsewhere [28].

4.1. Choose Zwitterionic Surfactants

The siloxane component chemical structures are depicted in Figure 2. They include tetrasiloxane-sulfobetaine (MD2062-54 and N10478-198) and trisiloxane-sulfobetaine (MD2102-16 and N10478-40),

cyclotetrasiloxane-sulfobetaine (N10477-81), t-butyltrisiloxane-sulfobetaine (CB-DTBS-SB), trisiloxane-sulfobutylbetaine with extra methylene in the linker (CB-1-123), tetrasilane-sulfobetaine (N10477-189), linear disilane-sulfobetaine (MD2102-90), t-butylidisiloxane-sulfobetaine (MD2102-99), and double headed hexasiloxane-disulfobetaine. Figure 2 shows variations of the siloxane tail structure and the sulfobetaine head structure.

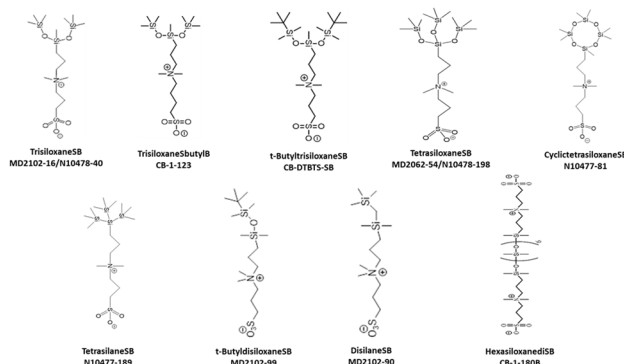


Figure 2. Siloxane-sulfobetaine structures synthesized and evaluated.

Premix solutions are prepared by mixing the siloxane-sulfobetaine surfactant with Guconon225DK and Diethyleneglycolbutylether (DGBE) in concentrations shown in Table 1. The premix is used for generating foams, foam degradation, fuel transport, and fire extinction measurements at bench scale and large scale testing. Premix formulations are typically prepared by mixing 12 g of Glucopon surfactant with 20 g of DGBE in relatively small quantity (30 g) of water in a 100 ml conical flask with a magnetic stirrer first. After all Glucopon is dissolved, the siloxane or fluorocarbon surfactant are added and stirred until complete dissolution. The mixture is then diluted with more water to the specified volume (4 liters).

Table 1. Compositions of the aqueous premix solutions of siloxane formulation versus fluorosurfactant formulations in weight %.

Key surfactant in formulation	% Siloxane surfactant	% Guconon225DK	% DGBE	x CMC _{form}	xCMC _{siloxane}
Tetrasiloxane-sulfobetaine MD2062-54, N10478-198	0.065	0.3	0.5	4.1	4.8
Cyclotetrasiloxane-sulfobetaine N10478-81	0.116	0.3	0.5	< 1.0	3.2
Tetrasilane-sulfobetaine N10477-189	0.05	0.3	0.5	8.5	10.7
Trisiloxane-sulfobetaine MD2102-16, N10478-40	0.2	0.3	0.5	2.3	0.8
t-butyl trisiloxane-sulfobetaine CB-DTBS-SB	0.02	0.3	0.5	5.2	< 0.7
Trisiloxane-sulfobutylbetaine CB-1-123	0.29	0.45	0.5	3.1	0.94
Disilane-sulfobetaine MD2102-90	0.2	0.3	0.5	5	0.67
t-butylidisiloxane-sulfobetaine MD2102-99	0.2	0.3	0.5	4.17	1
Hexasiloxane-disulfobetaine CB-1-1808	0.15	0.225	0.375	10.4	9.4
Trisiloxane-polyoxyethylene (S02W)	0.2	0.3	0.5	16.7	10
Glucopon225DK	0.0	0.3	0.5	1.9	N/A
Perfluorooctyl sulfonamide alkylbetaine Capstone1157	0.3	0.2 (Glucopon215UP)	0.5	6.3	7.5

4.2. Synthesis and Characterization of Siloxane-sulfobetaine Surfactants

We performed synthesis at grams scale in the laboratory initially and scaled the synthesis to tens of grams scale. The precursor starting materials are commercially available A tetrasiloxane-sulfobetaine (MD2062-54) synthesis was conducted as shown in Figure 3a. OTMS is an abbreviation for a trimethylsilyl ether group (O-Si(Me)₃) that are explicitly displayed in Figure 3a. The two-step synthesis gave 74% and 78% conversions for the first and second steps respectively. The first step in the synthesis was the platinum-catalyzed hydrosilation of N,N-dimethylallylamine with tris(trimethylsiloxy)silane. The particular platinum catalyst is the well-known Karstedt soluble complex that is commercially available [33]. The N,N-dimethylallylamine was purchased from Aldrich and used as received. The hydrosilation step usually gave about 70% yield. The mixture containing the product was cooled to room temperature and diluted with hexanes and the mixture containing the sulfobetaine was filtered or pelleted by centrifugation. The product was further purified by recrystallization from EtOAc/MeCN by heating up in the solvent and allowing to cool down which gave a crystalline appearing material that was easy to filter. Proton

NMR of product tetrasiloxane-sulfobetaine in CDCl_3 is shown in Figure 3b. This sample was also referred to as batch MD2062-54. Other siloxane-sulfobetaine surfactants are prepared following similar reaction steps but differed slightly in purification steps employed because of differences in their physical properties.

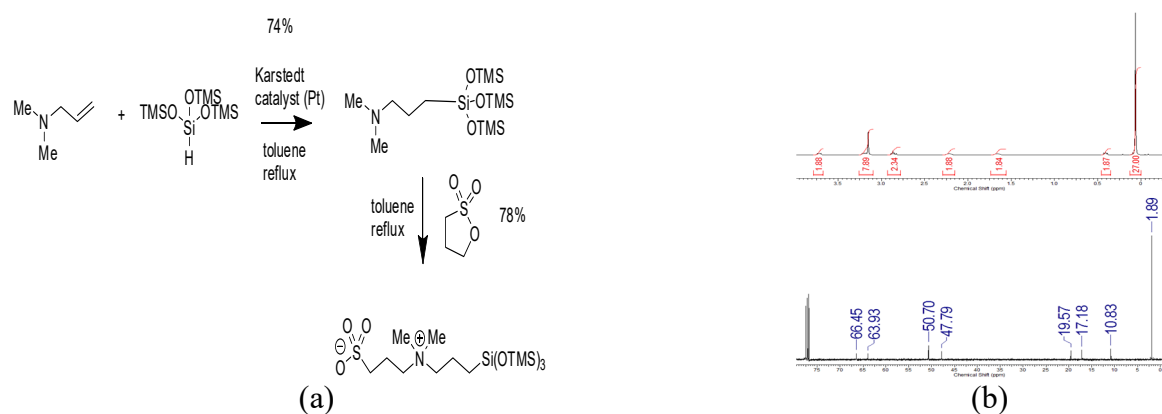


Figure 3. (a) Chemical route used to synthesize tetrasiloxane-sulfobetaine and (b) Proton (*top*) and carbon-13 (*bottom*) NMR spectra of tetrasiloxane-sulfobetaine compound (2062-54) in CDCl_3 .

4.3. Oleophobicity, Surface and Interfacial Tensions, and CMC

Table 2 shows surface tension, interfacial tension, and CMC for different sulfobetaine, trisiloxane-PEO (502W), and Capstone1157 surfactants alone in columns 2 to 5 and for formulations in columns 6 to 9. Table 2 shows surface tension, interfacial tension, and CMC for different sulfobetaine, trisiloxane-PEO (502W), and Capstone1157 surfactants alone in columns 2 to 5. For individual surfactant solutions, it shows changing the head from PEO to SB with a fixed trisiloxane tail has increased interfacial tensions and CMC dramatically. Changing it to SbutylB head from SB head has reduced the interfacial tensions and CMC somewhat. This could be because the zwitterionic head increases the hydrophilicity without increasing the hydrophobicity of the tail causing imbalance in amphiphilicity. The imbalance could cause the SB surfactant to migrate more into bulk water phase requiring greater CMC to saturate air-water interface. The zwitterionic head could also decrease surfactant concentration at the fuel-water interface leading to increased interfacial tension. Changing the tail from trisiloxane to t-butyltrisiloxane tail with the same SB head dramatically reduced the interfacial tensions and CMC but increased the surface tension. Changing to tetrasiloxane tail reduced the surface tension and CMC further while interfacial tensions did not change significantly compared to the t-butyltrisiloxane tail. This could be because they increase the hydrophobicity of the tail balancing it with the increased hydrophilicity of the SB head. Surprisingly, removing the oxygen from the tetrasiloxane tail with tetrasilane tail increased the surface and interfacial tensions significantly but further reduced CMC. This could be because it further increases hydrophobicity of the tail causing an overshoot and slight imbalance with the hydrophilicity of the SB head. Even more surprisingly, changing conformation of the tail from branched tetrasiloxane to cyclic tail could have potentially increased the tail's hydrophobicity causing significant increases in surface and interfacial tensions (with heptane) and in CMC. The precise reasons for this effect of tail's conformation on fire extinction are unclear. As mentioned above, trisiloxaneSB has increased CMC compared to trisiloxanePEO. Changing the tail to t-butyltrisiloxane or disilane further increased CMC as one might expect from the above discussion. Even though hexasiloxane-disulfobetaine is essentially twice the size of trisiloxane sulfobetaine and one might have expected similar CMC values, the double headed surfactant's CMC is much smaller. TrisiloxaneSB and trisiloxaneSbutylB stand out from the rest because of their high interfacial tensions of 10.8 and 8.5 mN/m respectively, especially with heptane. Similarly, trisiloxaneSB and tetrasilaneSB stand out from the rest because of very high or very low CMC values of 0.25 and 0.0047 % respectively. These uniquely different values may suggest imbalance in amphiphilicity and low surface activity. As the siloxane surfactant molecular structure is changed, the surface tension and CMC values of the formulation roughly follow the trends similar to the siloxane surfactant alone as described above. However, the interfacial tensions of the formulations seem to be insensitive to changes in siloxane structure unlike the siloxane surfactant alone and could be because Glucopon surfactant is adsorbing at the fuel-water interface and dominating the interfacial tension values unlike the surface tensions. TrisiloxaneSB and cyclictetrasiloxaneSB formulations stand out from the rest of the formulations because of their high CMC values of 0.22 % and > 0.46 % and may suggest imbalance in amphiphilicity and low surface activity.

Table 2. Surface and interfacial tensions and CMC for surfactant formulations with compositions shown in Table 1. Values for the individual siloxane (or fluorocarbon) surfactants are also shown.

Key surfactant	Solution with key surfactant only			Surfactant formulation in Table 1		
	Key surfactant in water % weight	Surface tension mN/m	Interfacial tension with gasoline, heptane mN/m	CMC % weight (mM)	Surface tension mN/m	Interfacial tension with gasoline, heptane mN/m
Tetrasiloxane-sulfobetaine MD2062-124, N10478-198	0.02	20.6	0.4, 0.7	0.0135 (0.27)	21.2	0, 0.1
Cyclotetrasiloxane-sulfobetaine N10478-81	0.04	24.0	0.4, 1.4	0.0363 (0.28)	24.3	0.4, 1.4
Tetrasilane-sulfobetaine N10477-189	0.005	25.7	2.9, 3.3	0.0047 (0.1)	25.0	0.1, 0.8
Trisiloxane-sulfobetaine MD2102-16, N10478-40	0.3	21.7	5.3, 10.4	0.23 (5.3)	22.7	0, 1.3
t-butyltrisiloxane-sulfobetaine, CB-DTBS-SB	0.022	24.2	0.4, 0.5	≥ 0.028 (≥ 0.59)	23.9	0.7, 1.3
Trisiloxane-sulfobutylbetaine, CB-1-123	0.35	20.8	4.1, 8.5	0.31 (7.0)	22.8	0.9, 1.5
Disilane-sulfobetaine MD2102-90	0.5	28.5	2.9, 5.6	0.3 (8.1)	26.5	1.3, 2.5
t-butylidisiloxane-sulfobetaine MD2102-99	0.5	23.8	N/A	0.2 (4.8)	25.1	0.9, 2.1
Hexasiloxane-disulfobetaine CB-1-180B	0.5	23.5	1.4, 3.1	0.016 (0.16)	24.0	0.6, 1.3
Trisiloxane-polyoxyethylene (502W)	0.5	20.5	3.0, 2.9	0.02 (average 0.28)	22.5	2.2, 2.9
0.3% Glucopon 225DK+0.5% DGBE	0.3	28.1	1.2, 2.9	0.16	N/A	N/A
Perfluorooctyl sulfonamide alkylbetaine (Capstone1157)	0.5	15.8	4.0, 5.5	0.04	16.7	1.0, 1.9

4.4. Foam Degradation on Fuel Pool and Fuel Vapor Permeation Through Foam

When foams are applied on to hot fuel pool (gasoline and heptane), the fuel vapors degrade the foams [2]. A 4-cm thick foam layer generated by sparging method is placed on a gasoline pool, which is held at 37 °C and the decrease in foam layer thickness is measured with time. Figure. 4a shows the percent change in foam layer thickness with time. As the siloxane structure is varied, foam lifetimes (100 % degradation) largely follow the trends in CMC as discussed for the data shown in Table 2 but not precisely. As the trisiloxane head is changed from PEO to SB, the foam lifetime decreases from 36 to 6 min due to reduced amphiphilic balance. When the head is changed further from SB to SbutylB the foam lifetime to 2 min due to further imbalance. With the SB head fixed, as the tail is changed from trisiloxane to t-butyltrisiloxane and tetrasiloxane the foam lifetime increases due somewhat restored amphiphilic balance. Changing the tail to tetrasilane does not appear to affect the foam lifetime very much. Figure 4b shows fuel vapor permeation rate through a 4-cm thick (initial thickness) foam layer placed on top a hot heptane (60 °C) pool. The faster the foam degradation, faster the fuel permeation.

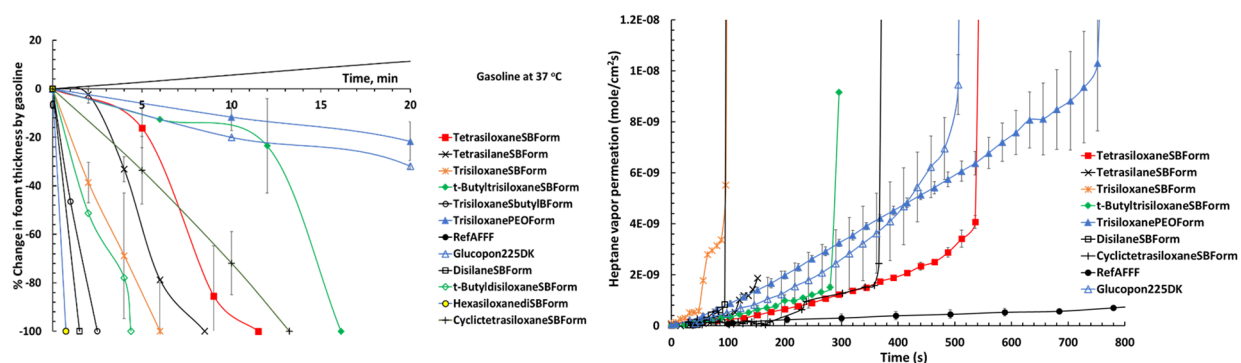


Figure 4. (a) Degradation of 4-cm thick (initial thickness) foam covering warm gasoline pool (37 °C) versus time, (b) heptane fuel mass flux emanating from the surface of a 4-cm thick (initial thickness) foam layer covering a hot (60 °C) heptane pool versus time.

4.5. Bench Scale Fire Performance

Fire extinction is conducted as described in section 2.2 with foams generated from surfactant formulations listed in Table 1. The formulations are tested on gasoline (alcohol-free), heptanes, Jet A and JP5 19-cm diameter fuel pools. Times for complete fire extinction, 90% fire extinction, and foam coverage of the pool are measured visually.

Figure 5a shows fire extinction time versus foam application rate for different sulfobetaine, trisiloxane-PEO (502W), and RefAFFF formulations. It shows changing the head from PEO to SB with a fixed trisiloxane tail has deteriorated fire suppression and changing it to SbutylB worsened. This could be because the ionic head increases the hydrophilicity without increasing the hydrophobicity of the tail causing imbalance in amphiphilicity. Changing the tail from Trisiloxane to t-butyltrisiloxane tail with the same SB head dramatically reduced the fire extinction times and changing to tetrasiloxane reduced the extinction times even further. This could be because they increase the hydrophobicity of the tail balancing it with the increased hydrophilicity of the SB head. Surprisingly, removing the oxygen from the tetrasiloxane tail with tetrasilane tail increased the extinction times moderately. This could be because it further increases hydrophobicity of the tail causing an overshoot and slight imbalance with the hydrophilicity of the SB head. Even more surprisingly, changing conformation of the tail from branched tetrasiloxane to cyclic tail potentially increased the tail's hydrophobicity and fire extinction times dramatically. The precise reasons for this effect of tail's conformation on fire extinction is unclear.

Figure 5a also shows the zwitterionic tetrasiloxane-sulfobetaine formulation (TetrasiloxaneSBForm) has a significantly faster fire extinction than the nonionic Trisiloxane-PEO formulation. TetrasiloxaneSBForm has 60% longer extinction times than RefAFFF and comes closest to RefAFFF fire extinction times among all of the sulfobetaine formulations tested. The fire extinction performance of TetrasiloxaneSBForm on gasoline fire relative to that of RefAFFF is comparable to the heptane fire extinction performance of Trisiloxane-PEO, which also exhibited 60% longer extinction times than RefAFFF on heptane fire. Trisiloxane-sulfobetaine (TrisiloxaneSBForm), Cyclitetrakisiloxane-sulfobetaine (CyclicTetrasiloxaneSBForm), and Trisiloxane-sulfobutylbetaine (TrisiloxaneSbutylBform) formulations have worse extinction times while the rest of sulfobetaines have comparable or improved fire extinction times than Trisiloxane-PEOForm.

Figure 5b shows the effect of siloxane molecular structure on foam expansion ratio. The effects of structure on expansion ratio follow the trends in fire extinction times discussed above. It shows changing the head from PEO to SB with a fixed trisiloxane tail has increased the foam expansion ratio in correlation with the increased fire extinction time. This could be because the surfactant concentration adsorbed at water-air interface of bubbles decreases because of the increased hydrophilicity of the head without increasing the hydrophobicity of the tail causing imbalance in amphiphilicity. However, changing the head to SbutylB had only a small effect on expansion ratio but a significant effect on fire extinction time. Changing the tail from trisiloxane to t-butyltrisiloxane tail with the same SB head dramatically reduced the expansion ratio but changing to tetrasiloxane reduced the expansion ratio even further in correlation with the reduced fire extinction times shown in Figure 6a. This could be because increased surfactant concentration at the water-air interface due to increased hydrophobicity of the tail balancing it with the increased hydrophilicity of the SB head. Surprisingly, removing the oxygen from the tetrasiloxane tail with tetrasilane tail increased the both the expansion ratio and extinction times moderately. This could be because it further increases hydrophobicity of the tail causing overshoot and imbalance with the hydrophilicity of the SB head causing decreased adsorption of surfactant at water-air interface of the bubbles. Even more surprisingly, changing conformation of the tail from branched tetrasiloxane to cyclic tail increased the expansion ratio and fire extinction times dramatically. The reason for this effect of tail's conformation on fire extinction is unclear. The tetrasiloxane-sulfobetaine, nonionic trisiloxane-PEO, and t-butyltrisiloxaneSB formulations have smaller expansion ratios than RefAFFF while other siloxane formulations have higher values. We do not have complete profiles for disiloxane and disilane or the double headed hexasiloxane foams to draw firm trends.

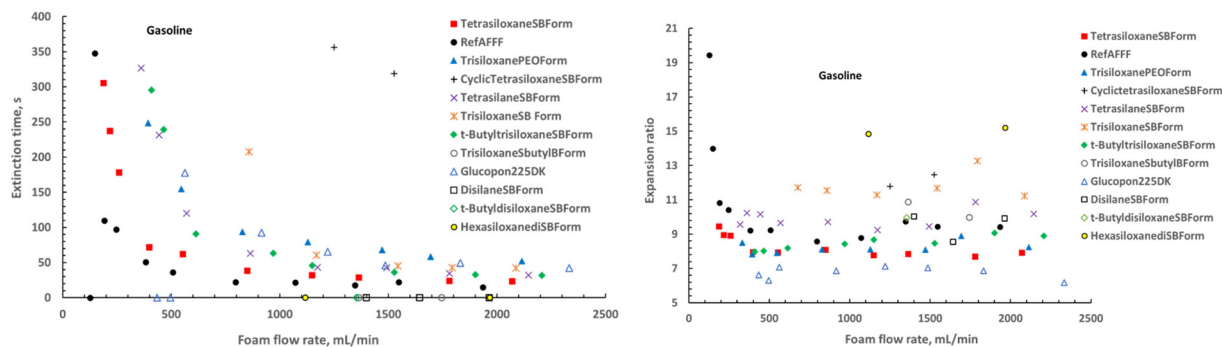


Figure 5. Gasoline fire performances (a) extinction time and (b) foam expansion ratio versus foam application rate onto the edge of a 19-cm diameter gasoline pool fire for the sulfobetaine formulations.

TetrasiloxaneSB formulation does exhibit significant synergistic fire suppression for gasoline fires as shown in Figures 6. Figures 6a shows that the 0.065 % tetrasiloxane with 0.5% DGBE did not extinguish the gasoline fire even at large foam flow rates as indicated by the data points along the x-axis. In fact, the foam could not even cover the pool. Figures 6a also shows that 0.3% Glucopon225DK with 0.5% DGBE could extinguish the gasoline fire but took more than twice the time than the mixture containing both siloxane and glucopon (tetrasiloxaneSB formulation). So, the mixture formulation clearly demonstrates the synergistic fire suppression effects on gasoline fires in sharp contrast to the heptane fire. Figure 6b shows that the sulfobetaine individually generates very dry foam with an expansion ratio of 14 and while Glucopon225DK individually generates a wetter foam with expansion ratio between 6 and 7. The tetrasiloxane-sulfobetaine formulation has an expansion ratio closer the that of Glucopon225DK foam and might help spread the foam more quickly on the pool surface.

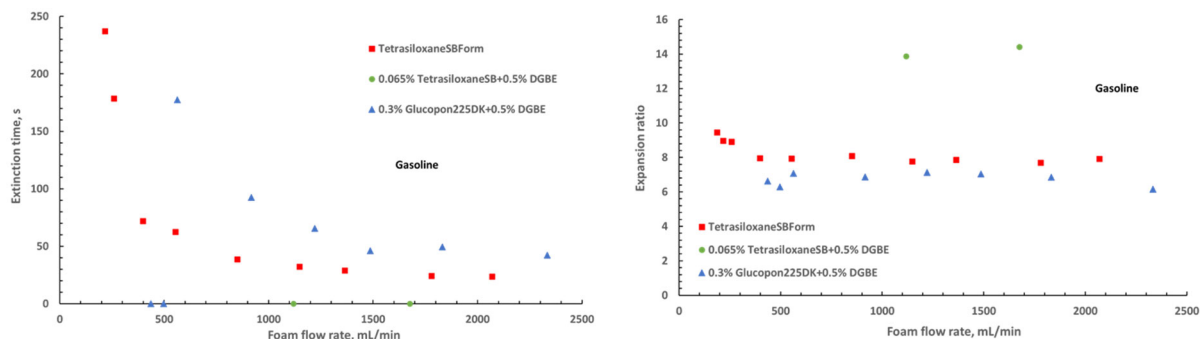


Figure 6. Comparison of individual surfactants versus mixture (formulation) showing synergistic fire suppression (a) extinction time and (b) foam expansion ratio versus foam application rate onto the edge of a 19-cm diameter gasoline pool fire for the sulfobetaine formulations.

4.6. 28ft² MilSpec Fire Extinction and Burnback Testing

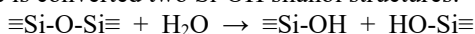
We conducted 28 ft² pool fire MilSpec testing on tetrasiloxaneSB formulation shown in Table 1. It included fire extinction tests on unleaded, alcohol-free, gasoline followed by a burnback test with a total of 90 seconds foam deposition including the extinction time. We also conducted a cold burnback test, where fresh fuel is used in the burnpan and foam is deposited for a fixed 60 s at 2 gallon per minute solution flow rate with a MilSpec aspirated nozzle. The fire extinction test was also conducted for Jet A pool fires. Table 3 lists the fire extinction and burnback times. The tetrasiloxaneSBForm is a clear improvement over the trisiloxanePEOForm in extinguishing a gasoline pool fire in 62 s while the trisiloxanePEOForm could not. The cold burnback times are also much longer for the tetrasiloxaneSBForm. The tetrasiloxaneSBForm also extinguishes Jet-A fire faster than compared to the trisiloxanePEOForm.

Table 3. 28 ft² 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

4.7. Hydrolytic Stability and Shelf Life

The hydrolytic susceptibility of silicone surfactants with its dependence on pH and CMC has been known for some time [42]. It is catalyzed by acid or base and is generally represented by the following reversible reaction wherein a Si-O-Si siloxane structure is converted two Si-OH silanol structures:



It is a very slow process in the pH range of 6-8 but accelerates markedly by acid or base catalysis outside of this range. Surfactants composed of a zwitterionic sulfobetaine hydrophile coupled to a siloxane hydrophobe represent a class of surfactants with exceptional properties, particularly with respect to aqueous surface activity and range of critical micelle concentration (CMC), and fire extinction. An unexpected and striking feature of this surfactant class is a hydrolysis of the siloxane tail caused by the sulfobetaine head in aqueous solution due to self-

created acidity. There is an interesting dependence of hydrolysis rate on the siloxane tail structure. We investigate the origin of the hydrolysis issue, its correlation with structure and possible methods for surfactant stabilization. The hydrolysis appears to be generated by a sheath of water molecules tightly bonded to the surfactant head which become acidic as a result of this bonding and large aggregate formation. New insight described below in detail involves documentation of a strongly bound hydration layer (4.3 to 8.6 water molecules based on measured pKa values) to the sulfobetaine moiety which is speculated to serve as a nucleation site for formation of an aqueous exclusion zone at a surfactant aggregate – water interface. The somewhat unique tendency of ionic siloxane surfactants to form large bilayer and/or vesicle aggregates [37] appears to be an enabling feature for an exclusion zone formation. Adjacent to the negatively charged exclusion zone is an acidic outer region [38] which is speculated to cause acceleration of the hydrolysis rate of siloxane tail of a sulfobetaine-siloxane surfactant. Protective measures investigated include use of a pH7 buffer and of an alkyl polyglucoside co-surfactant. Both of these were very significant in slowing the hydrolysis rate.

^1H NMR protocol focuses on the Si-CH₃ spectral region from a relatively dilute single surfactant in D₂O. Typically 3 mg surfactant is mixed into 2g D₂O followed by addition of a trace of tetramethylsilane (TMS) for chemical shift reference. Spectra are then recorded at intervals from several hours to a couple of weeks depending on magnitude of spectral changes. The Si-CH₃ region (0.25 to -0.02 ppm) of spectra recorded over a duration of 13 days are presented in Figure 7. Figure 7 contains several spectroscopic features of silicone surfactants dissolved in D₂O: a broadening of some Si-CH₃ resonances; the appearance and growth of new Si-CH₃ resonances coupled with decline of initial Si-CH₃ resonances with increasing hydrolysis time. The (OE)10 head structures correlate with a broadening of the Si-CH₃ resonances as compared with the SB head structures bonded to analogous silicone tails. Contributing to this effect is the larger molecular size of the of the (OE)10 surfactant molecules. Also their lower CMC values correlate with a larger population in the micelle environment. In APPENDIX I the micelle effect and resolution of nonequivalent SiCH₃ resonances are examined, but conditions for these data acquisitions deviate significantly from the simple protocol designed to make comparative assessments of surfactant hydrolytic stability under practical conditions. This hydrolytic stability is monitored by examining the spectra of each surfactant for systematic changes over a time of 0 to 13 days. When each of the three sulfobetaine-siloxane surfactants is compared with the polyoxyethylene-siloxane analog surfactant, it is clear that the sulfobetaine surfactant undergoes a much more rapid hydrolysis. For the first four surfactants in Figure 30, the order of hydrolytic susceptibility is: **Si4SB > Si3SB >> Si4(OE)10 > Si3(OE)10**. Also noted in the spectra of these four surfactants is the growth of a major hydrolysis product with a resonance at 0.147 ppm. Since this hydrolysis involves cleavage of a Si-O-Si bond structure by H₂O in these surfactant tail structures, two simple product possibilities are CH₃Si-OH and CH₃Si-O-SiCH₃.

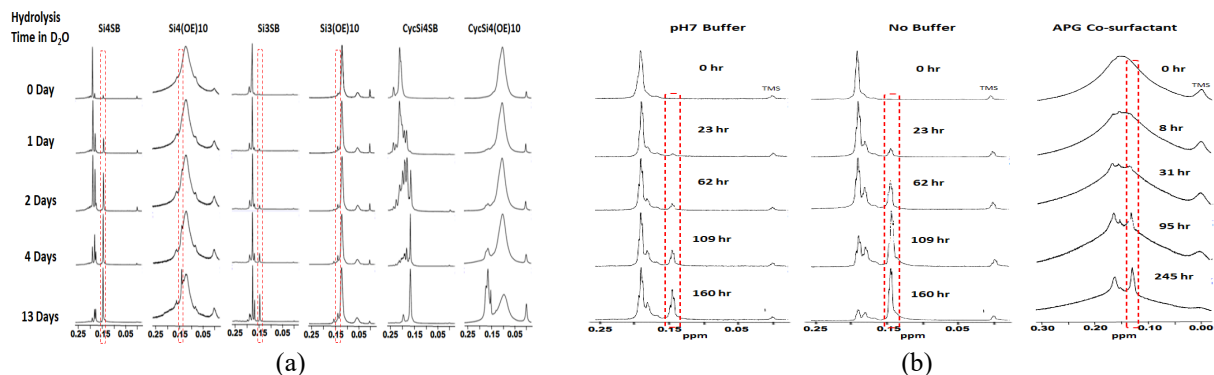


Figure 7. (a) ^1H NMR spectra of the Si-CH₃ region for six surfactants depicting the effects of hydrolysis over a 13 day period. The dashed line encircles a resonance at 0.147 ppm assigned to either of both the (CH₃)₃Si-OH and (CH₃)₃Si-O-Si(CH₃)₃ hydrolysis products. The small resonance at 0.00 ppm is from the trace of TMS reference. (b) ^1H NMR spectra depicting hydrolysis effects for **Si4SB** in pH7 buffered and unbuffered D₂O during a 160 hr period and in a formulation with an alkyl polyethylene glucoside surfactant and diethylene glycol monobutyl ether in D₂O.

To reduce the hydrolysis rate, buffer is added in sufficient quantity to maintain a neutral pH while maintaining dissolution of the surfactant. A pH 7 K₂HPO₄:KH₂PO₄ (1.6:1.0) buffer [40] was prepared in D₂O followed by **Si4SB** addition. The quantity of buffer used was a 10:1 buffer:**Si4SB** weight ratio, and a pH of 7 was measured before and after the experiment. The hydrolysis of this surfactant's tail in the Si-CH₃ region (0.25 to 0.05 ppm) is monitored over time at room temperature. These spectra along with those for a non-buffered control are presented. These results show that the hydrolysis reaction rate is significantly reduced by the buffer. In the NMR spectrum an extensive

broadening of the Si-CH₃ resonance as shown in the 0 hr spectrum. This broadening is attributed to incorporation of **Si4SB** into a large APG micelle, and it is a hypothesis that this APG micelle may afford hydrolysis protection. Over a 245 hr monitoring period small narrow resonances begin to slowly emerge, one of which correlates the trisiloxane hydrolysis products indicated by encircling dashed line in the series of spectra. The bulk of the area of this group of resonances is associated with the initial broad indicating that the degree of hydrolysis is significantly less than that for the non-buffered control and also less than that for the pH 7 buffer which have durations of 160 hr. However, the hydrolysis was not completely suppressed.

4.8. Assess Aquatic Toxicities (Dr. David Moore, USACE ERDC, Vicksburg, MS)

We quantified acute and chronic toxicities of individual siloxane, hydrocarbon, fluorocarbon surfactants and RefAFFF using *P. promelas* and *C. dubia* species following standard methods (U.S. Environmental Protection Agency, 2002. EPA/821/R/012. U.S. Environmental Protection Agency, Office of Water, Washington, DC and U.S. Environmental Protection Agency, 2002. Short-term methods for estimating the chronic toxicity of effluents and receiving waters to freshwater organisms. Fourth Edition. EPA/821/R-02/013). Based on these results the least toxic of the compounds/formulations evaluated included DGBE, 502W sulfate, NRL 502, MD2062-124 and MD2086-1, which generally fell in the slightly toxic to practically nontoxic range (i.e., >10 mg/L). Conversely the most toxic compounds/formulations evaluated included the Capstone mix, HMTS, N10477-09, and Silwett-77, which generally fell in the highly to moderately toxic range (i.e., 0-10 mg/L) for the test species and endpoints evaluated. Based on results of the most complete data set (*C. dubia*) the relative order of toxicity of the tested compounds from least toxic to most toxic for acute survival is as follows: Capstone 1157, 502W Sulfate < NRL502W, MD2062-124, MD-2086-1 < DGBE < 502W < Glucopon 225DK, Glucopon 215UP < Silwett-77 < N10477-09 < HMTS < Capstone mix. The order of relative toxicity was similar in chronic tests with *C. dubia* was similar with the exception of Capstone which was comparatively more toxic in relation to the other compounds/formulation evaluated with a reproductive IC₅₀ value of 5.28 mg/L. The relative order of toxicity for the common set of compounds/formulation (Capstone 1157, DGBE, and NRL502W) tested across all species and endpoints was similar though there were pronounced differences in toxicity between species for some compounds (e.g., DGBE LC₅₀ for an LC₅₀'s of 75mg/L for survival in acute tests with *C. dubia* survival vs. and LC₅₀ of 2092 mg/L for *P. promelas*).

5. Implications for Future Research and Benefits

Further work is needed to improve the fire suppression of siloxane based formulation on gasoline and heptane matching that of AFFF. If successful, it has the potential to be a drop-in replacement for AFFF because of low viscosity of the 3% concentrate, unlike many of today's commercial fluorine-free formulations. The new surfactants and foams have the potential to meet MIL-F-24385F performance standards and have acceptable persistence and aquatic toxicity in order to replace current environmentally hazardous AFFF.

Future works should examine broader variations of head and tail structures of both silicone and hydrocarbon surfactants to strengthen the bubble lamellae so that they contain the fuel vapors within the foams and cut-off fuel vapor supply to the fire. Experiments designed to measure the lamellae strength and suitable metrics should be developed. Hydrogen bonding between surfactants and with water should be quantified experimentally and theoretically using molecular dynamics (MD) simulations to help design synergistic surfactants. Additives that can strengthen hydrogen bonding between the surfactants and foam boosters should also be considered. In addition to fire suppression, burnback performance including thermal degradation of foams should be measured at bench scale. Further improvements to bench scale methods are needed to better correlate with the large scale tests. This should include new bench scale methods for foam generation with the objective of simulating the quality and properties of foams generated by the MilSpec nozzle. In terms of aquatic toxicity, toxicities of formulations should be assessed in addition to the individual components.

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

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Abstract

Zwitterionic-fluorocarbon surfactants have traditionally been used to generate aqueous firefighting foams and are extremely effective in suppressing pool fires on a number of hydrocarbon fuels. However, environmentally-friendly fluorine-free alternatives are being developed because the fluorosurfactants belong to a class of per- and polyfluoroalkyl substances (PFAS), which pose significant threats to environment and human health. It has been shown previously that surfactant interactions with a fuel and water play a crucial role in suppressing degradation of foams exposed to hydrocarbons during fire suppression. In the present work, changes to siloxane-sulfobetaine (siloxaneSB) surfactant's head and tail structures are made gradually, one step at a time, to vary hydrophilicity of the head and hydrophobicity of the tail. Several closely related surfactant structures are synthesized to affect the amphiphilic balance between the head and tail. The surfactant concentrations in water are kept much higher than critical micelle concentrations (CMC) and identical methods and conditions are used across all the surfactants allowing us to correlate surfactant structure to interfacial and foam properties, and fire suppression. The results suggest that the amphiphilic balance of the siloxane surfactant can have dramatic effects on CMC, interfacial tension, foam expansion ratio, foam degradation, heptane vapor permeation through a foam layer, and fire suppression. They show synergism between siloxaneSB and APG in gasoline fire suppression but not on heptane unlike the trisiloxanePEO, which exhibited synergism in heptane fire suppression but not on gasoline as reported previously. A large scale 28 ft² pool-fire suppression demonstrates tetrasiloxaneSB formulation's effectiveness on gasoline but not heptane consistent with the bench-scale measurements. Changes to surfactant structure do not seem to have large effects on foam quality at bench and large scales.. Small changes to surfactant molecular structure and synergisms with a co-surfactant resulted in improved effectiveness but they depend very much on the type of fuel unlike the fluorocarbon surfactants.

We also calculated packing parameter of 0.98 for the tetrasiloxaneSB that suggests aggregation into bilayer or vesicle shaped micelles. The sulfobetaine head exhibit strong electrostatic interaction with water forming a hydration layer containing 4 to 9 units of water surrounding the head as determined by titration method. The hydration layer is acidic (pKa 3.3) and catalyzes hydrolysis of the siloxane tail with time. While this can help degrade the siloxane in aqueous environment, it can limit shelf life. We found that glucopon component in the formulation as well as adding a pH buffer can slow the hydrolysis.

Measurements aquatic acute and chronic toxicities showed the least toxic of the compounds/formulations evaluated included DGBE, 502W sulfate, NRL 502, MD2062-124 and MD2086-1, which generally fell in the slightly toxic to practically nontoxic range (i.e., >10 mg/L). Conversely the most toxic compounds/formulations evaluated included the Capstone mix, HMTS, N10477-09, and Silwett-77, which generally fell in the highly to moderately toxic range (i.e., 0-10 mg/L) for the test species and endpoints evaluated.

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1. Objectives

Develop siloxane-betaine zwitterionic additives to enhance fire suppression and burnback resistance for gasoline, which contains aromatic and aliphatic components. Develop a new understanding of the synergistic intermolecular mechanisms at an interface controlling suppression. Specifically, vary siloxane-betaine's molecular structure to promote bilayer formation at an interface for increased surfactant packing density, and to suppress extraction by fuel. To vary the structure, synthesize new zwitterionic silicones, and evaluate commercial zwitterionic hydrocarbons as functional additives to glycoside foams.

Figure 1 shows a layer of large siloxane tails (red rectangles) on the airside aligned with a layer of large glycoside heads (blue rectangles) on the aqueous side of air-water interface of a bubble or at a fuel-water interface of the pool. The skinny betaine head (red line) of the siloxane and skinny alkyl tail of the glycoside lie in the aqueous and air phases of the interface respectively. The bilayer formation at an air-water interface of a bubble can suppress the rate of fuel permeation through bubbles in the foam layer covering a pool surface. As the rate of fuel vapor permeation through the foam is suppressed, the fire is suppressed because the foam layer more effectively blocks the fuel supply to the fire. Suppression of fuel vapor transport can reduce foam degradation by fuel vapors and increase burnback resistance.

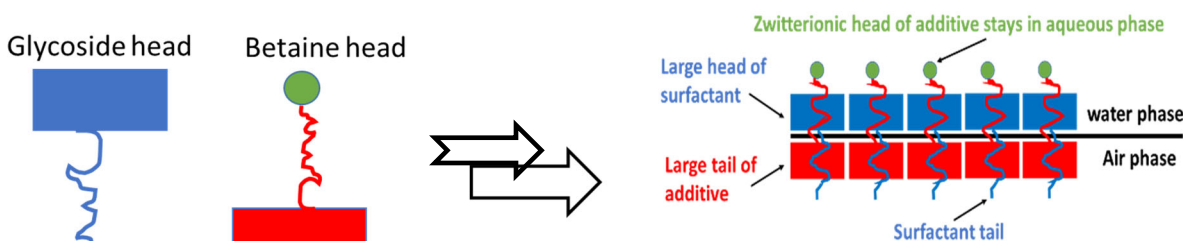


Fig. 1. Zwitterionic additive enables bilayer formation at bubble surfaces; the bilayers form additional barriers in foam to fuel feeding a fire.

Figure 1. Bilayer formation at air-water interface of bubbles in a foam. The bilayer acts as an additional barrier to fuel vapor permeation through a foam layer covering a burning fuel pool.

2. Background

Zwitterionic hydrocarbons (Alkyl betaines, alkylamid betaines, and alkylamine oxides) are well-known additives to foams as foam boosters, which help generate more foam per liter of solution. These amphoteric hydrocarbon surfactants consist of both the cationic (amine salt, quaternary ammonium) and anionic (carboxylate, sulfonate, phosphate) moieties within the same molecule (zwitterionic). The zwitterionic additives substantially improve the foamability, foam stability, and rheological behavior of foams especially in the presence of hydrocarbon and silicone oils, which are known to degrade foams [1]. High foam stability is critical when a foam is applied onto a burning fuel pool because the foam forms a barrier to fuel vapors feeding a fire and the fire is extinguished due to the lack of fuel vapor [2,3]. However, while the hydrocarbon tails of zwitterionic additives are hydrophobic, many lack the oleophobic property of a siloxane tail, which is both hydrophobic and oleophobic. The oleophobic siloxane moiety can be crucial to increasing the foam's ability to repel hydrocarbon-fuel vapors and the siloxane's hydrophobicity is crucial for surface activity (amphiphilicity) needed for foam stability [3]. Most commonly available

siloxane-polyoxyethylene or polyoxypropylene surfactants consist of permethylated siloxane tail coupled to non-ionic head group. These siloxanes are relatively less toxic than their hydrocarbon equivalents, and exhibit some unusual properties (high thermal stability, low surface tension, low surface viscosity, super-wetting, and UV resistance) due to the dual nature of the siloxane moiety [4]. They also form aggregates featuring surfactant bilayers, plate like micelles, and vesicles due to the conformational flexibility of the O-Si-O bonds [5] and can be important for synergistic fire suppression. The polar nature of the O-Si-O bonds shielded by the methyl groups allows for varying degrees of hydrophobic and oleophobic balance by varying the molecular structure of the silicone surfactants. Increasing the steric shielding can also increase the hydrolytic stability of the O-Si-O bonds, which are susceptible to hydrolysis in very dilute aqueous solutions. The dual nature (hydrophobic/oleophobic) of the permethylated siloxane tail is similar to that of a fluorocarbon surfactant, albeit to a significantly less degree, which could be altered by varying the siloxane molecular structure.

By coupling the siloxane tail to a zwitterion (instead of the non-ionic head), one can form amphoteric silicone additives, which are less common among commercial sources. The zwitterion can impart high foam quality and the siloxane can impart both hydrophobicity and oleophobicity in a single molecule. In addition, the zwitterionic moiety can suppress siloxane extraction into aromatic fuels, which is crucial for suppressing gasoline fires; gasoline contains various aromatic hydrocarbon components that extract silicones from the foams causing considerable foam degradation and poor fire suppression [6].

The zwitterionic siloxane-betaines could be used as additives to foams generated from carbohydrate surfactants to enhance their fire suppression. Carbohydrate foams such as *N*-alkyl glucosamides (NAGA) and alkylpolyglycosides (APG) are known to be less toxic, biodegradable, and are partially based on renewable resources [4]. Carbohydrate surfactants like commercial Glucopon-APGs make high quality aqueous foams but still suffer from foam degradation when exposed to aromatic fuels [6]. Addition of the siloxane-betaine can enhance their stability and suppress foam degradation against aromatic hydrocarbon fuels contained in gasoline. Other known stabilizers (polyvinyl alcohol, alcoholamines [7], cellulose, and nanoparticles [8], etc.) can also be used to reduce foam degradation.

Synergism between the siloxane additive and APG are crucial for enhancing fire suppression [9]. Synergism - when used individually, neither surfactant is effective in suppressing a fire but the degree of fire suppression increases dramatically for a mixture. The siloxane-betaines can be expected to exhibit synergism in enhancing gasoline fire suppression unlike the nonionic trisiloxane-polyoxyethylene, which exhibited synergism in suppressing n-alkane fuel fires only. As a part of WP2739 program, Ananth et al [9] discovered that OH-terminated-nonionic-trisiloxane and APG mixtures (0.2 % Glucopon225DK of BASF Co., 0.3% trisiloxane-polyoxyethylene or 502W Dowsil of Dow Silicones Co., and 0.5% diethyleneglycol butylether DGBE of Sigma-Aldrich) exhibited unique synergisms. This is indicated by much quicker heptane-fire suppression than aqueous solutions of the individual components at all foam application rates. They showed that this was due to enhancement of foam stability against heptane pools for the mixture. Even though the precise mechanisms of synergism are unclear, molecular dynamics simulations [10,11] showed that the area per molecule at heptane-water interface decreased (packing density increased) significantly when APG was added to the nonionic

trisiloxane. Varde et al. proposed that the formation bilayer vesicles slowed thinning of a lamella and increased packing density at the interface in a mixed ionic-surfactant system [12]. The geometrical compatibility between the two types of surfactant molecular structures and its effects were also noted in many technologically important applications [13]. The head and tail sizes and configurations in Figure 1 can be crucial for increasing the degree of synergism for gasoline fires.

The betaine head of the siloxane additive interacts with aqueous phase more strongly than a nonionic head and may help suppress siloxane extraction by the aromatic components in gasoline fuel. Snow et al. [6] showed that the mixture of nonionic trisiloxane-polyoxyethylene and APG did not exhibit synergism in extinguishing aromatic fuel fires (trimethylbenzene and toluene) unlike on linear-alkane fires (hexane to dodecane). Further investigations showed that the nonionic trisiloxane surfactant was being extracted from the foams by the aromatic fuels causing excessive foam degradation. In a series of experiments, Snow et al [6] brought trimethylbenzene in contact with aqueous solutions containing a mixture of nonionic trisiloxane and Glucopon, and measured the depletion of siloxane in the aqueous phase with time using NMR. A similar measurement showed negligible depletion of siloxane when the trimethylbenzene was replaced with heptane fuel [6]. The addition of siloxane-betaine to Glucopon 225DK, may not only suppress the siloxane extraction into gasoline but also exhibit synergisms enhancing suppression of fires especially for gasoline.

2.1. Sulfobetaine's water hydration layer

For almost two decades, polysulfobetaines have been investigated for a water hydration layer that is strongly bonded to its zwitterionic structural feature [14-20], especially as marine antifouling or fouling-release coatings [21-25]. The positive and negative charges held in close proximity but spaced apart generate a very strong electrostatic interaction with water molecules bonding them tightly to this region. This phenomenon is sometimes referred to as a superhydrophilicity. The tightly bound water hydration layer has been found to be resistant to protein attachment, making it a good fouling release candidate. Figure 2 shows a comparison of the oxyethylene repeat unit in polyethylene glycol with the sulfobetaine unit in poly(sulfobetaine methacrylate) and was discussed by Wu et al [18]. This depiction may have a direct analogy with the polyoxyethylene-trisiloxane surfactant (502W) and the sulfobetaine-tetrasiloxane.

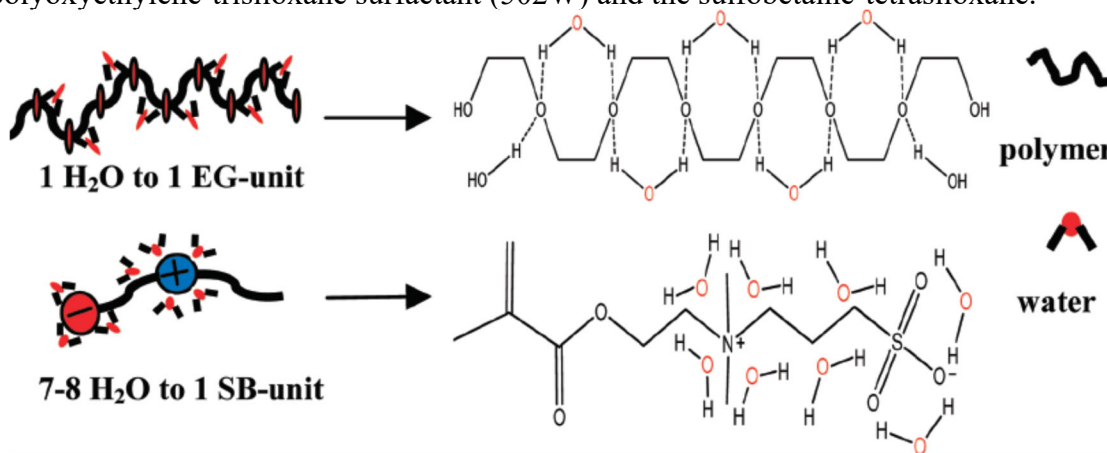


Figure 2. A model for the hydration of polyethylene glycol (EG) and poly(sulfobetaine methacrylate or SB) illustrating the 1:1 ratio of water molecule to oxyethylene repeat unit and the 8:1 ratio of water molecules to sulfobetaine unit as proposed by Wu et al [18].

This depiction in Figure 2 is based on NMR spin-spin relaxation measurements (T_2) and differential scanning calorimetry measurements. Water molecules via hydrogen bonding attach to the oxyethylene chain units and in the process cause the polymer chain to assume an extended conformation. Water molecules interact with the sulfobetaine structure via an electrostatic interaction. The NMR T_2 and DSC measurements indicate that there is a 1:1 ratio of water molecule to oxyethylene repeat unit and an 8:1 ratio of water molecules to sulfobetaine structural feature. The hydrogen-bonded interaction is much weaker than the electrostatic interaction. This correlates with mild heating of solutions of oxyethylene polymers or surfactants displaying a cloud point when the hydrogen-bonded sheath of water is broken and the oxyethylene chain coils into a more hydrophobic conformation and phase separates from water solvent resulting in a haze or cloudy appearance. No such cloud point is observed for sulfobetaine polymers or surfactants.

This physical picture of the sulfobetaine surfactant having a tightly bound water layer to its zwitterionic substructure may have important implications for their use in firefighting foam formulations as they have as antifouling agents [25]. A sulfobetaine surfactant with a siloxane tail group and strongly water hydrated head group would have greater disparity in amphiphilic character than most surfactants whose head is less hydrophilic and tail is less hydrophobic. As such, the sulfobetaine siloxane surfactant will have a relatively low CMC making it efficient at concentrating at the air-water interface, and that it carries a very strongly bound water layer around its head structure giving it better barrier properties against fuel vapor diffusion through a foam bubble lamella. Many of the best fluorocarbon surfactants have a betaine head structure, and this, along with its oleophobic tail structure, may contribute to their extraordinary lamella barrier properties to fuel vapor diffusion. Capstone 1157 is a good example of such a fluorocarbon sulfobetaine surfactant.

3. Approach

Our research to date has shown that small changes to the additive's molecular structure can have significant improvement in fire performance [26]. Three factors were found to be very important: (1) siloxane extraction from an interface by fuel, (2) synergism with the hydrocarbon surfactant (alkylglycoside), and (3) thickness of the hydration layer bound to the betaine head.

We hypothesize that the synergistic effects stem from intermolecular forces between the two types of molecules adsorbed at an interface (bubble surface or fuel-water interface). They include geometrical alignment of the two types of surfactant molecules where the large glycoside head of the alkylpolyglycoside (APG) on the water side of the interface aligns with the large permethylatedtetrasiloxane tail on the air side (or fuel side) to form a bilayer as shown in Figure 1. The bilayer formation at an interface can increase packing density and suppress fuel permeation. The dipole interactions between the alkyl tail of the APG and the siloxane tail could also contribute to the increased packing density at an interface promoting the bilayer formation. Similarly, the bilayer formation could also occur in mixed micelles, which contain both types of surfactant molecules in solution; stable micelles can slow the thin-film rupture, which occurs in steps [12,13]. The bilayer also interacts with fuel vapor molecules. The polar Si-O bonds of a siloxane tail can interact more strongly with the polarity of the aromatic components in gasoline (versus a nonpolar alkane fuel like heptane), and result in extraction of the siloxane from the interface or micelle by gasoline. The ionic sulfobetaine head of the siloxane additive interacts very strongly with water

forming a hydrated water layer [18]. We hypothesize that the hydrated water layer overpowers the electrostatic interactions between the Si-O bonds and the aromatic components of the gasoline. Thus, the ionic betaine head can suppress extraction of the siloxane from the air-water (or fuel-water) interface (or from mixed micelles) by gasoline. This can promote the bilayer formation that increases surfactant-additive packing density at bubble surfaces, resulting in increased fire suppression. Also, increasing the thickness of the hydration layer of water around sulfobetaine head of the siloxane additive for suppressing fuel vapor permeation through foam.

We systematically varied the siloxane-betaine additive's chemical structure by synthesis. In this 1-year research project, we selected only a few head and tail variations of the betaine additive molecule to determine a promising direction having the most impact on fire suppression. We characterized fuel permeation through foams because surfactant micelles in water can carry fuel inside them, enhancing fuel permeation. We performed measurements of foam dynamics and gasoline-fire suppression/burnback at bench scale. Furthermore, any fluorine-free formulation must have low toxicity and acceptable biodegradation. Varying molecular structure of the siloxane additive can affect the hydrolysis of the siloxane tails. The hydrolysis in aqueous solutions may help increase biodegradation, but can affect shelf life adversely, and also affect toxicity. Therefore, we measure hydrolysis of siloxane surfactants. We also measured acute lethality endpoints (LC₅₀), chronic sublethal toxicity endpoints (EC₅₀, IC₅₀), and biodegradation using standard methods. The approach consists of different tasks as depicted in Figure 3.

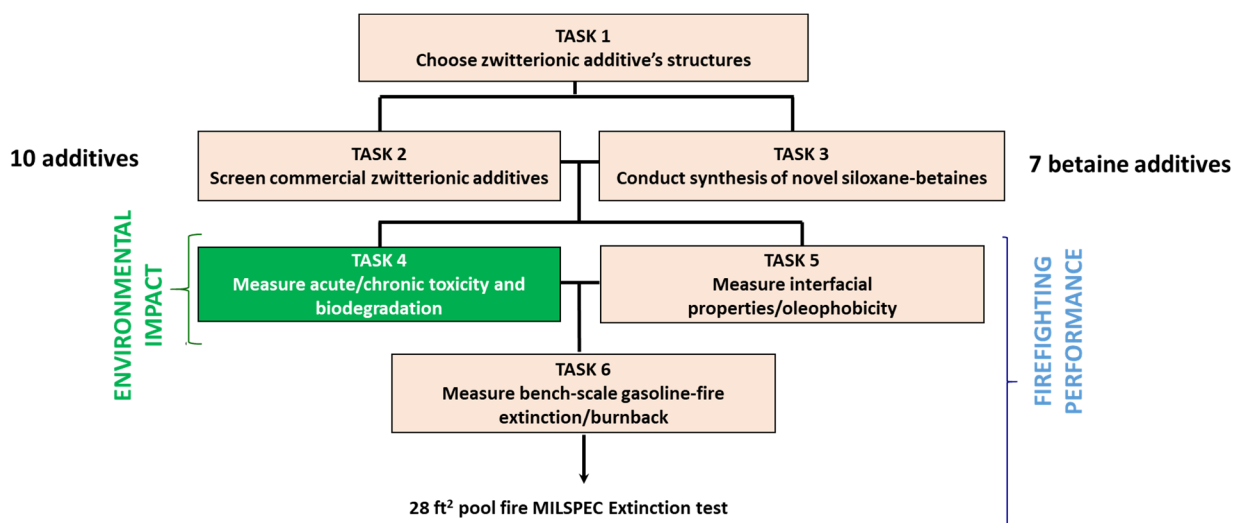


Figure 3. Approach to the development of zwitterionic siloxane additives for enhancing gasoline fire suppression.

4. Materials and Methods

The methods are described in detail in our previous paper on siloxane-polyoxyethylene surfactant formulation [2]. CMC and static surface tensions were measured using a Du Nouy ring (radius 9.58 mm, wire radius 0.185 mm) tensiometer at 20°C (Du Nouy Model Sigma 701, Biolin Scientific Inc., Gothenburg, Sweden) as well as with Wilhelmy plate instrument (NIMA Inc. Helsinki, Finland). Surface tension was measured at different concentrations of the total surfactant (siloxane and glucopon). CMC values were determined from the log plot of surface tension against weight % of the sum of siloxane and glucopon surfactant concentrates supplied by the

manufacturers. Interfacial tensions were measured with the Du Nouy ring tensiometer between a fuel and the siloxane formulations at 20°C. The viscosity was measured at 20°C using a CannonTM-Fenske viscometer (Fisher Model 50 13616B, capillary size #50).

Foams were generated by air sparging method and foams are characterized by expansion ratio, liquid drainage, foam degradation when placed on fuel pool, and fuel vapor permeation rate through a foam layer using methods developed in our laboratory [2, 3]. Fire extinction experiments were conducted on a 19-cm diameter pool as described in detail elsewhere [9, 20]. In this method, foams are generated by sparging air continuously at a constant rate through a porous disc while feeding solution continuously to maintain a constant liquid column height (3-cm) above the porous disc (25-50 μm pores, 1.9-cm diameter) by using a leveling system. Foam collects to form 5.5-cm thick layer above the solution surface while flowing out from a 2.5-cm diameter outlet tube connected to the cap of a 0.7-liter plastic bottle (7.6-cm diameter, 15.9-cm height). Foam flow rate is maintained constant during fire extinction and are measured by recording time taken to collect 500 mL volume before and after fire extinction. Foam expansion ratio (volume of foam/weight of foam) is also measured before and after each fire extinction experiment in order to calculate liquid flow rate (foam flow rate/expansion ratio). To apply the foam continuously on to burning fuel pool, the outlet tube from the foam generating plastic bottle is placed about 2-inches above the pool surface. The foam is applied directly at the near-edge of a burning gasoline (alcohol-free) or heptane or Jet fuel pool (circular shape) and allowed to spread across the pool to cover it and until fire extinction, or a maximum time of 5 minutes if there is no extinction. Extinction experiments are conducted at different values of foam flow rates. The jet fuel pool is ignited by pouring about 10 mL of heptane just before lighting. The fuel pool is allowed to burn for 60 s (preburn time) prior to the foam application. The pool consisted of 1-cm thick fuel layer above a 5-cm thick water layer. The fuel level is maintained at 1-cm below the rim of the 19-cm diameter crystallizing dish to accommodate the foam and prevent overflow of the fuel by using a leveling system. The apparatus used for generating the foams and conducting fire extinction were developed previously by us [27]. Large scale 28 ft² pool fire testing followed MilSpec methods described elsewhere [28].

4.1. Task 1 – Choose zwitterionic and other additives

4.1.1. Individual surfactants

The siloxane component chemical structures are depicted in Figure 4. They include branched tetrasiloxane-sulfobetaine (MD2062-54 and N10478-198), trisiloxane-sulfobetaine (MD2102-16 and N10478-40), t-butyltrisiloxane-sulfobetaine (CB-DTBTS-SB), trisiloxane-sulfobutylbetaine with extra methylene in the linker (CB-1-123), and tetrasilane-sulfobetaine (N10477-189). Also included are cyclic tetrasiloxane-sulfobetaine (N10477-81), linear disilane-sulfobetaine (MD2102-90), and t-butylidisiloxane-sulfobetaine (MD2102-99). A double headed hexasiloxane-disulfobetaine (CB-1-180B) is also included. Figure 4 shows variations of the siloxane tail structure and the sulfobetaine head structure.

Other materials include Glucopon[®] 215 CS UP and Glucopon 225DK (68 to 72 weight % alkyl polyglycoside concentrates contributed by BASF Corporation, Ludwigshafen, Germany and referred to as “Gluc215” and “Gluc225” [27]). CapstoneTM 1157 (35 weight % fluorotelomer sulfonamide alkylbetaine concentrate contributed by Chemours Inc., Wilmington, DE and referred to as “Cap”) [27]; Dowsil 502W additive (100 weight % trisiloxane polyoxyethylene, Dow

Chemical Co., Midland MI); Butyl Carbitol™ (98 weight % diethyleneglycol butylether, “DGBE”, from Sigma Aldrich, St. Louis, MO) [27]. The RefAFFF and 502W-Gluc225DK compositions and properties have been previously characterized in reference [27, 9]. Figure 5 shows chemical structures of trisiloxane-polyoxyethylene surfactant ($y=1$, $z=1$) with a distribution of polyoxyethylene (OCH_2) chain lengths with an average $m=8$ to 12 and a hydroxyl functional group (R-OH).

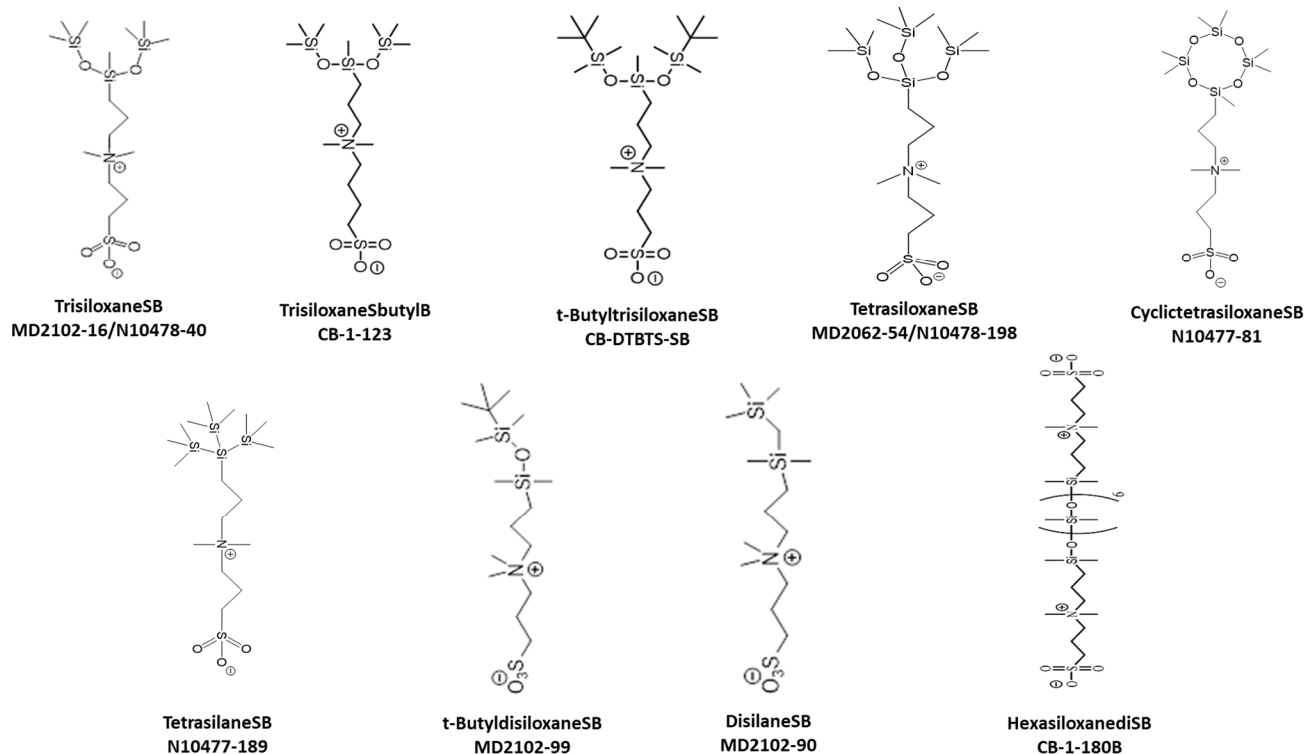


Figure 4. Siloxane-sulfobetaine structures synthesized and evaluated.

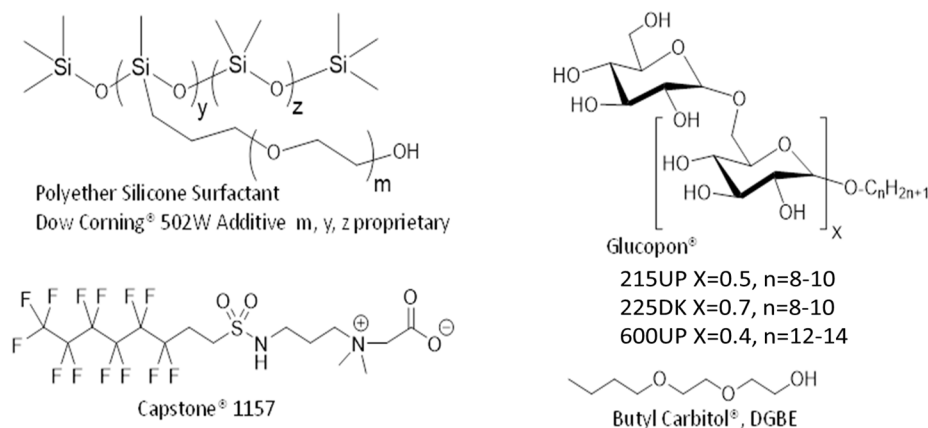


Figure 5. Structures of surfactant components in Siloxane-Glucopon [27, 29, 30] and RefAFFF [27] and Siloxanesulfobetaine-Glucopon formulations.

All three Glucopons have a distribution in both the number of glycoside structural units and in the number of methylene units in the alkyl tail structure as represented in Figure 5, but differ only in the average number of glycoside units of the head group according to BASF literature [30]. Glucopon[®] 600 CS UP, Glucopon[®] 215 CS UP, and Glucopon[®] 225 DK have $x=0.4$, 0.5 , and 0.7 respectively and have $n=8$ to 10 except Glucopon[®] 600 CS UP, which has $n=12$ to 14 . Increased glycoside head size increases the number of OH functional groups on the hydrophilic head. The hydrocarbon surfactant's structures shown in Figure 5 are poly-D-glucopyranose with octyl and decyl alkyl chains [30]. DGBE chemical structure shown in Figure 5 has a relatively long history as a component in AFFF formulations [31] being a good solvent for fluorocarbon surfactants, hydrocarbon surfactants and water. The fluorosurfactant's structure shown in Figure 5 is tridecafluorooctyl sulfonamide alkylbetaine. Comparative analytical data of the Capstone[™] 1157 and the Ref AFFF formulations are displayed in the supporting material provided in Reference [27].

4.1.2. Premix formulations

Table 1. Compositions of the aqueous premix solutions of siloxane formulation versus fluorosurfactant formulations in weight %.

Key surfactant in formulation	% Siloxane surfactant	% Glucopon225DK	% DGBE	x CMC _{Form}	x CMC _{siloxane}
Tetrasiloxane-sulfobetaine MD2062-54, N10478-198	0.065	0.3	0.5	4.1	4.8
Cyclotetrasiloxane-sulfobetaine N10478-81	0.116	0.3	0.5	< 1.0	3.2
Tetrasilane-sulfobetaine N10477-189	0.05	0.3	0.5	8.5	10.7
Trisiloxane-sulfobetaine MD2102-16, N10478-40	0.2	0.3	0.5	2.3	0.8
t-butyl trisiloxane-sulfobetaine CB-DTBTS-SB	0.02	0.3	0.5	5.2	< 0.7
Trisiloxane-sulfobutylbetaine CB-1-123	0.29	0.45	0.5	3.1	0.94
Disilane-sulfobetaine MD2102-90	0.2	0.3	0.5	5	0.67
t-butyl disiloxane-sulfobetaine MD2102-99	0.2	0.3	0.5	4.17	1
Hexasiloxane-disulfobetaine CB-1-180B	0.15	0.225	0.375	10.4	9.4
Trisiloxane-polyoxyethylene (502W)	0.2	0.3	0.5	16.7	10
Glucopon225DK	0.0	0.3	0.5	1.9	N/A
Perfluorooctyl sulfonamide alkylbetaine Capstone1157	0.3	0.2 (Glucopn215UP)	0.5	6.3	7.5

Table 1 shows the compositions of the synthesized siloxane formulations tested for generating foams and used for measuring foam degradation, fuel transport, and fire extinction at

bench scale and large scale testing. Premix formulations are typically prepared by mixing 12 g of Glucopon surfactant with 20 g of DGBE in relatively small quantity (30 g) of water in a 100 ml conical flask with a magnetic stirrer first. After all Glucopon is dissolved, the siloxane or fluorocarbon surfactant are added and stirred until complete dissolution. The mixture is then diluted with more water to the specified volume (4 liters).

Because the siloxane surfactants are custom synthesized at laboratory scale in small quantities, their concentration in a formulation is kept small to achieve a measurable effect over that of Glucopon surfactant only solution. Attempt is made to completely dissolve the siloxane into the aqueous premix solution and not use excessive quantities, which are too costly for use in practice. Therefore, the siloxane to Glucopon ratio and ratio with CMC may vary among the formulations tested. The presumption is that the siloxane surfactant molecular structure has a much larger effect on fire suppression than the effects of variations in composition of the premix formulation, which are kept much higher than corresponding CMC values as shown in the fifth and sixth columns of Table 1.

5. Results and Discussion

5.1. Tasks 2 and 3 – Synthesis and Structural Characterization

5.1.1. Tetrasiloxane-sulfobetaine (MD2062-54)

The siloxane-sulfobetaines are not available commercially and we very briefly describe general synthesis for this class of chemical structures because they are well established in chemical synthesis literature [32]. We performed synthesis at grams scale in the laboratory initially and scaled the synthesis to tens of grams scale. The precursor starting materials are commercially available as shown in Figure 6. Hydroxyl terminated allylethylene reagents are commercially available and are shown in Figure 6. The hydroxyl group can be converted to the dimethylamine group via a chloro-intermediate. Using SciFinder for the amine- and chloro-structures below indicated that they are also available commercially.

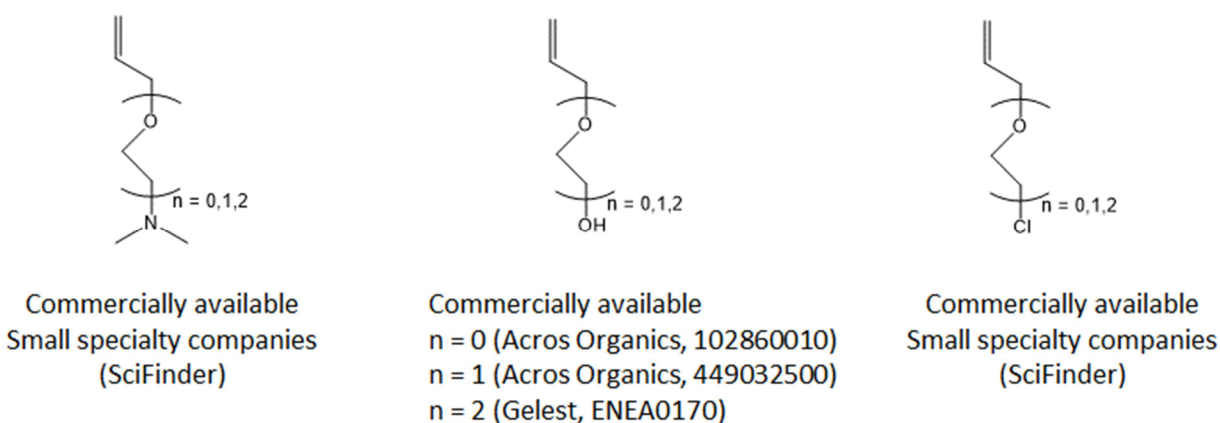


Figure 6. Structures of commercially available precursor materials used in the synthesis.

A tetrasiloxane-sulfobetaine synthesis was conducted as shown in Figure 7. OTMS is an abbreviation for a trimethylsilyl ether group ($\text{O-Si}(\text{Me})_3$) that are explicitly displayed in Figure 7. The two-step synthesis gave 74% and 78% conversions for the first and second steps respectively.

The first step in the synthesis was the platinum-catalyzed hydrosilylation of N,N-dimethylallylamine with tris(trimethylsiloxy)silane. The particular platinum catalyst is the well-known Karstedt soluble complex that is commercially available. The N,N-dimethylallylamine was purchased from Aldrich and used as received. The hydrosilylation step usually gave about 70% yield. The 3-dimethylaminopropyl-1-tris(trimethylsiloxy)silane was separated from the starting material silane by reduced pressure fractional distillation. The proton NMR of the product is shown in Figure 8.

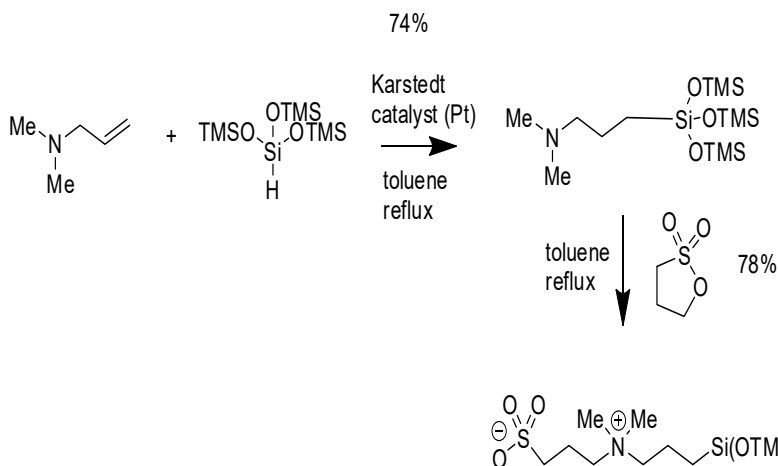


Figure 7. Chemical route used to synthesize tetrasiloxane-sulfobetaine.

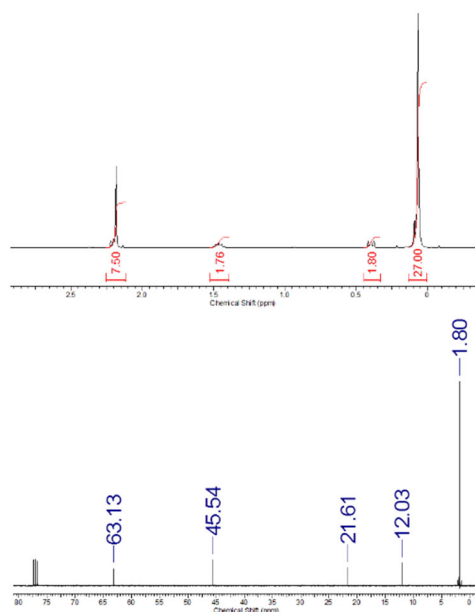


Figure 8. Proton (*top*) and carbon-13 (*bottom*) NMR spectra of 3-dimethylaminopropyl-1-tris(trimethylsiloxy)silane intermediate.

In the initial preparations of the sulfobetaine, equimolar quantities of the 3-dimethylaminopropyl-1-tris(trimethylsiloxy)silane and 1,3-propanesultone were heated to 100 °C in toluene. After the mixture reached 80 °C typically the sulfobetaine had precipitated out and stirring was difficult. Then the reaction mixture was cooled to room temperature and diluted with hexanes and the mixture containing the sulfobetaine was filtered or pelleted by centrifugation. The

product was further purified by recrystallization from EtOAc/MeCN by heating up in the solvent and allowing to cool down which gave a crystalline appearing material that was easy to filter. Proton NMR of product tetrasiloxane-sulfobetaine in CDCl₃ is shown in Figure 9. It appeared correct for the desired structure, although the integrations were not perfect. This sample was also referred to as batch MD2062-54.

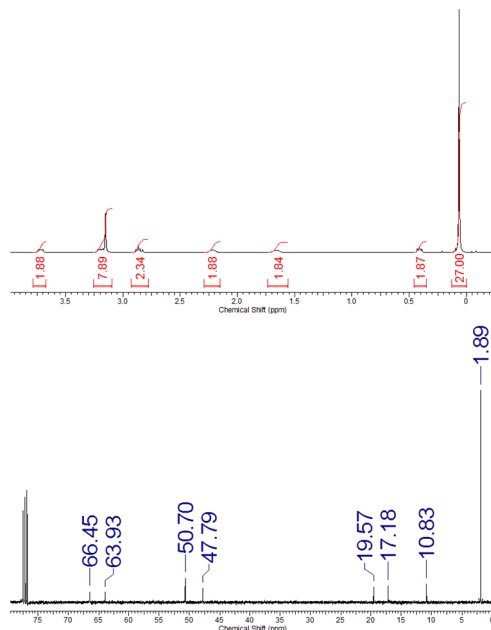


Figure 9. Proton and carbon-13 NMR spectra of tetrasiloxane-sulfobetaine compound **1** (MD2062-54) in CDCl₃.

5.1.2. Other Siloxane-Sulfobetaines

The preparation of the trisiloxane-sulfobetaine and cyclotetrasiloxane-sulfobetaine surfactants involved two steps, hydrosilylation reaction of the tri- and tetrasilane reagents with N,N-dimethyl allylamine followed by reaction of this dimethylaminetrimethylene siloxane intermediate with 1,3-propanesultone to yield the respective surfactant products shown in Figure 10. The intermediates were purified by reduced pressure distillation, and surfactant products were purified by precipitation and diethyl ether washing. Yields were between 75 and 85%, and structures were confirmed by NMR and IR spectroscopies.

Procedures for sulfobetaine-siloxane and the polyoxyethylene-siloxane surfactant syntheses described below are adaptations from those described in the literature [32, 33, 34]. The catalyst selected for the hydrosilylation reaction is an issue of particular importance. The two used in this report are the Speier catalyst (H₂PtCl₆·6H₂O 1 wt% in 2-propanol) and the Karstedt catalyst (platinum-divinyl tetramethyl disiloxane complex 5 wt% in xylenes). The former has a low activity relative to the latter. The use of either frequently involves an induction period followed by an exotherm when the reaction starts. The selection frequently depends on the reactivity of the reagents with the (Me₃OSi)₂(Me)Si-H and the allyl-polyoxyethylene having the higher reactivity, and the (Me₃OSi)₃Si-H and the allyl-amine having the lower reactivity. The heptamethylcyclotetrasiloxane is intermediate. If the Speier catalyst is used with a lower reactive

reagent combination, no reaction occurs, and if the Karstedt catalyst is used with a higher reactive reagent combination, a strong discoloration of the reaction mixture and byproducts can occur.

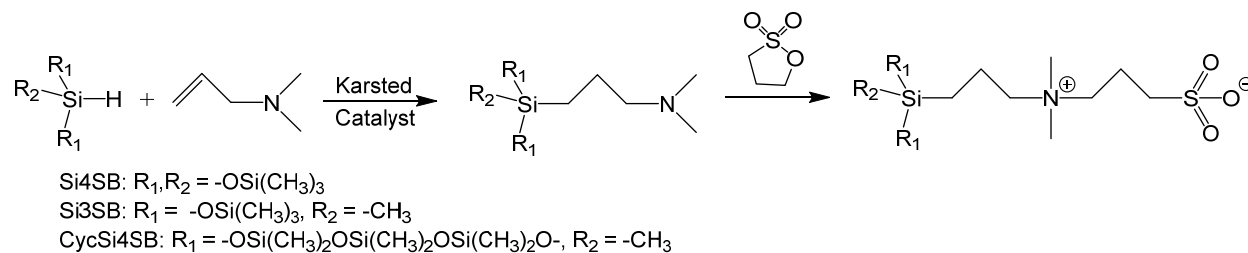
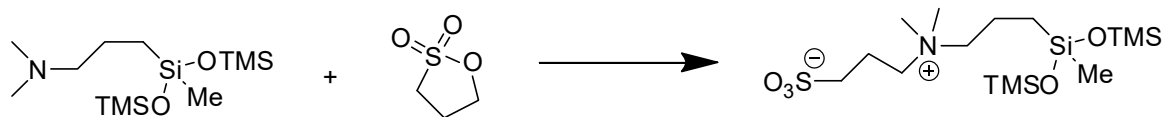


Figure 10. Two step synthesis of trisiloxane-sulfobetaine and cyclictetrasiloxane-sulfobetaine surfactants.

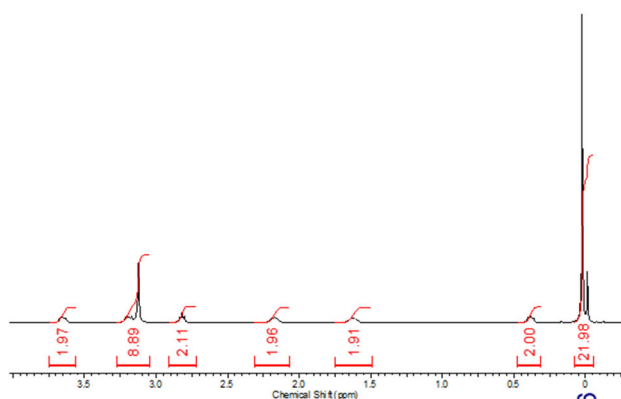
5.1.2.1. Trisiloxane-sulfobetaine (N10478-038 and N10478-040), *N*-[3'-bis(trimethylsiloxy)(methyl)silyl-1'-propylene]-*N,N*-dimethylammonium-*N*-propane-3-sulfonate): First *N*-[3-bis(trimethylsiloxy)(methyl)silyl-1-propylene]-*N,N*-dimethylamine intermediate was prepared by adding 22.31 g (100.1 mmol) bis(trimethylsiloxy)methylsilane, 8.51 g (99.9 mmol) *N,N*-dimethylallylamine and 0.057 g Speier catalyst to a 3-neck 50 ml round bottom flask fitted with thermometer, magnetic stirring bar, condenser and N_2 inlet. The stirred reaction mixture was gradually heated with an initial 65 °C oil bath while monitoring temperature for an exotherm which was observed as a short 10 °C rise and fall after 1 hr. The oil bath temperature was then gradually increased to 110 °C and the reaction continued for an additional 4 hrs. Conversion was monitored by =C-H and Si-H NMR resonances. This intermediate product was isolated by fractional distillation (72 °C/1 mm) to yield 23.08 g (75 %). Product is characterized by NMR (for details see APPENDIX I). Trisiloxane-sulfobetaine was prepared by adding 11.01 g (35.7 mmol) *N*-[3-bis(trimethylsiloxy)(methyl)silyl-1-propylene]-*N,N*-dimethylamine intermediate, 4.50 g (36.8 mmol) 1,3-propanesultone and 14 ml CH_2Cl_2 to a 50 ml Erlenmeyer followed by a large magnetic stirring bar. The flask was tightly capped and vigorously stirred. After 30 min the clear reaction solution became opaque, and coarse precipitate particulates formed after one hr. Stirring continued for a total of 5 hrs. The product was collected by filtration, washed 5x with 10ml portions of diethyl ether and vacuum dried to yield 6.73 g (44 %) colorless product. The CH_2Cl_2 filtrate was evaporated to dryness to yield 4.05 g (26 %) colorless product, and the diethyl ether combined wash was evaporated to dryness to yield 4.15 g (27 %) colorless product. See APPENDIX I for NMR spectra of these three fractions. For reasons similar to the tetrasiloxane analog the latter two fractions were discarded.

Alternatively, trisiloxane-sulfobetaine MD2102-16 was prepared by the following method (Figure 11). A reaction vial equipped with a magnetic stirring bar was filled with *N,N*-dimethylaminopropyl-3-bis(trimethylsiloxy)methylsilane (1.54 g, 5 mmol) and anhydrous toluene (15 mL). Next, 1,3-propanesultone (0.6 g, 5 mmol, 1 equiv) was added to the mixture in one portion. The vial was capped with a pressure relief style cap and then vigorously stirred and heated (100 °C) in an aluminum heating block. Afterwards (2 h), the mixture was removed from the block and allowed to cool to room temperature whereupon the reaction mixture solidified. Next, anhydrous hexanes (15 mL) was added to the mixture and the white solid product 2102-16 was isolated by filtration (1.73 g, 80 %). NMR spectra of the product is shown in Figure 12.



2102-16 and N10478-40

Figure 11. Synthesis of trisiloxane-sulfobetaine (MD2102-16) surfactant.



NMR 2102-16 (CDCl₃)

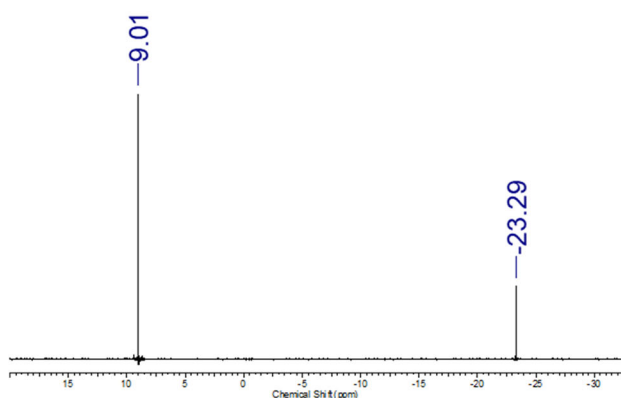
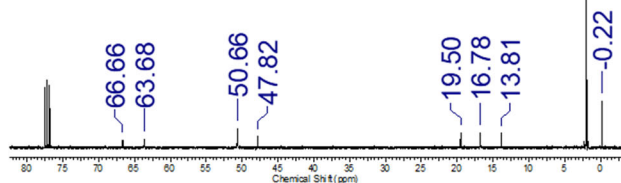


Figure 12. NMR spectra of the product trisiloxane-sulfobetaine (MD2102-16)

5.1.2.2. Cyclotetrasiloxane-sulfobetaine (N10478-079 and N10478-081, *N*-[3'-heptamethylcyclotetrasiloxo-1'-propylene]-*N,N*-dimethylammonium-*N*-propane-3-sulfonate): *N*-[3- heptamethylcyclotetrasiloxo-1-propylene]-*N,N*-dimethylamine intermediate was prepared by adding 3.34 g (11.8 mmol) heptamethylcyclotetrasiloxane, 1.01 g (11.8 mmol)

N,N-dimethylallylamine and 0.005 g Karstedt catalyst to 3-neck 25 ml round bottom flask fitted with thermometer, magnetic stirring bar, condenser and N₂ inlet. An exotherm to 60 °C occurred during addition of this catalyst accompanied by clear dark yellow color development. The reaction was cooled quickly to room temperature then gradually warmed to 110 °C with an oil bath over a 3 hr period at which time NMR indicated reaction completed. This intermediate product was isolated by fractional distillation (80 °C/1 mm) to yield 3.69 g (85 %). Cyclictetrasiloxane-sulfobetaine was prepared by adding 6.00 g (16.3 mmol) N-[3- heptamethylcyclotetrasiloxyl-1-propylene]-N,N-dimethylamine, 2.02 g (16.5 mmol) 1,3-propanesultone and 8 ml CH₂Cl₂ to a 25 ml Erlenmeyer. The flask was tightly capped and vigorously stirred. After 30 min the clear reaction solution became opaque. After 6 hr, the reaction was stopped, product collected by filtration and washed 5x with ether and vacuum dried to yield 5.73 g (71 %), and coarse precipitate particulates formed after one hr. Stirring continued for a total of 5 hr. The CH₂Cl₂ filtrate was evaporated to dryness to yield 1.36 g (17 %) colorless product. See APPENDIX I for NMR spectra of these two fractions. The CH₂Cl₂ filtrate fraction contained a significant quantity of impurities.

5.1.2.3. Tetrasilane-Sulfobetaine (N10477-189)

The synthesis of the tetrasilane-sulfobetaine surfactant consisted of a two-step preparation. The first step is the preparation of a tetrasilane-amine intermediate, and the second step is the conversion of this intermediate to the sulfobetaine surfactant product. These steps are individually reported below along with purification procedures and characterization data.

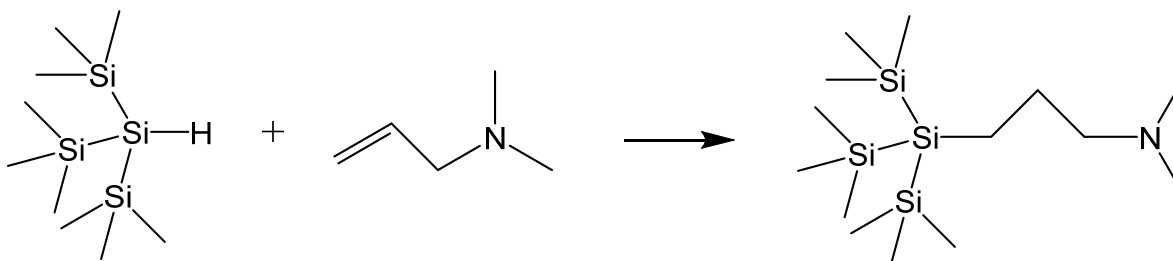


Figure 13. Synthesis of tetrasilane-amine (N-[3-tris(trimethylsiloxy)silyl-1-propylene]-N,N-dimethylamine) intermediate.

The reaction shown in Figure 13 is conducted in a 25ml sealed reaction apparatus due to reagent volatility. Reagents added were 5.840g (23.5mmol) tris(trimethylsilyl)silane, 2.006g (23.5mmol) dimethylallylamine, and initial 11mg of Karstedt catalyst (5% platinum divinyltetramethyldisiloxane complex in xylene). The catalyst is added in small increments as indicated in Table 2 to control the temperature rise caused by the exothermic reaction. The reaction progress is monitored by NMR, and the allyl proton resonances show a gradual reduction in intensity with reaction time. The NMR spectra are depicted in Figure 14.

The reaction mixture was transferred to a short path length distillation apparatus and fractionally distilled under vacuum conditions as described in Table 3. Figure 15 shows NMR spectra of fractions. Fractions F#3 and F#4 represent the purified product with a yield of 4.706g (60.0%). The ²⁹Si NMR spectrum of this purified intermediate product is presented in Figure 16 verifying its chemical structure.

Table 2. Monitoring of tetrasilane-amine intermediate preparation reaction.

Time (hr)	0	0.25	1.0	1.5	2.0	2.5	3.0	4.5	5.5	6.5	7.25	8.5	10.25
Temp (°C)	22	95	99	99	120	122	123	123	125	125	125	125	135
Observ	clear	slight haze	slight haze	slight haze	dark haze	dark haze	dark haze	amber clear	amber clear	amber clear	amber clear	amber clear	amber clear
Catalyst(mg)	11mg						32mg		30mg		47mg	57mg	Rx stop
NMR Spec	#1		#2			#3		#4		#5		#6	#7

Table 3. Tetrasilane-amine intermediate product workup.

Fraction #	Temp/Pressure	Quantity (g)	NMR Spectrum #
F#1	77°C/<1mm	0.634g	#8
F#2	77-81°C/<1mm	0.679g	#9
F#3	85-95°C/<1mm	3.074g	#10
F#4	95-96°C/<1mm	1.632g	#11
F#5	96-105°C/<1mm	0.071g	#12
Distilland		0.567g	

Reaction shown in Figure 17 is conducted by adding reagents, 3.339g (10.0 mmol) tetrasilane-amine intermediate, 1.238g (10.1 mmol) 1,3-propanesultone and 2ml methylene chloride to a 15ml round bottom flask fitted with a magnetic stirring bar. The reaction flask was fitted with a 14 cm column and N₂ inlet. The stirring rate was set for half vortex and reaction run at room temperature with following observations and adjustments made. After 1-2 minutes the clear reaction solution developed a haze. At 30 minutes the reaction became a thick white paste and difficult to stir but remained at room temperature. A 1 ml addition of CH₂Cl₂ was made to facilitate stirring and reaction continued. After 60 minutes reaction time, the reaction mixture became a very thick paste and six successive 1ml CH₂Cl₂ additions were made to restore stirring action. After 2hr reaction time the reaction was stopped. The thick mixture was transferred to a 15ml coarse sintered glass filter and filtered with gentle water aspiration. The filtrate was collected and evaporated to dryness. The was then dispersed/washed in 4ml ethyl acetate for 15 min followed by filtering and vacuum drying for 12 hr to yield 3.986g (87.0%). The ¹H NMR spectrum with structural resonance assignments is presented in Figure 18. This tetrasilane-sulfobetaine surfactant was characterized by surface tension measurements with the surface tension – concentration plot, CMC, CMC surface tension, and via the Gibbs equation surface excess concentration and air-water surfactant interfacial area presented in Figure 19.

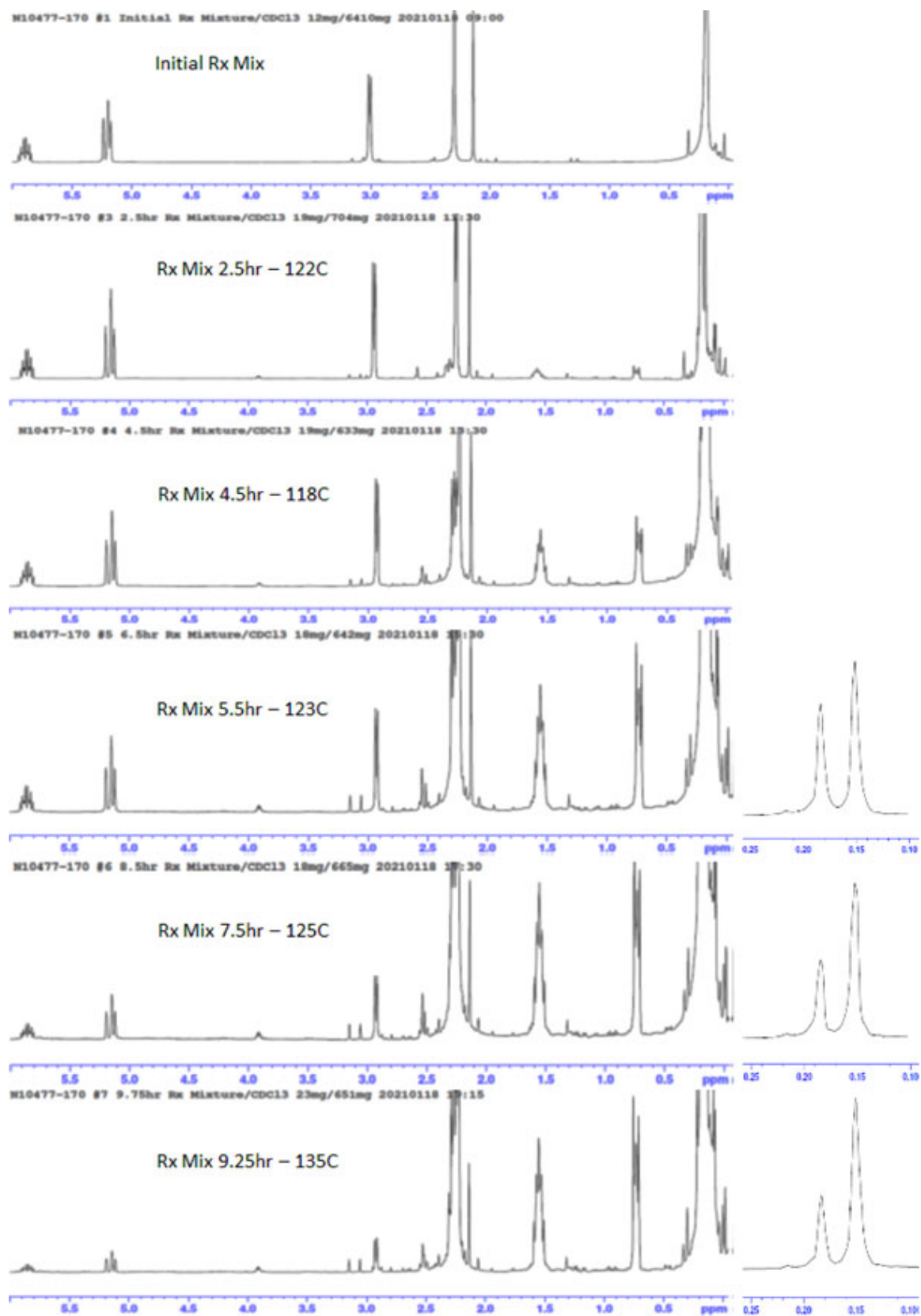


Figure 14. NMR spectra of tetrasilane-amine intermediate product reaction monitoring.

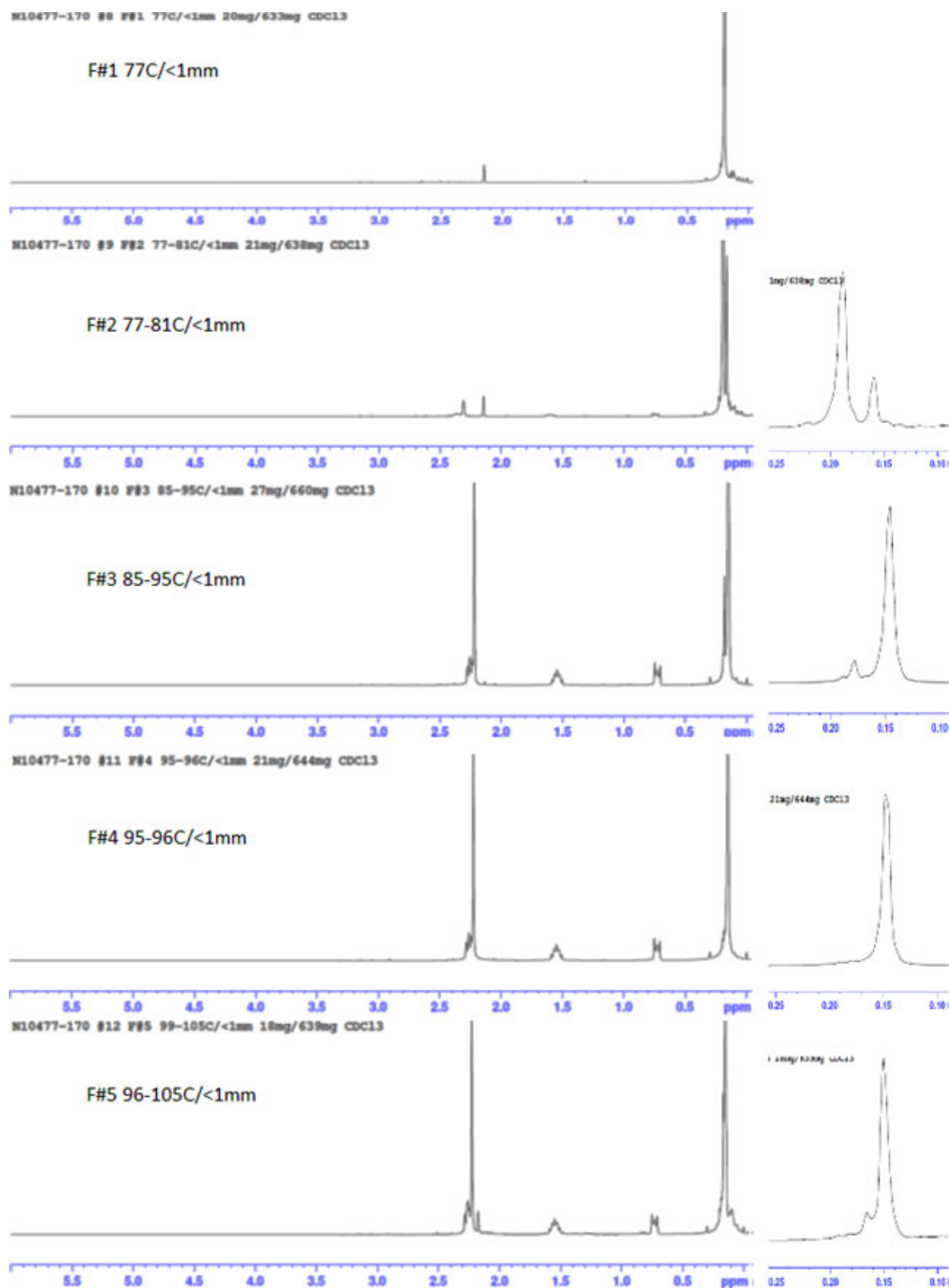


Figure 15. NMR spectra of tetrasilane-amine intermediate product distillation fractions.

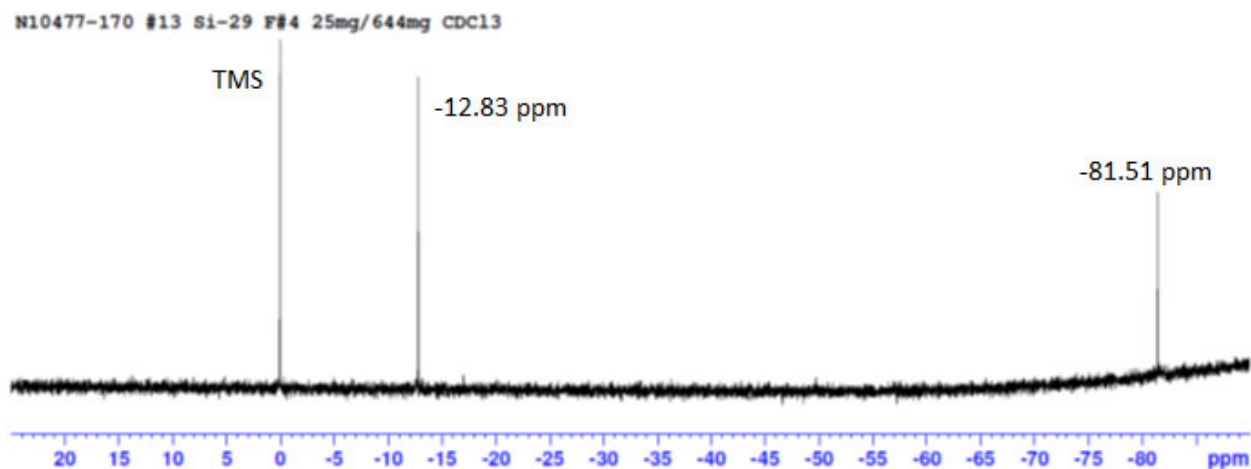


Figure 16. ^{29}Si NMR spectra of purified tetrasilane-amine intermediate product.

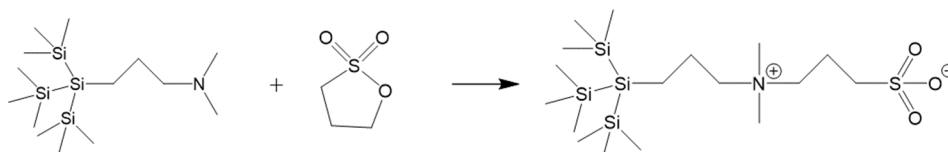


Figure 17. Synthesis of tetrasilane-sulfobetaine (*N*-[3'-tris(trimethylsilyl)silyl-1'-propylene]-*N,N*-dimethylammonium-*N*-propane-3-sulfonate) surfactant.

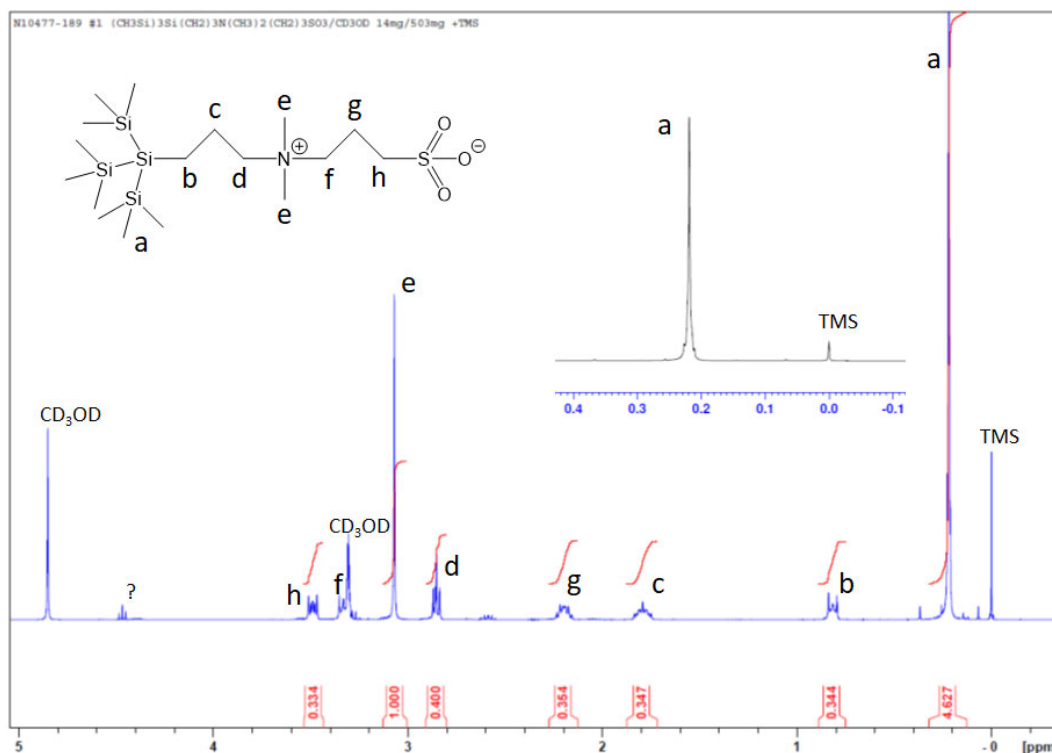


Figure 18. ^1H NMR spectrum of tetrasilane-sulfobetaine surfactant product (N10477-189).

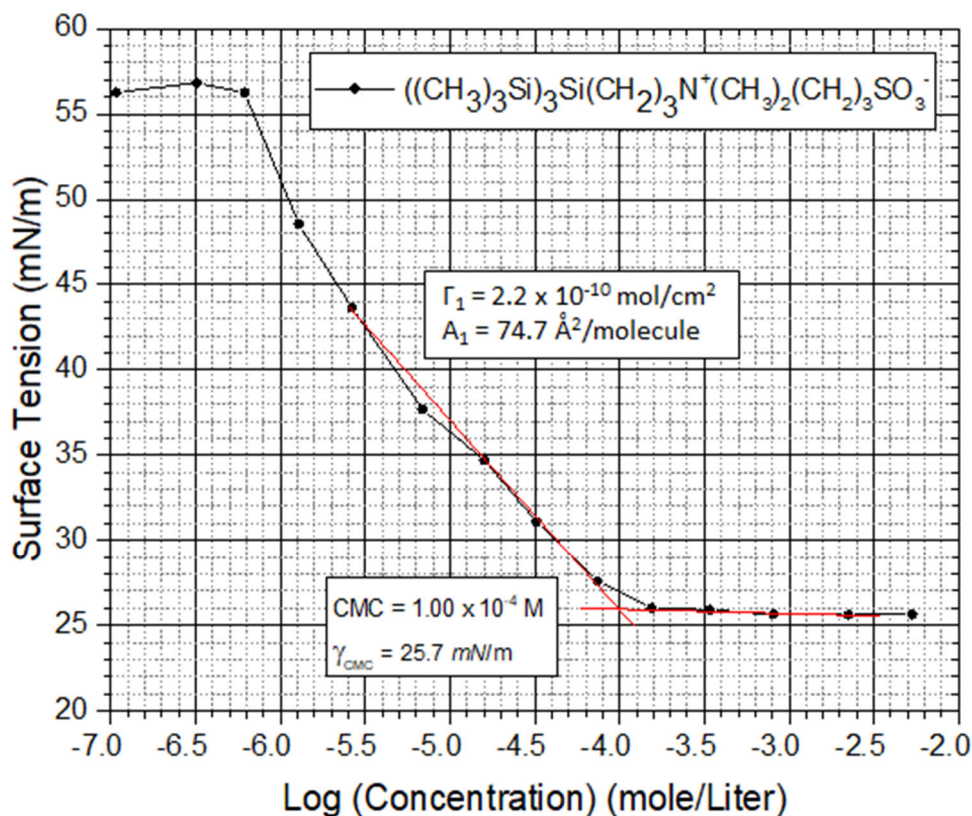


Figure 19. Plot of tetrasilane-sulfobetaine (N10477-189) surfactant surface tension vs concentration depicting critical micelle concentration (CMC), surface tension at CMC (γ_{CMC}), surface excess concentration (Γ_1) and air-water surfactant interfacial area (A_1).

5.1.2.4. t-Butyltrisiloxane-Sulfobetaine (CB-DTBTS-SB): The synthesis of 3-[[3-[Di(tert-butyl)dimethylsiloxy)methylsilanyl]propyl]dimethylamino]propane-1-sulfonate CB-DTBTS-SB required three steps. First, to a 500 mL round-bottom flask was added 200 mL isopropyl ether (IPE) and 10 mL distilled water. The flask was then equipped with a magnetic stirring bar, pressure equalizing dropping funnel, and reflux condenser. To the dropping funnel was added *tert*-butyldimethylchlorosilane (20 g, 132.7 mmol) and dichloromethylsilane (6.9 mL, 66.3 mmol) in 100 mL IPE. While stirring vigorously the silane in ether mixture was added to the IPE/H₂O dropwise at room temperature over an hour. After the addition, the mixture was heated to 50 °C and stirred overnight. The reaction mixture was cooled to room temperature then partitioned between diethyl ether and H₂O. The organic phase was separated, washed with 25 mL brine, dried with MgSO₄, then filtered over a frit. Volatiles were removed via rotary evaporation and distilled under reduced pressure. The major fraction was collected (0.8 Torr, 82-86 °C) to yield a clear colorless oil (27.7 g, 68%), with structure confirmed by ¹H NMR. Second, to a 250 mL flask was added *tert*-butylhexamethyltrisiloxane intermediate (20 g, 65.2 mmol) and the flask was equipped with a magnetic stirring bar, reflux condenser, nitrogen inlet, and placed into an oil bath. Then *N,N*-dimethylallylamine (15.2 mL, 130.3 mmol) was added dropwise with vigorous stirring. The

reaction mixture was heated to 30 °C and Karstedt's catalyst (2% Pt in xylene, 0.04 mL) was added dropwise. The reaction mixture was then heated to 90 °C for four hours then the mixture was left to stir overnight at room temperature. Excess dimethylallylamine was removed via rotary evaporation to yield a clear, colorless oil intermediate (23.8 g, 93%). Third, to a new 250 mL flask was added the dimethylaminetrimethylene *tert*-butylhexamethyltrisiloxane intermediate (23.8 g, 60.7 mmol), magnetic stirring bar, and 150 mL dry toluene. The flask was then equipped with a reflux condenser and nitrogen gas inlet then 1,3-propane sultone (7.5 g, 61.4 mmol) was added dropwise with vigorous stirring. The reaction mixture was placed into an oil bath and heated to 80 °C for five hours. During this time the reaction mixture became progressively cloudy, slightly opaque, with increased viscosity. Volatiles were then removed via rotary evaporation to yield a colorless opaque gel-like product. Then 150 mL diethyl ether was added to the flask and the product was suspended using a spatula. The suspension was then filtered over a frit and the product was washed with additional diethyl ether, then dried in a vacuum oven to yield a colorless powder (26.8 g, 86%). NMR spectra of the product is shown in APPENDIX I.

5.1.2.5. Trisiloxane-Sulfobutylbetaine (CB-1-123): The synthesis of *N,N*-dimethyl-4-sulfo-*N*-[3-[1,3,3,3-tetramethyl-1-[(trimethylsilyl)oxy]-1-disiloxanyl]propyl]-1-butanaminium CB-1-123 required two steps. First, to a 250 mL round-bottom flask was added heptamethyltrisiloxane (Sigma, 10 mL, 36.8 mmol). The flask was equipped with a reflux condenser, nitrogen gas inlet, and placed into an oil bath. While stirring vigorously *N,N*-dimethylallylamine (8.6 mL, 73.73 mmol) was added dropwise. The reaction mixture was heated to 30 °C and Karstedt's catalyst (2% Pt in xylene, 0.03 mL) was added dropwise. The reaction mixture was then heated to 80 °C for four hours then the mixture was left to stir overnight at room temperature. Excess dimethylallylamine was removed via rotary evaporation to yield a clear, colorless oil intermediate (10.4 g, 92%). Second, to a new 250 mL flask was added the dimethylaminetrimethylene-heptamethyltrisiloxane intermediate (10.4 g, 33.8 mmol), magnetic stirring bar, and 150 mL dry toluene. The flask was then equipped with a reflux condenser and nitrogen gas inlet then 1,4-butane sultone (Sigma, 4.7 g, 34.5 mmol) was added dropwise with vigorous stirring. The reaction mixture was placed into an oil bath and heated to 90 °C for five hours. During this time the reaction mixture became progressively cloudy, slightly opaque, with increased viscosity. Volatiles were then removed from the mixture via rotary evaporation to yield a colorless opaque gel-like product. Then 150 mL diethyl ether was added to the reaction flask and the product was suspended using a spatula. The suspension was then filtered over a frit, washed with additional diethyl ether, then dried in a vacuum oven to yield a colorless powder (9.6 g, 64 %). NMR spectra of the product is shown in APPENDIX I.

5.1.2.6. Hexasiloxane-Disulfobetaine, dual headed (CB-1-180B): The synthesis of bis(sulfobetaine)hexadecamethyloctasiloxane (CB-1-123) required two steps. First, to a 250 mL round-bottom flask was added silylhydride-terminated hexadecamethyloctasiloxane (Gelest DMS-H03, 10 g, 22.2 mmol). The flask was equipped with a reflux condenser, nitrogen gas inlet, and placed into an oil bath. While stirring vigorously *N,N*-dimethylallylamine (6.5 mL, 55.7 mmol) was added dropwise. The reaction mixture was heated to 30 °C and Karstedt's catalyst (2% Pt in xylene, 0.04 mL) was added dropwise. The reaction mixture was then heated to 80 °C for four hours then left to stir overnight at room temperature. Excess dimethylallylamine was then removed via rotary evaporation to yield a clear, colorless oil intermediate (13.2 g, 96%). Second, to a new 250 mL flask was added the bis-dimethylaminetrimethylene-hexadecamethyloctasiloxane

intermediate (13.2 g, 21.3 mmol), magnetic stirring bar, and 150 mL dry toluene. The flask was then equipped with a reflux condenser and nitrogen gas inlet then 1,3-propane sultone (5.3 g, 43.4 mmol) was added dropwise with vigorous stirring. The reaction flask was placed into an oil bath and heated to 70 °C for five hours. During this time the mixture became progressively cloudy, slightly opaque, with increased viscosity. Volatiles were then removed via rotary evaporation to yield a colorless opaque gel-like product. Then 150 mL diethyl ether was added to the reaction flask and the product was suspended using a spatula. The suspension was then filtered over a frit, washed with additional diethyl ether, then dried in a vacuum oven to yield a colorless powder (14.6 g, 79%). NMR spectra of the product is shown in APPENDIX I.

5.1.2.7. Disilane-Sulfobetaine (MD2102-90)

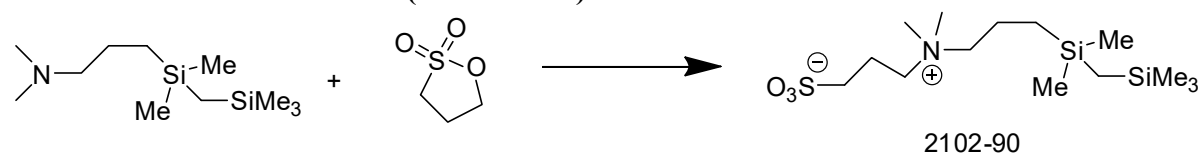


Figure 20. Synthesis of disilane-sulfobetaine (MD2102-90) surfactant.

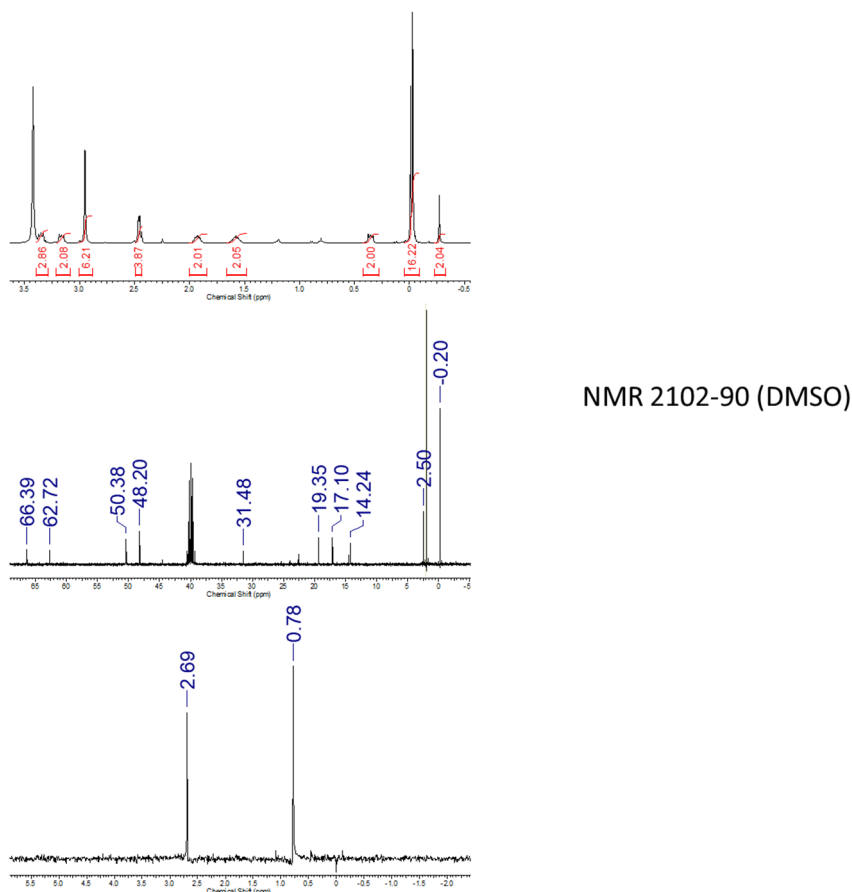


Figure 21. NMR spectra for the product disilane-sulfobetaine (MD2102-90) surfactant.

A reaction vial equipped with a magnetic stirring bar was filled with 3-(dimethyl((trimethylsilyl)methyl)silyl)-N,N-dimethylpropan-1-amine (2.31 g, 10 mmol) and anhydrous toluene (15 mL). Next, 1,3-propanesultone (1.22 g, 10 mmol, 1 equiv) was added to

the mixture in one portion. The vial was capped with a pressure relief style cap and then vigorously stirred and heated (100 °C) in an aluminum heating block. Afterwards (2 h), the mixture was removed from the block and allowed to cool to room temperature whereupon the reaction mixture solidified. Next, anhydrous hexanes (15 mL) was added to the mixture and the white solid product 2102–90 was isolated by filtration (2.78 g, 78 %).

5.1.2.8. t-Butyldisiloxane-Sulfobetaine (MD2102-99)

Figure 22. Synthesis of butyldisiloxane-sulfobetaine (MD2102-99) surfactant.

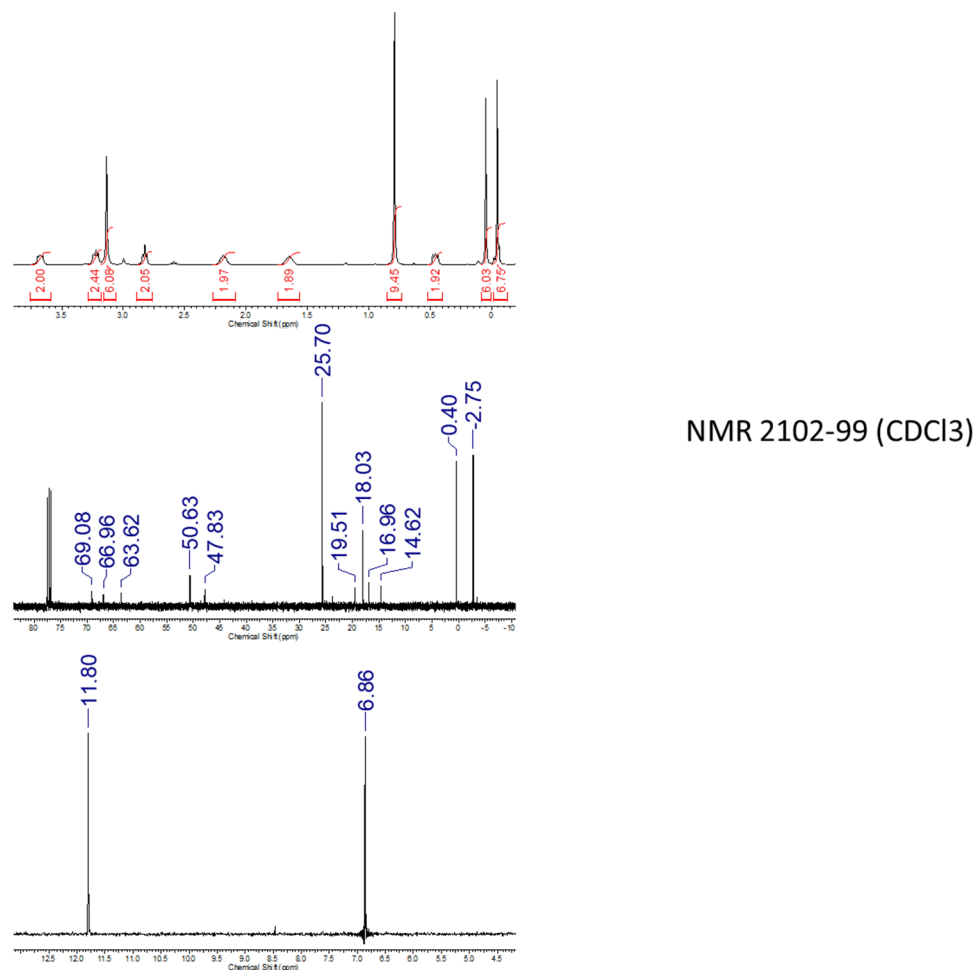


Figure 23. NMR spectra for the product t-butyldisiloxane-sulfobetaine (MD2102-99) surfactant.

A reaction vial equipped with a magnetic stirring bar was filled with 3-(3-(tert-butyl)-1,1,3,3-tetramethyldisiloxanyl)-N,N-dimethylpropan-1-amine (3.58 g, 13 mmol) and anhydrous toluene (15 mL). Next, 1,3-propanesultone (1.6 g, 13 mmol, 1 equiv) was added to the mixture in one portion. The vial was capped with a pressure relief style cap and then vigorously stirred and

heated (80 °C) in an aluminum heating block. Afterwards (2 h), the mixture was removed from the block and allowed to cool to room temperature whereupon the reaction mixture solidified. Next, anhydrous hexanes (15 mL) was added to the mixture and the white solid product 2102–99 was isolated by filtration (3.93 g, 76 %). NMR spectra are shown in Figure 23.

5.2. Task 4 – Assess Environmental Impact (Dr. David Moore, USACE ERDC, Vicksburg, MS)

The objective of this task is to perform toxicity measurements on select compounds/formulations. Toxicity assessments were performed with three freshwater species, the water flea *Ceriodaphnia dubia*, the fathead minnow *Pimephales promelas*, and the algae *Radopholocelis capitata*. Acute and chronic tests were performed with *C. dubia* (48hour survival & 7 day reproduction, respectively) and with *P. promelas* (48hr survival and 7 day growth, respectively), while a chronic endpoint of 96hr cell growth was measured in test with *R. capitata*. All testing was performed in accordance with prescribed standardized testing protocols summarized in Table 4. Not all compounds/formulations were tested with each species. The most complete data set is for *C. dubia* where toxicity (both acute and chronic) was assessed for 13 compounds/formulations (e.g., capstone 1157, a capstone based fluorosurfactant mixture, glucopon 215UP, glucopon 225DK, DGBE, HMTS-PEO-TMACL, N10466-09, silwet-77, 502W, 502 sulfate, NRL 502W, MD-2062-124 and MD-2086-1). Tests with the fish *P. promelas* were performed on 9 of the 13 compounds/ formulations these included capstone 1157, glucopon 215UP (acute only), glucopon 225DK (acute only), DGBE, HMTS-PEO-TMACL, silwet-77, 502W, 502W sulfate (acute only), and NRL 502W. Tests with the algae *R. capitata* were performed on 5 of the compounds/formulations including capstone 1157, Glucopon 215UP, DGBE, silwet-77 and NRL 502W. All tests met acceptability criteria, all water quality criteria were within prescribed protocol limits, and test animal sensitivity as indicated by LC50 measures in concurrent reference toxicant exposures were within ± 2 standard deviations of laboratory historical reference toxicity control.

Table 4. Summary of toxicity tests conducted and associated standardized testing protocols.

Test Species	Test type	Protocol	Comments
<i>C. dubia</i>	Acute (48h survival)	EPA-821-R-02-012 ; OECD 202	<i>C. dubia</i> selected as a more suitable test species relative to <i>D. magna</i> based on sensitivity and testing requirements.
	Chronic (7d reproduction)	EPA-821-R-02-013 ; EPA 1002.0	
<i>P. promelas</i>	Acute (48h survival)	EPA-821-R-02-012 , OECD 203	
	Chronic (7d growth, biomass)	EPA-821-R-02-013 ; EPA 1000.0	
<i>R. subcapitata</i>	Chronic (96h growth, cell count)	EPA-821-R-02-013 ; OECD 201	

Nominal concentrations for each of the compounds/formulations evaluated in each of the tests are summarized in Tables 5-7 below. Standard toxicity endpoints (i.e., concentration lethal to 50% of the test population, the LC50; concentration producing statistically significant effect [e.g., growth or reproduction] the IC50) as well as no observable effect concentrations (NOEC) and lowest observable effect concentration (LOEC) calculated based on the results of each of the

tests are summarized in Tables 8-12. Finally, plots of toxicity acute and chronic test endpoints (LC50 and IC50) for each of the species referenced against USEPA aquatic toxicity categories (i.e., <1mg/L = Highly Toxic, 1-10mg/L = Moderately toxic, 10-100mg/L = Slightly Toxic, 100-1000 mg/L = Practically non-toxic, >1000 mg/L = Relatively Harmless) are presented in Figures 24- 28.

Table 5. Nominal exposure concentrations (mg/L) used in acute and chronic tests with *C. dubia*.

Test Material	Acute Conc. (mg/L)	Chronic Conc. (mg/L)
Capstone 1157	25, 50, 100, 200, 400	3.12, 6.25, 12.5, 50
Fluorosurfactant Mixture (Capstone Mix)	0.2, 0.39, 0.78, 1.56, 3.13	0.04, 0.09, 0.19, 0.39, 0.78, 1.56
Glucopon 215UP	5.1, 10.2, 20.4, 40.8, 81.62	0.80, 1.6, 3.2, 6.3, 12.6
Glucopon 225DK	3.9, 7.8, 15.6, 31.2, 62.5	3.12, 6.25, 12.5, 25, 50
DGBE	18.8, 37.5, 75, 150, 300	4.7, 9.4, 18.8, 37.5, 75
HMTS-PEO-TMACL (HMTS)	0.91, 1.82, 3.64, 7.28, 14.56	0.09, 0.19, 0.39, 0.78, 1.56
N10477-09	0.19, 0.38, 0.77, 1.55, 3.60	0.10, 0.20, 0.40, 0.80, 1.6
Silwet-77	0.625, 3.25, 2.5, 5, 10	0.31, 0.62, 1.25, 2.5, 5
502W	6.25, 12.5, 25, 50, 100	3.12, 6.25, 12.5, 25, 50
502W Sulfate	6.25, 12.5, 25, 50, 100	6.25, 12.5, 25, 50, 100
NRL 502W	25, 50, 100, 200, 400	6.25, 12.5, 25, 50, 100
MD-2062-124	25.1, 50.2, 100.4, 200.8, 401	12.5, 25, 50, 100, 200
MD-2086-1	25.6, 51.3, 102.6, 205.3, 410.6	12.5, 25, 50, 100, 200

Table 6. Nominal exposure concentrations (mg/L) used in acute and chronic tests with *P. promelas*. Shaded cell = not tested.

Test Material	Acute Conc. (mg/L)	Chronic Conc. (mg/L)
Capstone 1157	5.86, 11.72, 23.44, 46.88, 93.75	2.81, 5.62, 11.24, 22.48, 45
Fluorosurfactant Mixture (Capstone Mix)		
Glucopon 215UP	6.25, 12.5, 25, 50, 100	
Glucopon 225DK	6.25, 12.5, 25, 50, 100	
DGBE	187.5, 375, 750, 1500, 3000	125, 250, 500, 1000, 2000
HMTS-PEO-TMACL (HMTS)	0.313, 0.625, 1.250, 2.5, 5	0.156, 0.313, 0.625, 1.250, 2.5
N10477-09		
Silwet-77	0.24, 0.48, 0.96, 1.92, 3.9	0.11, 0.22, 0.44, 0.875, 1.75
502W	0.190, 0.380, 0.750, 1.5, 3	0.187, 0.375, 0.750, 1.5, 3
502W Sulfate	6.25, 12.5, 25, 50, 100	
NRL 502W	6.25, 12.5, 25, 50, 100	6.25, 12.5, 25, 50, 100
MD-2062-124		
MD-2086-1		

Table 7. Nominal exposure concentrations (mg/L) used in chronic tests with *R. capitata*. Shaded cell=not tested.

Test Material	Chronic Conc. (mg/L)
Capstone 1157	25, 50, 100, 200, 400
Fluorosurfactant Mixture (Capstone Mix)	
Glucopon 215UP	3.13, 6.25, 12.5, 25, 50
Glucopon 225DK	
DGBE	31.3, 62.5, 125, 250, 500
HMTS-PEO-TMACL (HMTS)	
N10477-09	
Silwet-77	0.94, 1.88, 3.75, 7.5, 15
502W	
502W Sulfate	
NRL 502W	25, 50, 100, 200, 400
MD-2062-124	
MD-2086-1	

Table 8. Summary of acute lethality endpoint measures (mg/L) for tests with *C. dubia*. All endpoints derived using nominal concentrations. NC= Not Calculated, absence of dose-response relationship precluded calculation.

Test Material	Mean LC50 (mg/L) (95% CI) (Survival)	NOEC (Survival)	LOEC (Survival)
Capstone 1157	263.9 (231.2-301.1)	100	200
Fluorosurfactant Mixture (Capstone Mix)	0.6 (0.5-0.6)	0.39	0.78
Glucopon 215UP	19 (16.4-22.2)	10.2	20.4
Glucopon 225DK	22.3 (19.3-25.7)	15.6	31.25
DGBE	75 (62.8-89.6)	37.5	75
HMTS-PEO- TMACL (HMTS)	1.5 (1.3-1.8)	0.91	1.82
N10477-09	1.9 (1.6-2.3)	0.77	1.55
Silwet-77	7.9 (6.9-9)	5	10
502W	26.7 (22.6-31.6)	12.5	25
502W Sulfate	>100 NC	100	>100
NRL 502W	103.9 (82.9-130.1)	50	100
MD-2062-124	119.40 (95.95-148.58)	50.2	100.4
MD-2086-1	102.65 (86.74-121.47)	51.3	102.6

Table 9. Summary of chronic toxicity endpoints (mg/L) for tests with *C. dubia*. All endpoints were derived using nominal concentrations. NC= Not Calculated, absence of dose-response relationship precluded calculation.

Test Material	Mean LC50 (95% CI) (Survival)	Mean IC50 (95% CI) (Reproduction)	NOEC (Reproduction)	LOEC (Reproduction)
Capstone 1157	11.6 (9.1-16.6)	5.28 (4.3-7.18)	<3.12	3.12
Fluorosurfactant Mixture (Capstone Mix)	1.3 (0.7-1.8)	1.26 (0.370-18.83)	0.391	0.7825
Glucopon 215UP	7 (5.2-9)	6.82 (5.16-8.74)	3.2	6.3
Glucopon 225DK	13.8 (11.2-17.02)	7.6 (6.6-8.6)	<3.12	3.12
DGBE	>75 NC	>75 NC	75	>75
HMTS-PEO-TMACL (HMTS)	>1.56 NC	>1.56 NC	1.56	>1.56
N10477-09	1.33 (0.99-1.80)	1.02 (0.83-1.14)	0.1	0.2
Silwet-77	2.32 (1.7-3.1)	0.6 (0.5-0.8)	0.31	0.62
502W	19.2 (15.5-23.9)	7 (6.4-8.1)	<3.12	3.12
502W Sulfate	>100 NC	>100 NC	100	>100
NRL 502W	70.7 (54.5-91.7)	67 (56.9-75.3)	25	50
MD-2062-124	52.8 (43.52- 55.99)	36.55 (11.73-69.97)	<12.5	12.5
MD-2086-1	43.43 (33.69- 55.99)	17.76 (15.51-18.81)	12.5	25

Table 10. Summary of acute toxicity endpoints (mg/L) for tests with *P. promelas*. All endpoints derived using nominal concentrations. NC= Not Calculated, absence of dose-response relationship precluded calculation. Shaded cell = not tested.

Test Material	Mean LC50 (mg/L) (95% CI) (Survival)	NOEC (Survival)	LOEC (Survival)
Capstone 1157	38.1 (34.5-42.0)	23.4	46.9
Fluorosurfactant Mixture (Capstone Mix)			
Glucopon 215UP	>100 NC	100	>100
Glucopon 225DK	>100 NC	100	>100
DGBE	2092 (2035-2151)	1500	3000
HMTS-PEO- TMACL (HMTS)	3.08 (2.8-3.34)	1.25	2.5
N10477-09			
Silwet-77	1.5 (1.4-1.7)	0.96	1.92
502W	2.3 (2.1-2.6)	1.5	3
502W Sulfate	>100	100	>100
NRL 502W	>100	100	>100
MD-2062-124			
MD-2086-1			

Table 11. Summary of chronic toxicity (growth as biomass) endpoints (mg/L) for tests with *P. promelas*. All endpoints derived using nominal concentrations. NC= Not Calculated, absence of dose-response relationship precluded calculation. Shaded cells = materials not tested.

Test Material	Mean LC50 (95% CI) (Survival)	Mean IC50 (95% CI) (Growth)	NOEC (Survival)	LOEC (Survival)	NOEC (Growth)	LOEC (Growth)
Capstone 1157	23.89 (17.32-32.96)	11.6 (7.37-15.33)	12.5	25	3.12	6.25
Fluorosurfactant Mixture (Capstone Mix)						
Glucopon 215UP						
Glucopon 225DK						
DGBE	1333 (1122.5-1583.3)	>2000 NC	500	1000	2000	>2000
HMTS-PEO-TMACL (HMTS)	1.9 (1.8-2)	1.98 (1.7-2.13)	1.25	2.5	1.25	2.5
N10477-09						
Silwet-77	1.24 (1.16-1.40)	>0.438 NC	0.875	1.175	0.219	>0.438
502W	2 (1.9-2.2)	2.28 (1.14-2.62)	1.5	3	1.5	3
502W Sulfate						
NRL 502W	>100	>100	100	>100	100	>100
MD-2062-124						
MD-2086-1						

Table 12. Summary of chronic toxicity (growth as cell counts) endpoints (mg/L) for tests with *R. subcapitata*. All endpoints derived using nominal concentrations. NC= Not Calculated, absence of dose-response relationship precluded calculation. Shaded cells = materials not tested.

Test Material	Mean IC50 (mg/L) (95% CI) (Growth)		NOEC (Growth)	LOEC (Growth)
Capstone 1157	>400	100	200	
Fluorosurfactant Mixture (Capstone Mix)				
Glucopon 215UP	31.2 (28.0 – 36.4)	25	50	
Glucopon 225DK				
DGBE	310.2 (176.9 – 246.2)	125	250	
HMTS-PEO-TMACL (HMTS)				
N10477-09				
Silwet-77	6.8 (6.4 – 7.4)	3.75	7.5	
502W				
502W Sulfate				
NRL 502W	174.3 (160.7 – 190.2)	50	100	
MD-2062-124				

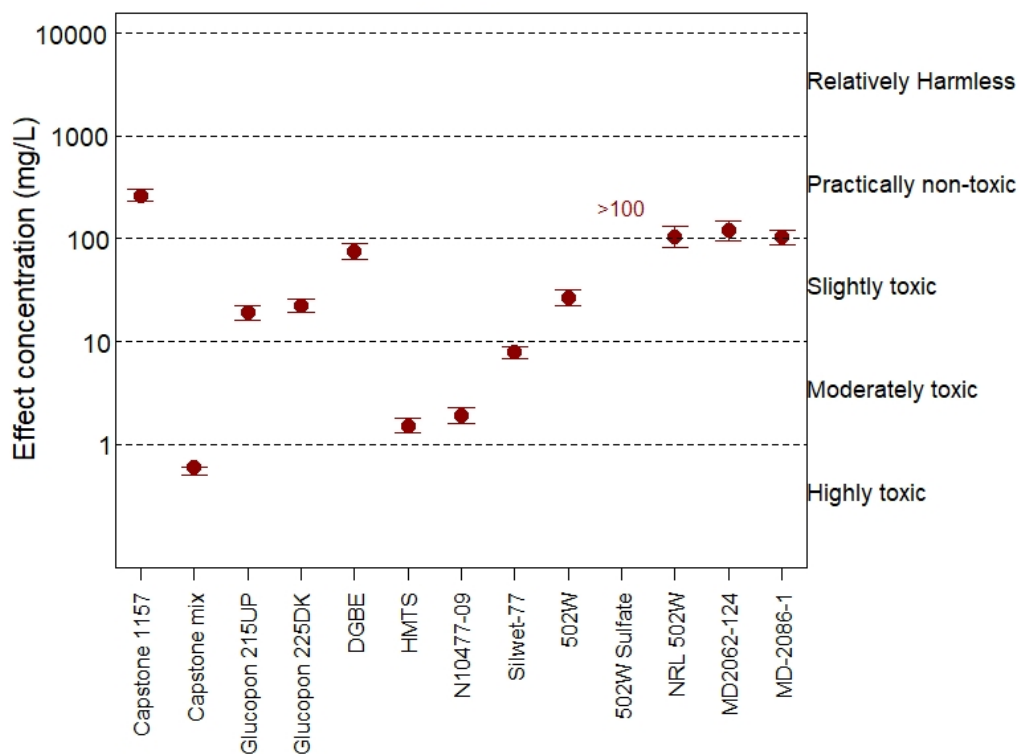


Figure 24. *C. dubia* acute survival LC50 values (mg/L) plotted against USEPA aquatic hazard categories.

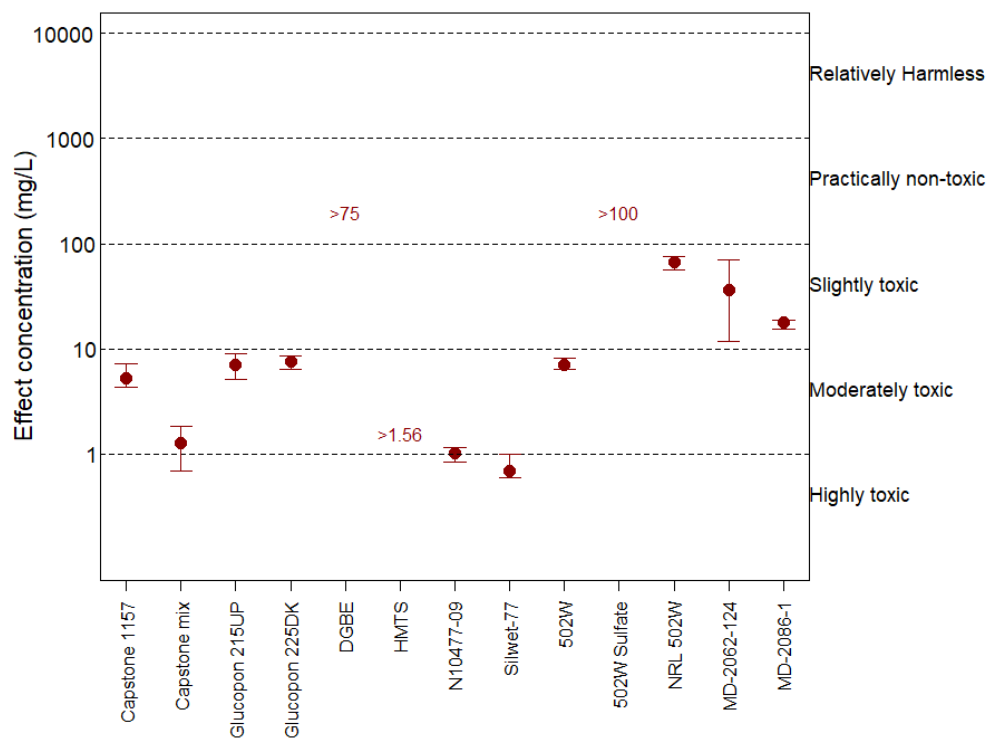


Figure 25. *C. dubia* chronic reproduction IC50 values (mg/L) plotted against USEPA aquatic hazard categories.

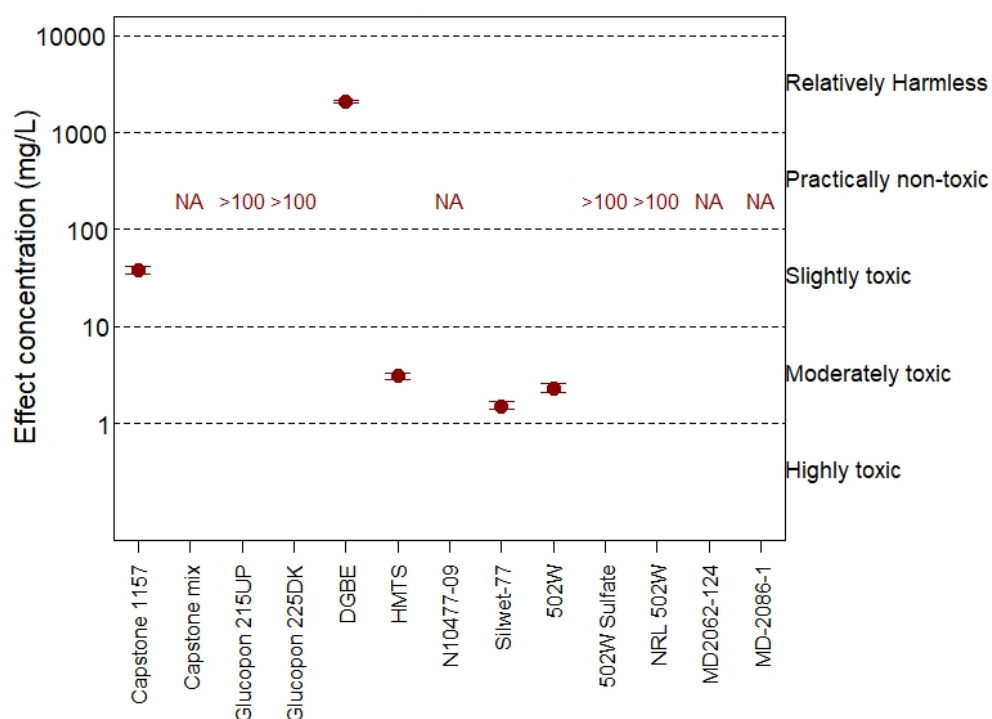


Figure 26. *P. promelas* acute survival LC50 values (mg/L) plotted against USEPA aquatic hazard categories. NA = not tested. > values indicate LC50 could not be calculated and exceeded highest concentration tested.

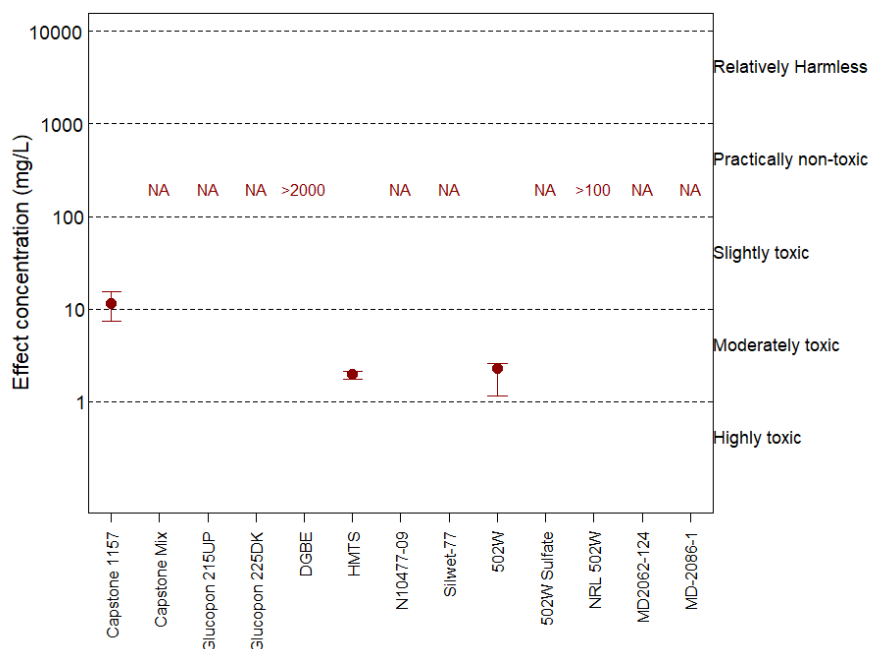


Figure 27. *P. promelas* chronic (growth as biomass) IC50 values (mg/L) plotted against USEPA aquatic hazard categories. NA = not tested. > values indicate LC50 could not be calculated and exceeded highest concentration tested.

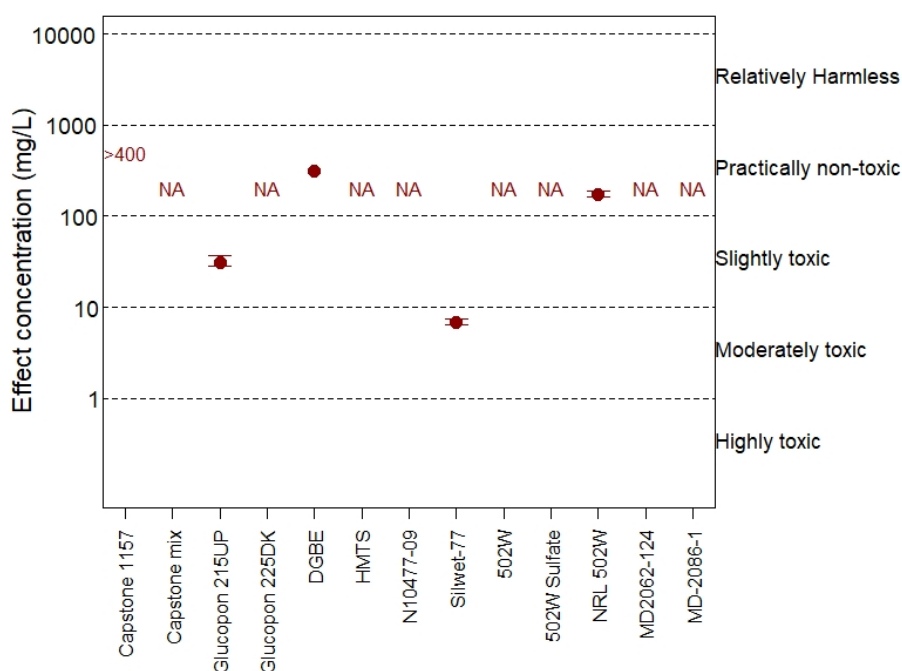


Figure 28. *R. subcapitata* chronic (growth as cell counts) IC50 values (mg/L) plotted against USEPA aquatic hazard categories. NA = not tested. > values indicate LC50 could not be calculated and exceeded highest concentration tested.

Based on these results the least toxic of the compounds/formulations evaluated included DGBE, 502W sulfate, NRL 502, MD2062-124 and MD2086-1, which generally fell in the slightly toxic to practically nontoxic range (i.e., >10 mg/L). Conversely the most toxic compounds/formulations evaluated included the Capstone mix, HMTS, N10477-09, and Silwett-77, which generally fell in the highly to moderately toxic range (i.e., 0-10 mg/L) for the test species and endpoints evaluated. Based on results of the most complete data set (*C. dubia*) the relative order of toxicity of the tested compounds from least toxic to most toxic for acute survival (Figure 24, Table 8) is as follows: Capstone 1157, 502W Sulfate < NRL502W, MD2062-124, MD-2086-1 < DGBE < 502W < Glucopon 225DK, Glucopon 215UP < Silwett-77 < N10477-09 < HMTS < Capstone mix. The order of relative toxicity was similar in chronic tests with *C. dubia* was similar with the exception of Capstone which was comparatively more toxic in relation to the other compounds/formulation evaluated with a reproductive IC50 value of 5.28 mg/L (Table 9). The relative order of toxicity for the common set of compounds/formulation (Capstone 1157, DGBE, and NRL502W) tested across all species and endpoints was similar though there were pronounced differences in toxicity between species for some compounds (e.g., DGBE LC50 for an LC50's of 75mg/L for survival in acute tests with *C. dubia* survival vs. and LC50 of 2092 mg/L for *P. promelas*) (Tables 8 & 10).

5.3. Task 5.1. – Interfacial and foam properties

This section describes results obtained from measurements of interfacial and foam properties.

5.3.1. Task 5.2. – Oleophobicity, Surface and interfacial tensions, and CMC

The premix formulations should have low enough surface tension and CMC values to be used in practice. The formulations should contain surfactants in well excess over the CMC values to ensure saturation of the newly created interfaces of bubbles in a foam. It is also crucial to know the interfacial tension as a measure of thermodynamic driving force for emulsification with a fuel. Table 13 shows properties of premix formulations including surface tension, interfacial tensions with heptane and gasoline, and CMC values. It also shows the properties of individual siloxane surfactants in water. For comparison, Table 13 also includes fluorocarbon surfactant formulation (RefAFFF) and individual fluorocarbon surfactant (Capstone1157). Properties for Glucopon225DK and Glucopon215UP were reported previously [9, 27].

Surface and interfacial tensions and CMC are affected by the siloxane surfactant molecular structure despite differences in compositions shown in Table 13. Variations in surfactant structure affects intermolecular forces such as hydrophilic, hydrophobic, and oleophobic interactions with water, fuel, and other surfactants in the formulation. Interfacial properties are affected by competition between two effects which are coupled in a complex manner and is difficult to separate. One of the effects is changing the trisiloxane-PEO's nonionic PEO head to ionic head increases the hydrophilicity and tends to pull the siloxane surfactant more on to the aqueous side of water-air interface of a bubble. The second effect is an imbalance between hydrophobicity of the tail and hydrophilicity of the head that deteriorates amphiphilicity of the surfactant. The imbalance tends to pull the surfactant more to water or air side of the interface depending on whether tail is relatively more hydrophobic than the hydrophilicity of the head or the head is relatively more hydrophilic than the hydrophobicity of the tail. Given that perfectly balanced amphiphilicity is difficult to predict a priori and is difficult to synthesize such a molecule in practice, we attempted to look for patterns in how the interfacial properties are affected by the changes in molecular structure of the siloxane surfactant empirically as illustrated below.

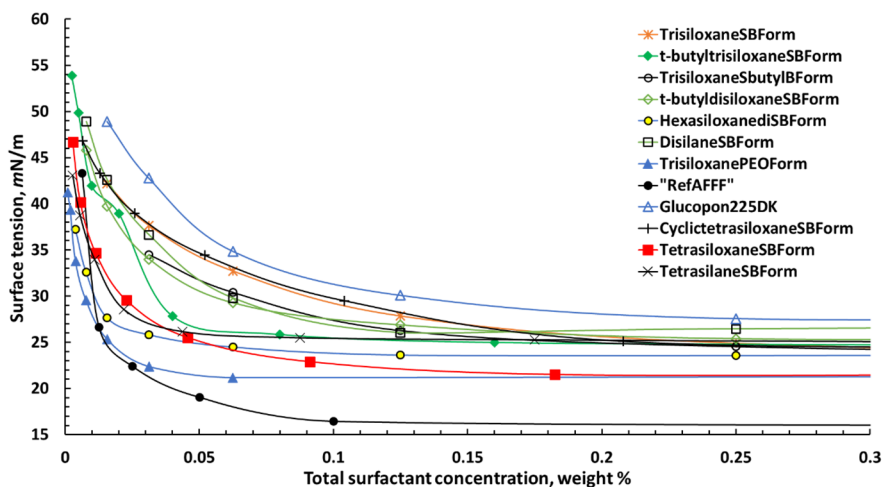
Table 13 also shows surface tension, interfacial tension, and CMC (as weight %) for different sulfobetaine (SB), trisiloxane-PEO (502W), and Capstone1157 surfactants alone in columns 2 to 5. CMCs in weight % and molar concentration follow roughly similar trends. For individual surfactant solutions, it shows changing the head from PEO to SB with a fixed trisiloxane tail has increased interfacial tensions and CMC (weight % in column 4) dramatically. This could be because the zwitterionic head increases the hydrophilicity without increasing the hydrophobicity of the tail causing imbalance in amphiphilicity. The imbalance could cause the SB surfactant to migrate more into bulk water phase requiring greater CMC to saturate air-water interface. The zwitterionic head could also decrease surfactant concentration at the fuel-water interface leading to increased interfacial tension; changing SbutylB head from SB head with the trisiloxane tail fixed has reduced the interfacial tensions somewhat. Changing the tail from trisiloxane to t-butyltrisiloxane tail with the same SB head dramatically reduced the interfacial tensions and CMC but increased the surface tension. Changing to tetrasiloxane tail reduced the surface tension and CMC further while interfacial tensions did not change significantly compared to the t-butyltrisiloxane tail. This could be because they increase the hydrophobicity of the tail balancing it with the increased hydrophilicity of the SB head. Surprisingly, removing the oxygen from the tetrasiloxane tail with tetrasilane tail increased the surface and interfacial tensions significantly but further reduced CMC. A further increase in hydrophobicity of the tail may cause an overshoot and slight imbalance with the hydrophilicity of the SB head. Even more surprisingly,

Table 13. Surface and interfacial tensions and CMC for surfactant formulations with compositions shown in Table 1. Values for the individual siloxane (or fluorocarbon) surfactants are also shown.

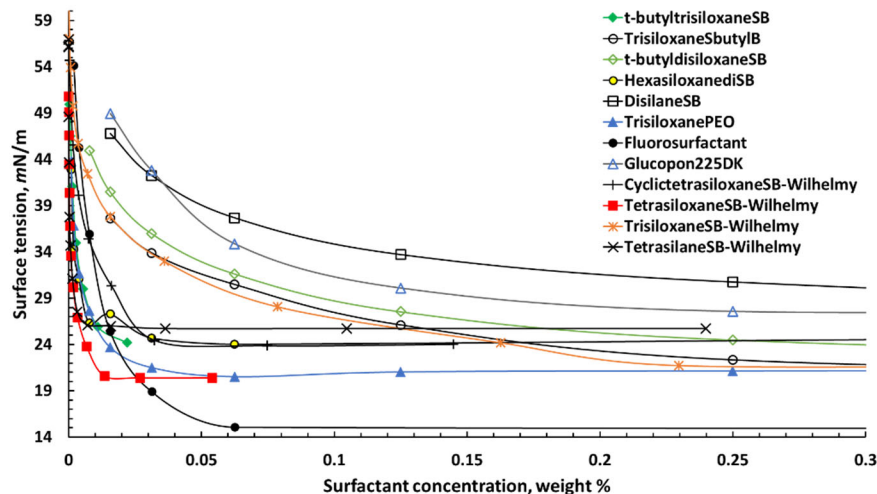
Key surfactant	Solution with key surfactant only				Surfactant formulation in Table 1		
	Key surfactant in water % weight	Surface tension mN/m	Interfacial tension with gasoline, heptane mN/m	CMC % weight (mM)	Surface tension mN/m	Interfacial tension with gasoline, heptane mN/m	CMC % weight
Tetrasiloxane-sulfobetaine MD2062-124, N10478-198	0.02	20.6	0.4, 0.7	0.0135 (0.27)	21.2	0, 0.1	0.088
Cyclictetrasiloxane-sulfobetaine N10478-81	0.04	24.0	0.4, 1.4	0.0363 (0.28)	24.3	0.4, 1.4	≥ 0.42
Tetrasilane-sulfobetaine N10477-189	0.005	25.7	2.9, 3.3	0.0047 (0.1)	25.0	0.1, 0.8	0.041
Trisiloxane-sulfobetaine MD2102-16, N10478-40	0.3	21.7	5.3, 10.4	0.23 (5.3)	22.7	0, 1.3	0.22
t-butyltrisiloxane-sulfobetaine, CB-DTBTS-SB	0.022	24.2	0.4, 0.5	≥0.028 (≥0.59)	23.9	0.7, 1.3	0.062
Trisiloxane-sulfobutylbetaine, CB-1-123	0.35	20.8	4.1, 8.5	0.31 (7.0)	22.8	0.9, 1.5	0.24
Disilane-sulfobetaine MD2102-90	0.5	28.5	2.9, 5.6	0.3 (8.1)	26.5	1.3, 2.5	0.1
t-butylidisiloxane-sulfobetaine MD2102-99	0.5	23.8	N/A	0.2 (4.8)	25.1	0.9, 2.1	0.12
Hexasiloxane-disulfobetaine CB-1-180B	0.5	23.5	1.4, 3.1	0.016 (0.16)	24.0	0.6, 1.3	0.036
Trisiloxane-polyoxyethylene (502W)	0.5	20.5	3.0, 2.9	0.02 (average 0.28)	22.5	2.2, 2.9	0.030
0.3% Glucopon 225DK+0.5% DGBE	0.3	28.1	1.2, 2.9	0.16	N/A	N/A	N/A
Perfluorooctyl sulfonamide alkylbetaine (Capstone1157)	0.5	15.8	4.0, 5.5	0.04	16.7	1.0, 1.9	0.080

changing conformation of the tail from branched tetrasiloxane to cyclic tail could have potentially increased the tail's hydrophobicity causing significant increases in surface and interfacial tensions (with heptane) and a slight increase in CMC. The precise reasons for this effect of tail's conformation are unclear. As mentioned above, trisiloxaneSB has increased CMC and interfacial tensions compared to trisiloxanePEO. Changing the tail from trisiloxane to t-butylidisiloxane or disilane further increased CMC as one might expect from the above discussion of reduced

amphiphilicity but it decreased interfacial tensions. Even though hexasiloxane-disulfobetaine is essentially twice the size of trisiloxane sulfobetaine and one might have expected similar CMC values, the double headed surfactant's CMC is much smaller than a factor of 2. TrisiloxaneSB and trisiloxaneSbutylB stand out from the rest because of their high interfacial tensions of 10.4 and 8.5 mN/m respectively, especially with heptane. Similarly, trisiloxaneSB and tetrasilaneSB stand out from the rest because of very high or very low CMC values of 0.25 and 0.0047 % respectively. These uniquely different values may suggest imbalance in amphiphilicity and low surface activity.



(a)



(b)

Figure 29. (a) Surface tension versus total surfactant (Siloxane+Glucopon) concentration for surfactant formulations listed in Table 1, (b) Surface tension versus surfactant concentration for aqueous solutions containing one surfactant only. Wilhelmy plate and Du Noy ring methods were used as indicated.

Table 13 also shows surface tension, interfacial tension, and CMC for different sulfobetaine, trisiloxane-PEO (502W), and Capstone1157 surfactant formulations in columns 6 to 9 with compositions listed in Table 1. As the siloxane surfactant molecular structure is changed,

the surface tension and CMC values of the formulation roughly follow the trends similar to the siloxane surfactant alone as described above with the exceptions of disilaneSB and t-butylidisiloxaneSB. However, the interfacial tensions of the formulations seem to be relatively insensitive to changes in siloxane structure unlike the siloxane surfactant alone and could be because Glucopon surfactant is adsorbing at the fuel-water interface and dominating the interfacial tension values unlike the surface tensions. TrisiloxaneSB and cyclictetrasiloxaneSB formulations stand out from the rest of the formulations because of their high CMC values of 0.22 % and > 0.42 % and may suggest imbalance in amphiphilicity and low surface activity.

CMC values listed in Table 13 are determined from surface tension versus surfactant concentration plots. Figure 29a shows surface tension versus total surfactant concentration for the formulations. The total surfactant concentration includes the siloxane and Glucopon225DK surfactants. The curves are fitted to two straight lines following the standard procedure for determining CMC at the intersection values as shown in Table 13. Figure 29b shows similar plot for individual surfactants for determining their CMC values shown in Table 13.

5.3.2. Task 5.1.1. Foam expansion ratio, bubble size, and liquid drainage

Foam quality could be very important affecting its ability to extinguish a fire. Quality depends on foam generation methods used at bench and large scales and could be assessed by measuring initial bubble size distributions, bubble coarsening with time, and liquid drainage with time using DFA instrument. The foams are generated externally using methods similar to those used for fire extinction rather than using internal mechanisms provided within the DFA instrument. At the large scale, foams are generated using the aspirated MilSpec nozzle at 2 gallon per minute solution flow under 100 psi pressure. The foams are sprayed on to a flat vertical panel with grooves to direct the foam flow at the bottom using a standard method. The foam is collected at the bottom of the groove into the DFA cylinder. At the bench scale, foams are generated at 1000 mL/min air flow rate by using sparging method at atmospheric condition and are fed into the DFA cylinder directly from the generator.

Table 14 lists foam properties including expansion ratios for the sulfobetaine formulations. At large scale, the expansion ratio and 25% liquid drainage times are measured following MilSpec methods described in MIL-PRF-24385SH. In the MilSpec method, foam from the MilSpec nozzle is sprayed on to a slanted aluminum plate and the foam drained from the plate is collected into two graduated cylinders for measuring the 25% liquid drainage times and initial expansion ratio as reported in Table 14. We also collected the same foam into DFA cylinder and measured liquid drainage, bubble size distributions, and average bubble size versus time for the large scale foam generation as shown in Table 14. In addition, we collected the foam from the MilSpec nozzle into a 5 gallon bucket and measured foam flow rate and foam's weight to obtain expansion ratio, which is reported in parentheses in Table 14. Liquid drainage, bubble size distributions, and average bubble size versus time are measured using the DFA as reported in Table 14.

The large scale data show only slight differences in average initial bubble radius, expansion ratio (4.5 to 6.7), and 25% liquid drainage times depending on the formulation's composition. For example, changing the head and tail of trisiloxanePEO to tetrasiloxaneSB appears to have reduced the average initial bubble radius only slightly (54 to 40 μm), if at all, comparable to that of RefAFFF. The bench scale data also show small differences in liquid drainage (<10% variation),

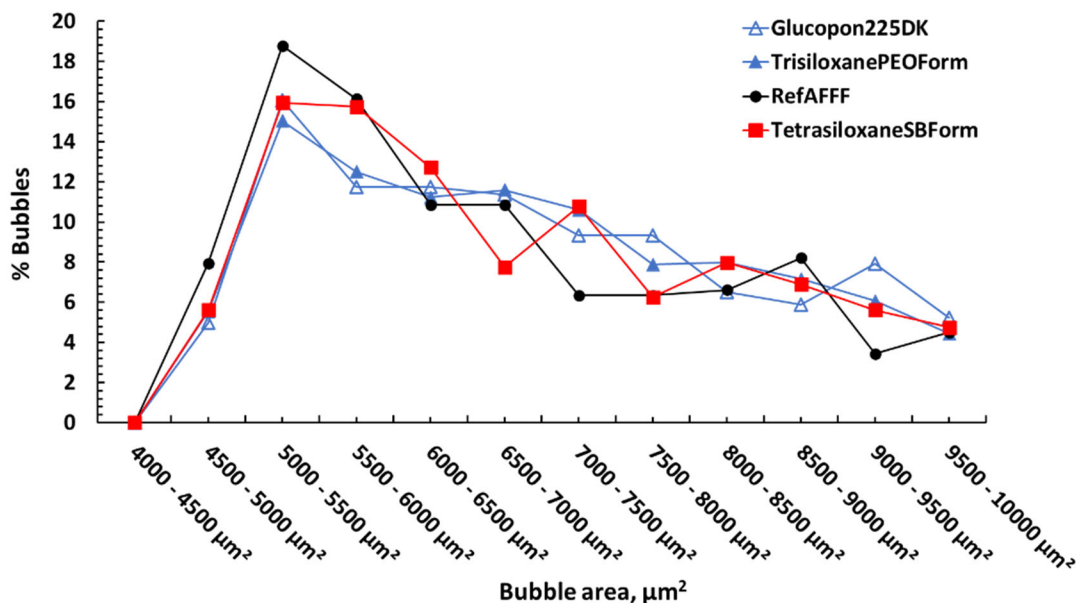
initial average bubble size (40 % variation), and expansion ratio (8.5 to 12 variation) depending on the formulation's composition. But for a given formulation, expansion ratios are smaller for large scale compared to small scale foam generation. More importantly, the initial bubble sizes are 3 to 4 times smaller at large scale than at bench scale foams. The 25% liquid drainage times measured by DFA are also longer by a factor of 3 to 4 at the large scale than at the bench scale.

Table 14. Foam quality as measured by initial expansion ratio, initial average bubble radius, and time for 25% liquid drainage at large (28 ft² pool MilSpec) scale and bench scale.

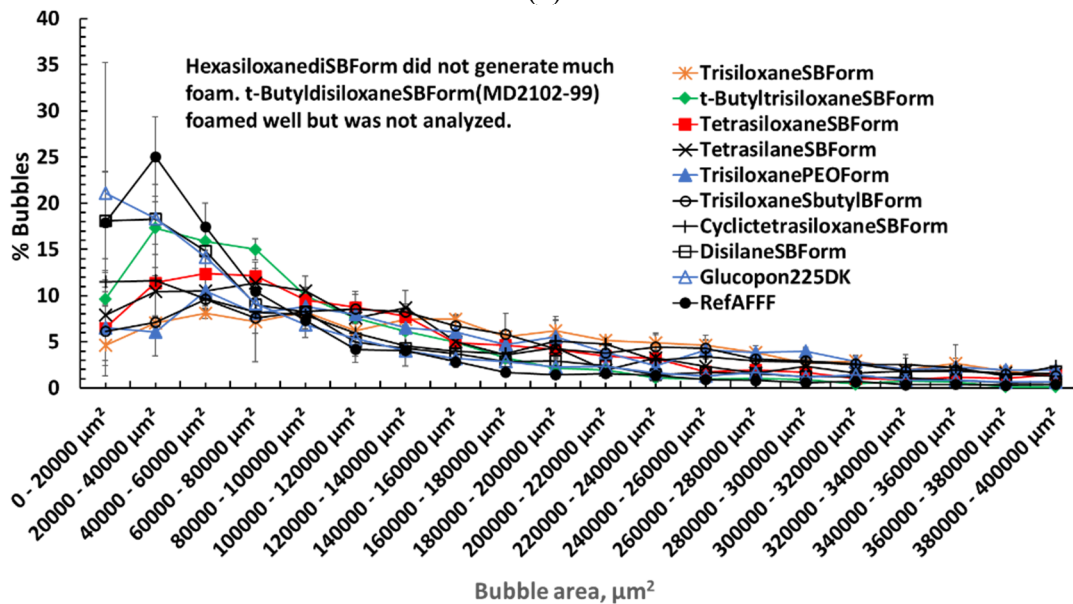
Key surfactant	Large scale MilSpec nozzle at 2 gpm solution flow			Bench scale sparging at 1000 mL/min air flow			
	MilSpec Expansion ratio, (Expansion ratio measured by foam weight)	Initial bubble radius by DFA, μm	MilSpec 25% liquid drainage time, s (25% drainage by DFA)	Expansion ratio measured by foam weight, Ex	Initial bubble radius by DFA, μm	25% liquid drainage time by DFA, s	% Liquid drained at 60 s
Tetrasiloxane-sulfobetaine MD2062-124, N10478-198	4.5 (5.7)	40 $\pm$ 15	216 (150)	9.0	197 $\pm$ 2	< 50	72 $\pm$ 1
Cyclotetrasiloxane-sulfobetaine N10478-81				11.7	215 $\pm$ 6	< 50	68 $\pm$ 3
Tetrasilane-sulfobetaine N10477-189				9.7	219 $\pm$ 20	< 50	74 $\pm$ 2
Trisiloxane-sulfobetaine MD2102-16, N10478-40				11.0	222 $\pm$ 30	< 50	72 $\pm$ 4
t-butyltrisiloxane-sulfobetaine, CB-DTBTS-SB				8.5	173 $\pm$ 23	< 50	65 $\pm$ 1
Trisiloxane-sulfobutylbetaine, CB-1-123				10.9	215 $\pm$ 8	< 50	69 $\pm$ 1
Disilane-sulfobetaine MD2102-90				9.6	183 $\pm$ 16	< 50	74 $\pm$ 1
Hexasiloxane-disulfobetaine CB-1-180B				14.0	292 $\pm$ 36	Non-Foaming	Non-Foaming
Trisiloxane-polyoxyethylene (502W)	5.0 $\pm$ 0.4	54 $\pm$ 1	234 (127)	8.5	233 $\pm$ 6	< 50	71 $\pm$ 1
0.3 % Glucopon 225DK+0.5 % DGBE	6.7 $\pm$ 0.1	54 $\pm$ 1	230 (170)	7.6	165 $\pm$ 20	< 50	70 $\pm$ 3
Perfluorooctyl sulfonamide alkylbetaine (Capstone1157)	6.6 $\pm$ 0.1	53 $\pm$ 1	317, 180 (190)	9.3	149 $\pm$ 9	< 50	78 $\pm$ 4

Figures 30a and b show initial bubble size distributions measured within a minute of generating the foams at large and bench scales respectively. Even though the bubble size distributions have similar shape at both scales, the size ranges are very different. At large scale, the bubble area falls between 4000 to 10000 μm^2 while at bench scale they fall between 10,000 to 400,000 μm^2 . Despite a factor of 2 to 3 difference in bubble radii between large and bench scale foam generation, the distributions among different formulations are very similar. Also, RefAFFF

has a narrower distribution than the fluorine-free formulations at both scales. The distributions for trisiloxane-PEO and RefAFFF formulations using DFA are very different from those reported previously [9] where a digital camera and ImageJ software were used to calculate the bubble size distributions from the pictures. The digital camera pictures showed very similar distributions between large and bench scale unlike the DFA measurements presented here.



(a)



(b)

Figure 30. Initial bubble size distribution for sulfobetaine formulations listed in Table 1 (a) large-scale foam generation at 2 gpm foam solution flow rates through an air-aspirated nozzle, (b) bench-scale foam generation using sparging method at 1000 mL/min air flow rate and fed into the DFA cylinder.

The DFA also measures bubble coarsening where the air from smaller bubbles diffuses into larger bubbles resulting in an increase in average bubble radius with time as shown in Figures 31a and b at large and bench scales respectively. We discussed before the changes in surfactant structure and the associated amphiphilicity correlated to CMC in reference to Table 13. We do not find similar correlations between bubble radius or coarsening with amphiphilicity or CMC or surface tension of surfactants. Instead, we find the foam properties vary some (factor of 2 or less) as the surfactant structure is changed but are much more (up to a factor of 5) dependent on the nozzle and pressure used to generate the foams. At large scale, the RefAFFF and glucopon have similar average bubble radii initially, while tetrasiloxaneSB and commercial AFFF have slightly smaller initial bubble radii. The bubble radius increases by 60% for RefAFFF with time while it increases by 2 to 3 times for all other formulations shown in Figure 31a including the commercial AFFF. At bench scale, the initial bubble radius and increase in bubble radius with time remain

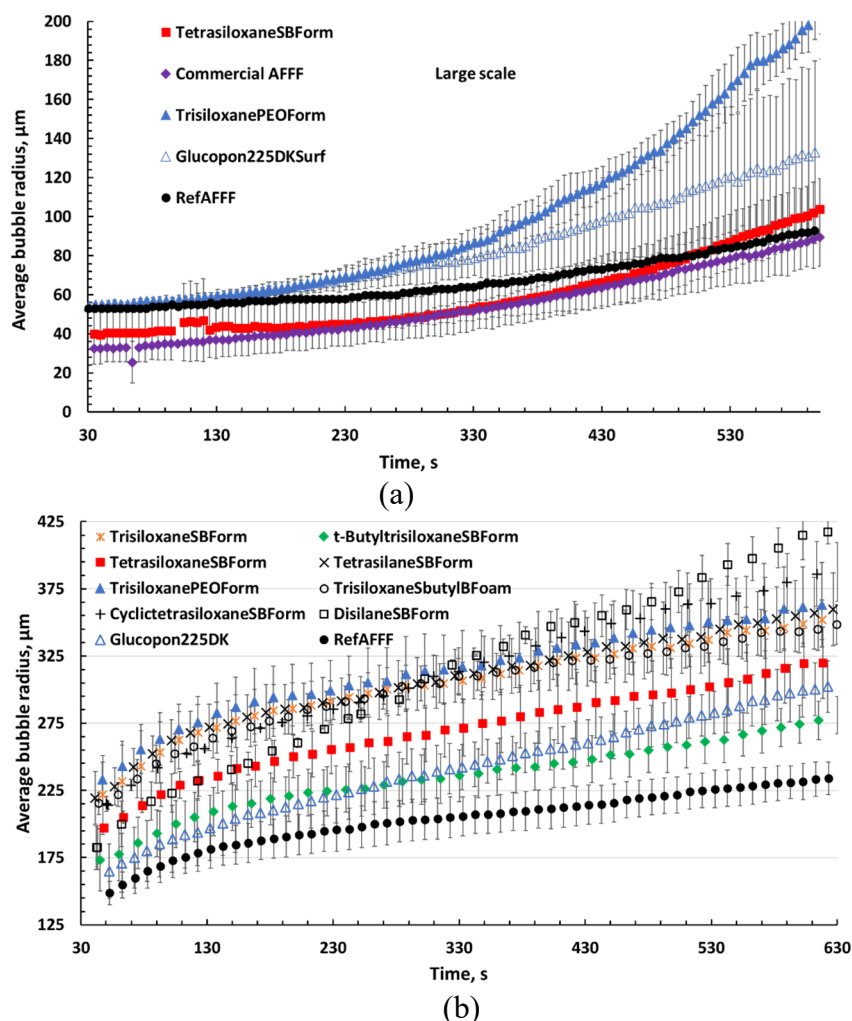


Figure 31. Initial average bubble diameters and coarsening measured using DFA for sulfo betaine formulations listed in Table 1 (a) large-scale foam generation, (b) bench-scale foam generation.

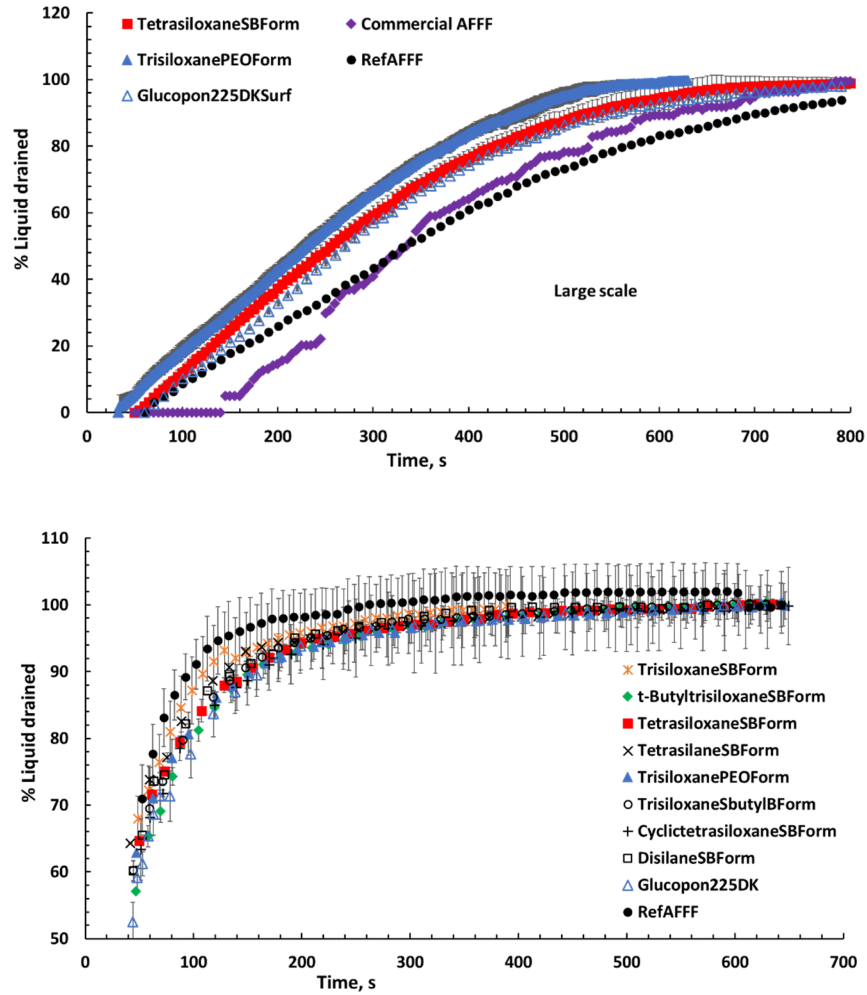


Figure 32. Liquid drainage profiles measured by DFA for sulfobetaine formulations listed in Table 1 (a) large-scale foam generation, (b) bench-scale foam generation.

unchanged as the surfactant head is changed from PEO to SB or SbutylB, with fixed trisiloxane tail in Figure 31b. With the SB head fixed, as the trisiloxane tail is changed to t-butyltrisiloxane or tetrasiloxane the initial bubble radius decreases, and coarsening rate remains the same. But as the tetrasiloxane tail is changed to tetrasilane or cyclic tetrasiloxane, the initial bubble radius and coarsening do not change significantly. However, as the trisiloxane tail is changed to disilane, bubble coarsening rate increases significantly. RefAFFF bubbles coarsen more slowly than siloxane foams or GlucoPON225DK consistent with the large scale. Clearly, the initial average bubble sizes for bench scale foams are 5 times larger than the large scale for the tetrasiloxaneSB foam. Consistently, the foams drain several times more quickly at bench scale as shown in Figure 32a than at the large scale shown Figure 32b.

5.3.3. Task 6.1. -Oleophobicity, foam degradation on fuel pools, and fuel permeation through foam

When foams are applied on to hot fuel pool, the fuel vapors degrade the foams [2]. The rate of foam degradation depends on compositions of fuel and surfactant formulation, and fuel

temperature. Increased fuel temperature increases the vapor pressure and accelerates foam degradation. A 4-cm thick foam layer generated by sparging method is placed on heptane and gasoline pools, which are held at 60 °C and 37 °C respectively and decrease in foam layer thickness is measured with time. The foam bubbles adjacent to pool surface coalesce and form a large bubble (gap) that lifts up the remaining foam above the gap and increases the total thickness (gap+remaining foam thickness). We plotted only the remaining foam thickness excluding the gap. The reported error bars represent 2 standard deviations from 4 averaged trials for the tetrasiloxanesulfobetaineForm and 2 averaged trials for the 0.3%G225DK 0.5%DGBE.

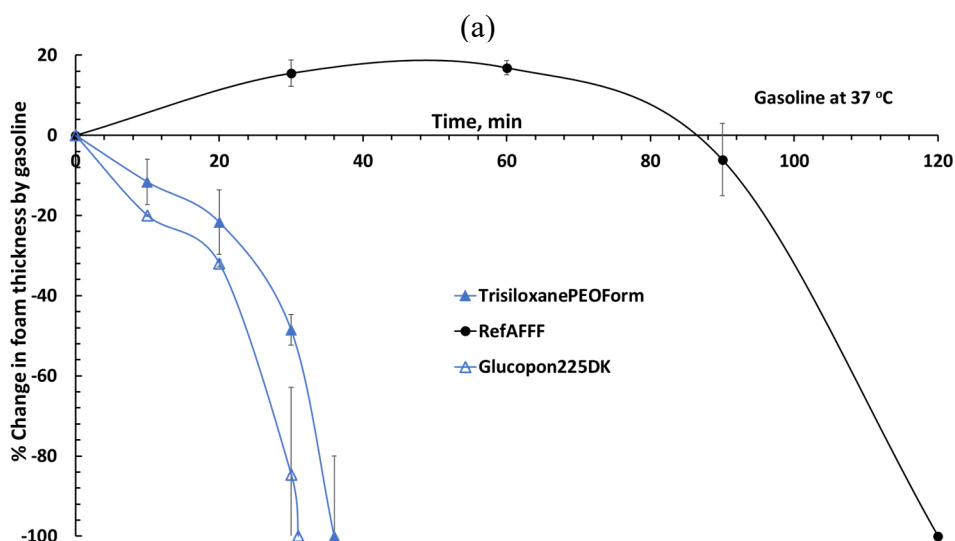
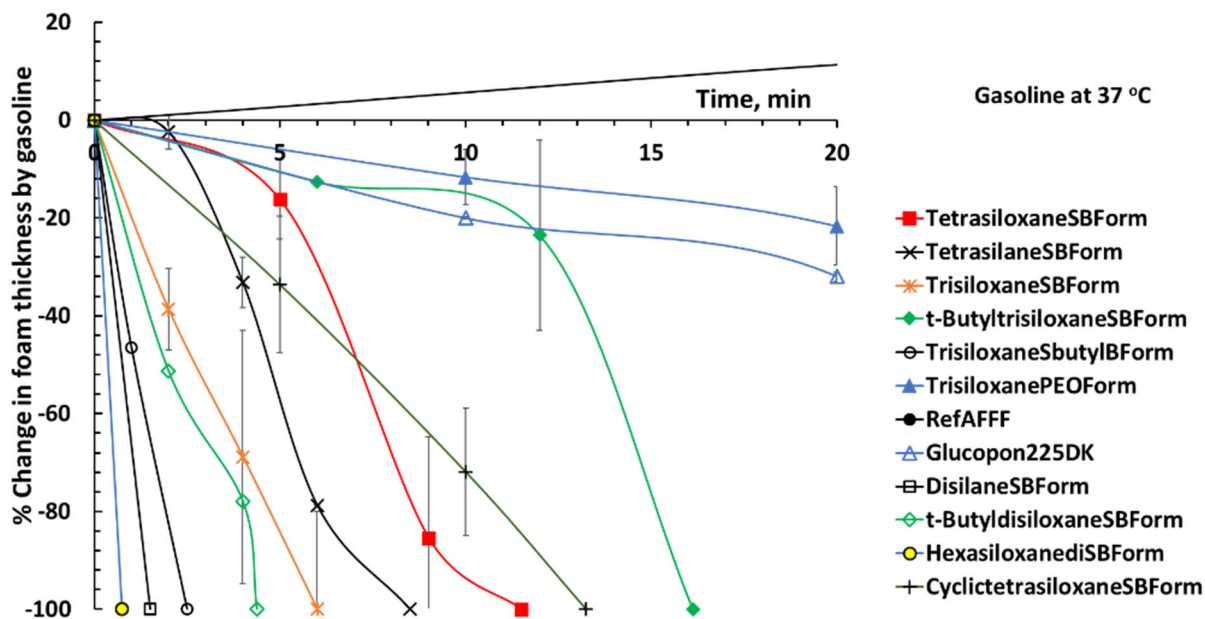
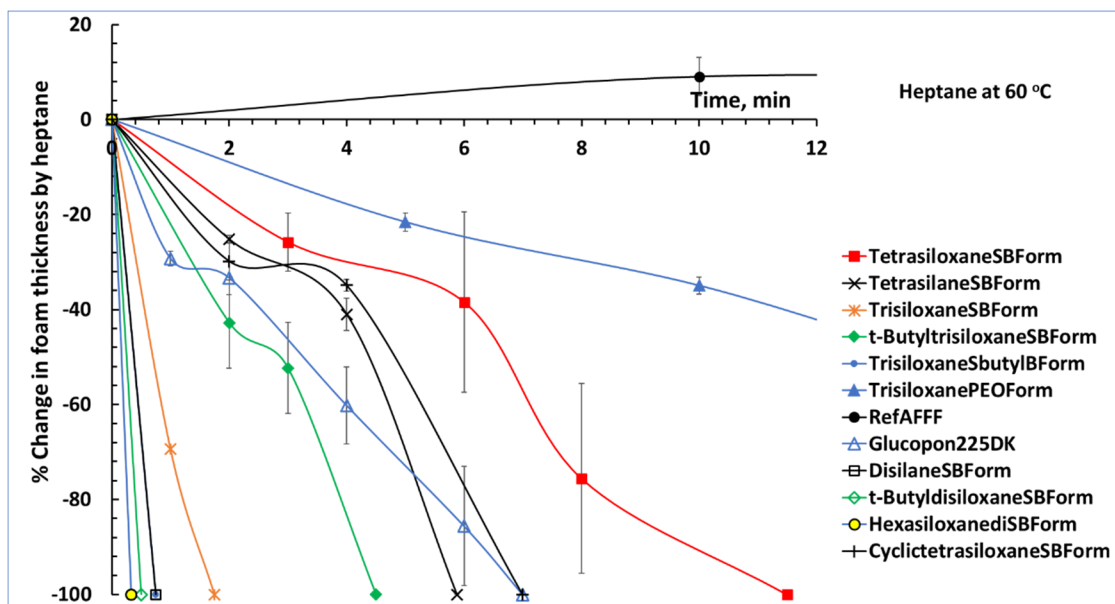
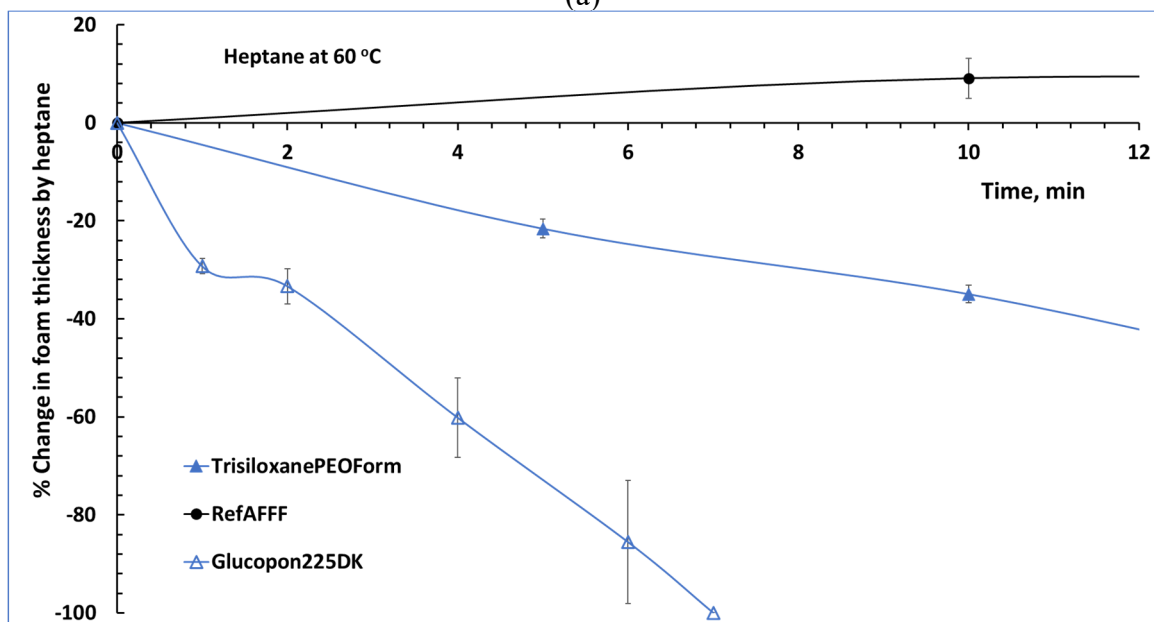


Figure 33. Degradation of 4-cm thick (initial thickness) foam covering warm gasoline pool (37 °C) versus time: (a) 0 to 20 min, (b) 0 to 120 min.



(a)



(b)

Figure 34. Degradation of 4-cm thick (initial thickness) foam covering hot heptane pool (60 °C) versus time: (a) 0 to 20 min, (b) 0 to 120 min.

The plots shown in Figure 33a and 33b report the percent change in foam layer thickness with time for gasoline at 37 °C . As the siloxane structure is varied, foam lifetimes (time at 100 % degradation) largely follow the trends in CMC as discussed for the data shown in column 8 of Table 13 but in reverse order (i.e., as the CMCs increase, foam lifetimes decrease). But, the foam lifetimes do not follow the trends in CMCs precisely or to the same degree likely because foam lifetime is also affected by the presence of gasoline vapors unlike the CMCs. When the CMC is decreased by the structural change, the foam degradation time increases making the foam more stable on gasoline. As the trisiloxane head is changed from PEO to SB, the foam lifetime decreases

from 36 to 6 min due to reduced amphiphilic balance and the CMC increases because the zwitterionic head increases the hydrophilicity without increasing the hydrophobicity of the tail. When the head is changed further from SB to SbutylB the foam lifetime decreases to 2.5 min due to further imbalance, but the CMC increases only slightly. With the SB head fixed, as the tail is changed from trisiloxane to t-butyltrisiloxane and tetrasiloxane the foam lifetime increases from 6 to 16 and 11.5 min respectively due to somewhat restored amphiphilic balance and the CMC in column 8 of Table 13 decreases as well. But the foam lifetimes do not increase more than that of trisiloxanePEO foam. Changing the tail from tetrasiloxane to tetrasilane decreases foam lifetime from 11.5 to 8.5 min somewhat different from the tail effect on CMC, which also decreases. This could be because the lack of oxygen in tail reduces oleophobicity and increases interaction with gasoline. Changing tail conformation from branched tetrasiloxane to cyclictetrasiloxane reduces the number of CH₃ groups and surprisingly increases lifetime to from 11.5 to 13 min. However, the same change in tail also increases the CMC in column 8 of Table 13 significantly. Changing the trisiloxane tail to disilane or t-butylidisiloxane or hexasiloxane significantly reduced foam lifetime different from what is expected from the effects on CMC, which is also reduced. Interestingly, the foam lifetimes for sulfobetaine head are shorter than foams generated from Glucopon225DK or the trisiloxanePEO. Like in Figure 33a and b, Figure 34a and b shows very similar trends for heptane at 60 °C except that the foam lifetime for tetrasiloxane-sulfobetaine is longer than that for glucopon225DK foam. The lifetime for AFFF is much longer than the siloxane foams for both gasoline and heptane.

An attempt was made to measure foam lifetime for the tetrasiloxaneSB surfactant without the co-surfactant (APG). However the foam degraded so quickly that a 4 cm foam layer never accumulated, and the data collection was not possible. This means the foam lifetimes for the tetrasiloxanesulfobetaine-glucopon225DK mixture are between the foam lifetimes for the individual components on gasoline. Thus the addition of glucopon225DK increased the lifetime of siloxane foams on gasoline exhibiting a lack of synergistic effects in foam stability. On heptane however, the foam lifetimes for the mixture are longer than those for foams generated from tetrasiloxane-sulfobetaine or glucopon225DK individually. This synergistic effect in foam stability is similar to the trisiloxanePEO-Glucopon225DK mixture but to a lesser degree.

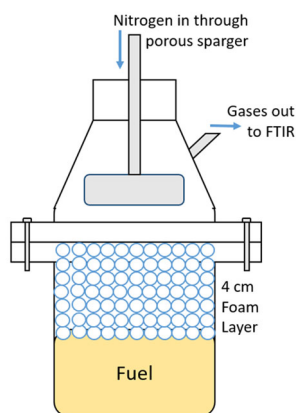


Figure 35. Experimental flux chamber used to measure fuel permeation through a foam layer placed on hot heptane pool at 60 °C. The fuel vapors emanating from the foam surface are carried by nitrogen gas into a FTIR [35].

Foams that can suppress the fuel vapor transport quickly will result in quicker fire extinction by cutting off the fuel supply to the fire. We previously designed an apparatus to measure a foam's ability to suppress fuel vapors as shown in Figure 35. This design is different from the one we reported on earlier [9]. The distance between the pool and vent to FTIR is shortened and shape is changed to rectangular plastic box. Heptane vapor permeation through a foam layer (4-cm initial thickness) placed on a hot heptane pool is measured inside a closed chamber shown in Figure 35 [3, 9]. Nitrogen is used as a carrier gas that carries heptane vapors emanating from the foam surface to a FTIR, which measures mole fraction of heptane in nitrogen with time. Fuel flux is obtained by multiplying the mole fraction with molar flow of the nitrogen gas stream.

The fuel flux profiles are shown in Figure 36 for the siloxane-sulfobetaine formulations. As the siloxane surfactant structure is varied, the fuel permeation follows the trends shown for foam degradation on heptane in Figure 33b as indicated by the rapid rise (vertical lines) in fuel flux as the fuel vapor breaks through the foam layer. As pointed out above, the foam thickness decreases with time causing fuel permeation rate to increase with time. A rapid rise in fuel flux profile indicates a breach in the foam layer because of degradation caused by the fuel vapors. The times when a rapid rise in fuel flux (breakthrough times) occurs in Figure 36 increases with increasing foam lifetimes in Figure 33b. Roughly similar trends are also observed at small times well before the breakthrough is reached. Figure 36 shows that the breakthrough times for a foam generated with tetrasiloxaneSB formulation is between trisiloxanePEO and Glucoptn225DK formulations but is still much higher than RefAFFF formulation. Foam degrades somewhat faster in the transport apparatus than in open beaker profiles shown in Figure 33 causing slight differences in trends between the degradation and heptane flux profiles as surfactant structure is varied. The flux profiles for trisiloxanePEO and Glucoptn225DK are different from our previously reported [9] data collected in a tall glass chamber because of differences in the design of the apparatus used and some changes could also arise from variation in compositions of surfactant batches received from the manufacturer. Therefore, RefAFFF is used as control to assess the flux profiles relative to one another in the current apparatus.

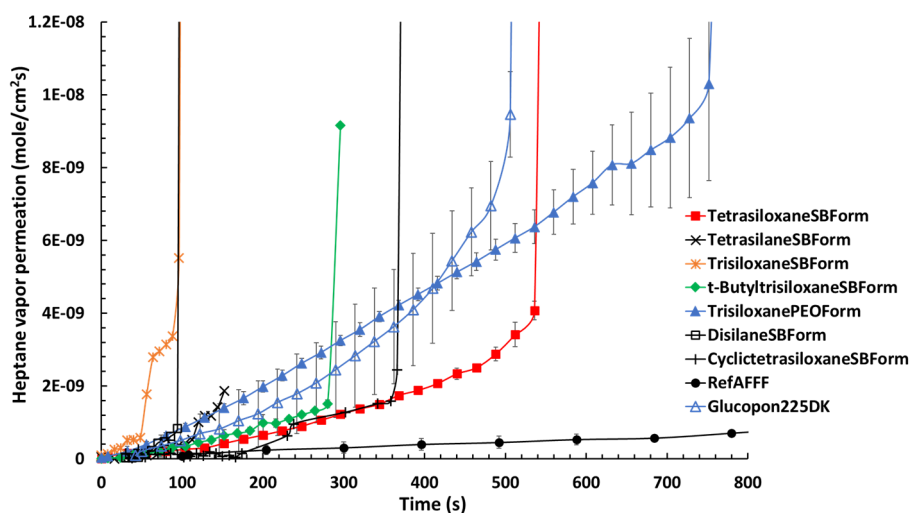


Figure 36. Heptane fuel mass flux emanating from the surface of a 4-cm thick (initial thickness) foam layer covering a hot (60 °C) heptane pool versus time. TrisiloxaneSbutylB foam degraded rapidly, and fuel flux measurements could not be made.

5.4. Task 6.2. – Bench scale fire performance

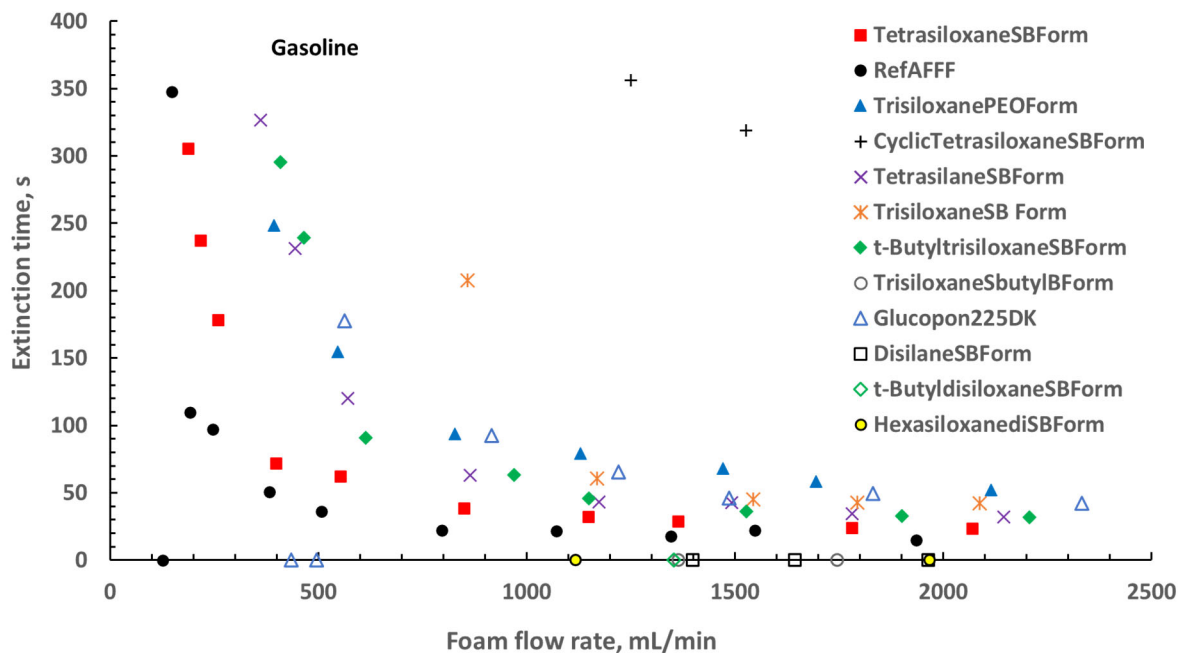
Fire extinction is conducted as described in section 2.2 with foams generated from surfactant formulations listed in Table 1. The formulations are tested on gasoline (alcohol-free), heptanes, Jet A and JP5 19-cm diameter fuel pools. Times for complete fire extinction, 90% fire extinction, and foam coverage of the pool are measured visually. The fuels are chosen because they are part of MIL-PRF-24385SH [28] and MIL-PRF-3389 [36]. Heptane is used in standardized testing for civilian firefighting applications and is also chosen because it is a mixture of its isomers only unlike the gasoline and Jet fuels, which contain a significant portion of aromatics [26].

5.4.1. Gasoline Fire

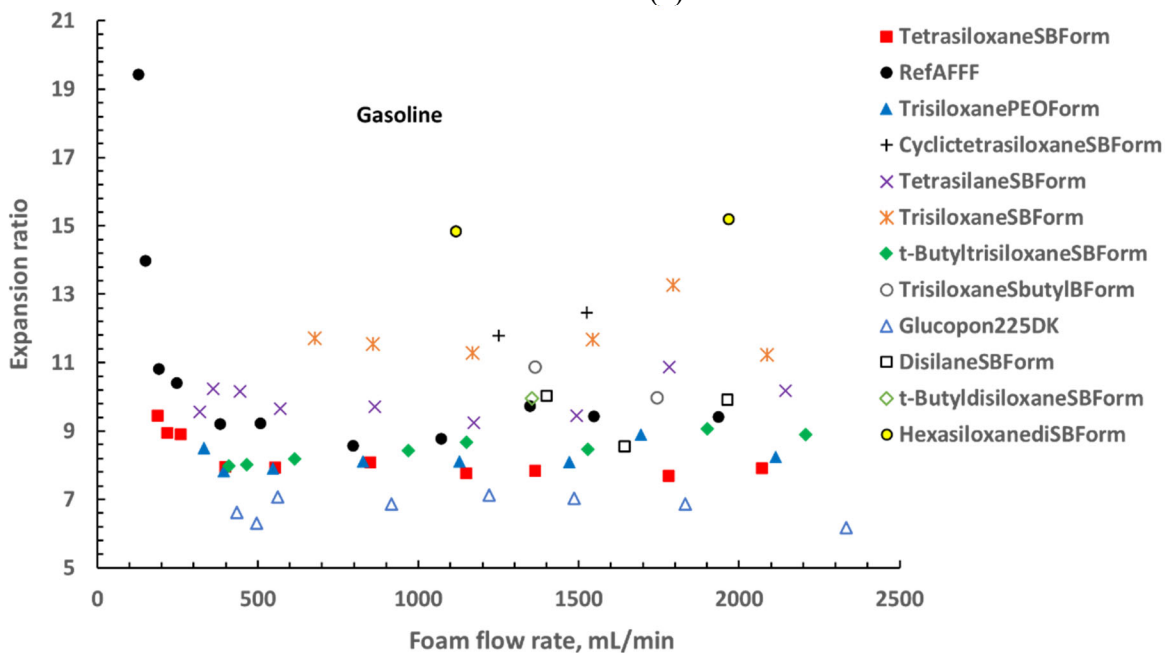
Fire extinction is affected by the siloxane surfactant molecular structure. Variations in surfactant structure affects intermolecular forces such as hydrophilic, hydrophobic, and oleophobic interactions with water, fuel, and other surfactants in the formulation. Fire extinction is affected by competition between two effects which are coupled in a complex manner and is difficult to separate. One of the effects is changing the nonionic head to ionic head that increases the hydrophilicity and tends to pull the siloxane surfactant more on to the aqueous side of water-air interface of a bubble. The second effect is an imbalance between hydrophobicity of the tail and hydrophilicity of the head that deteriorates amphiphilicity of the surfactant. The imbalance tends to pull the surfactant more to water or air side of the interface depending on whether tail is relatively more hydrophobic than the hydrophilicity of the head or the head is relatively more hydrophilic than the hydrophobicity of the tail. Given that perfectly balanced amphiphilicity is difficult to predict a priori and is difficult to synthesize such a molecule in practice, we took an empirical approach to reaching the optimum fire extinction performance as explained below.

Figure 37a shows fire extinction time versus foam application rate for different sulfobetaine, trisiloxane-PEO (502W), and RefAFFF formulations. It shows changing the head from PEO to SB with a fixed trisiloxane tail has increased fire extinction times especially at small foam application rates and changing it to SbutylB head worsened. This is consistent with decreased foam lifetimes in Figure 33a and with increased CMC in column 8 of Table 13. This could be because the ionic head increases the hydrophilicity without increasing the hydrophobicity of the tail causing imbalance in amphiphilicity. Changing the tail from Trisiloxane to t-butyltrisiloxane tail with the same SB head dramatically reduces the fire extinction times and changing to tetrasiloxane reduces the extinction times even further roughly consistent with increased foam lifetimes and reduced CMC (Figure 33a and Table 13 show that the effect is greater for t-butyltrisiloxane tail than for the tetrasiloxane tail). This could be because they increase the hydrophobicity of the tail balancing it with the increased hydrophilicity of the SB head. Surprisingly, removing the oxygen from the tetrasiloxane tail with tetrasilane tail increases the extinction times moderately consistent with reduced foam lifetime but not with reduced CMC. This could be because it further increases hydrophobicity of the tail causing an overshoot and slight imbalance with the hydrophilicity of the SB head. Even more surprisingly, changing conformation of the tail from branched tetrasiloxane to cyclic tail potentially increased the tail's hydrophobicity and fire extinction times dramatically. This is consistent with increased CMC but not with foam lifetime which increases as shown in Figure 33a. The precise reasons for this effect of tail's conformation on fire extinction is unclear. With the SB head fixed, changing the trisiloxane tail to disilane or t-butylldisilane resulted in no fire extinction in 5 min due to reduced amphiphilic balance between the head and tail consistent with trends in decreased foam lifetime

in Figure 33a but not with decreased CMC in Table 13. Even though hexasiloxane-disulfobetaine is essentially twice the size of trisiloxane sulfobetaine and one might have expected similar fire extinction times, the double headed surfactant does not extinguish the fire consistent with much smaller foam lifetime but not consistent with smaller CMC.



(a)



(b)

Figure 37. Gasoline fire performances (a) extinction time and (b) foam expansion ratio versus foam application rate onto the edge of a 19-cm diameter gasoline pool fire for the sulfobetaine formulations. Data points along the x-axis represent no fire extinction in 5 min.

Figure 37a shows the zwitterionic tetrasiloxane-sulfobetaine formulation (TetrasiloxaneSBForm) has a significantly faster fire extinction than the nonionic TrisiloxanePEO formulation. TetrasiloxaneSBForm has 60% longer extinction times than RefAFFF and comes closest to RefAFFF fire extinction times among all of the sulfobetaine formulations tested. The fire extinction performance of TetrasiloxaneSBForm on gasoline fire relative to that of RefAFFF is comparable to the heptane fire extinction performance of Trisiloxane-PEOForm, which also exhibited 60% longer extinction times than RefAFFF on heptane fire. Only Tetrasiloxane-sulfobetaine (TetrasiloxaneSBForm), t-Butyltrisiloxane-sulfobetaine (t-ButyltrisiloxaneSBForm), and Tetrasilane-sulfobetaine (TetrasilaneSBForm) formulations have better or comparable extinction times to TrisiloxanePEOForm.

Figure 37b shows the effect of siloxane molecular structure on foam expansion ratio. The effects of structure on expansion ratio roughly follow the trends in fire extinction times discussed above as the siloxane surfactant structure is changed. It shows changing the head from PEO to SB with a fixed trisiloxane tail has increased the foam expansion ratio in correlation with the increased fire extinction time. However, changing the head to SbutylB has only a small effect on expansion ratio but a significant effect on fire extinction time. Changing the tail from trisiloxane to t-butyltrisiloxane tail with the same SB head dramatically reduced the expansion ratio but changing to tetrasiloxane reduced the expansion ratio even further in correlation with the reduced fire extinction times shown in Figure 37a. Surprisingly, removing the oxygen from the tetrasiloxane tail with tetrasilane tail increased the both the expansion ratio and extinction times moderately. Even more surprisingly, changing conformation of the tail from branched tetrasiloxane to cyclic tail increased the expansion ratio and fire extinction times dramatically. Expansion ratios for hexasiloxanediSBForm are high consistent with no fire extinction but the moderate expansion ratios for disilaneSBForm and t-ButyldisiloxaneSBForm in Figure 37b are not consistent with no fire extinction observed in Figure 37a. Although expansion ratio and fire extinction times show similar trends as the siloxane structure is changed, smaller expansion ratio does not necessarily imply smaller fire extinction times. For example, Glucopon225DK has the smallest expansion ratio and addition of siloxane surfactant increases the expansion ratio. Also, The tetrasiloxane-sulfobetaine, nonionic trisiloxane-PEO, TetrasilaneSB, and t-butyltrisiloxaneSB formulations have similar or slightly smaller expansion ratios than RefAFFF, the fire extinction times are very different.

Figure 38a shows 90% fire extinction profile for the sulfobetaine formulations listed in Table 1. The extinction time data were collected when 90% of the pool area was extinguished but small edge flames linger before complete fire extinction as determined visually. The 90% data follows about the same trends as the 100 % data shown in Figure 38a. Edgeflames are small flamelets that linger on the pool surface and prolong complete fire extinction despite fire being extinguished on most of the pool surface. Most of the 90% extinction times vary between 70% to 96% of the extinction times except for the tetrasilanesulfobetaine formulation, which vary between 60% to 90% of the fire extinction times indicating relatively longer edge flame activity. For the tetrasilane formulation, the edge flames are more pronounced at foam flow rates less than 600 mL/min compared to 75% to 95% of extinction times at higher flow rates.

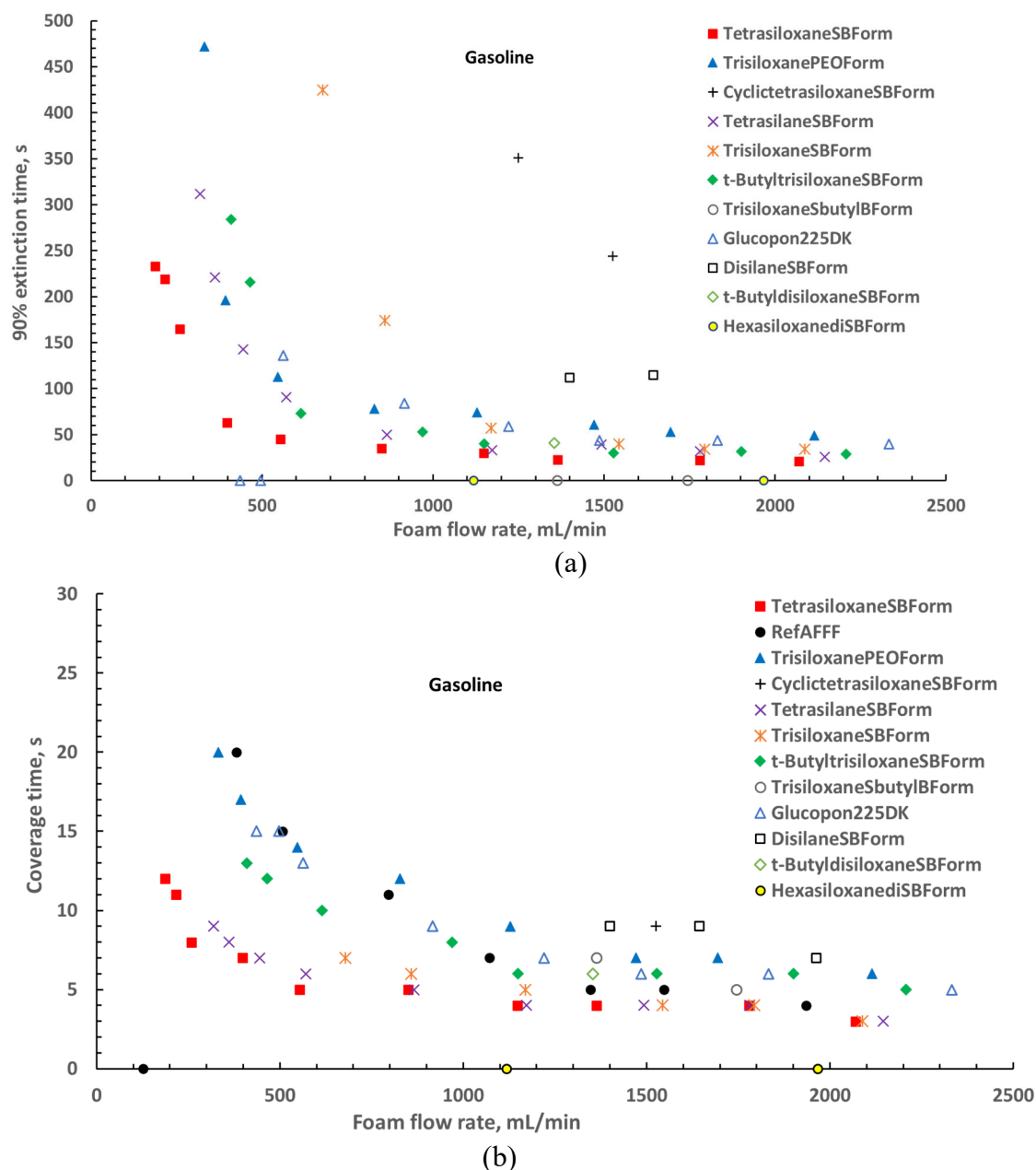


Figure 38. Gasoline fire performances (a) 90% fire extinction time and (b) pool coverage time versus foam application rate onto the edge of a 19-cm diameter gasoline pool fire for the sulfobetaine formulations. Data points along the x-axis represent no fire extinction in 5 min.

Foams must cover the burning pool surface in order to completely extinguish the fire. So, the coverage times are less than or equal to the fire extinction times. Figure 38b shows time for foam to cover the entire pool surface. It shows most sulfobetaine foams cover the pool about the same or faster than RefAFFF and trisiloxane-PEO formulations except for the cyclic siloxane foam, which is unable to cover the pool at smaller foam flow rates and hexasiloxanediSB does not cover even at high foam flow rates. The coverage times decrease from 40% to about 25% of the extinction times as the foam flow rate is increased for RefAFFF. For most sulfobetaine formulations the coverage times increase from 3% to about 15% of the fire extinction times with the increased

foam flow rate. So, the betaines spread very quickly but take longer to extinguish compared to RefAFFF, which takes longer for the foams to cover the burning pool.

5.4.2. Heptane Fire

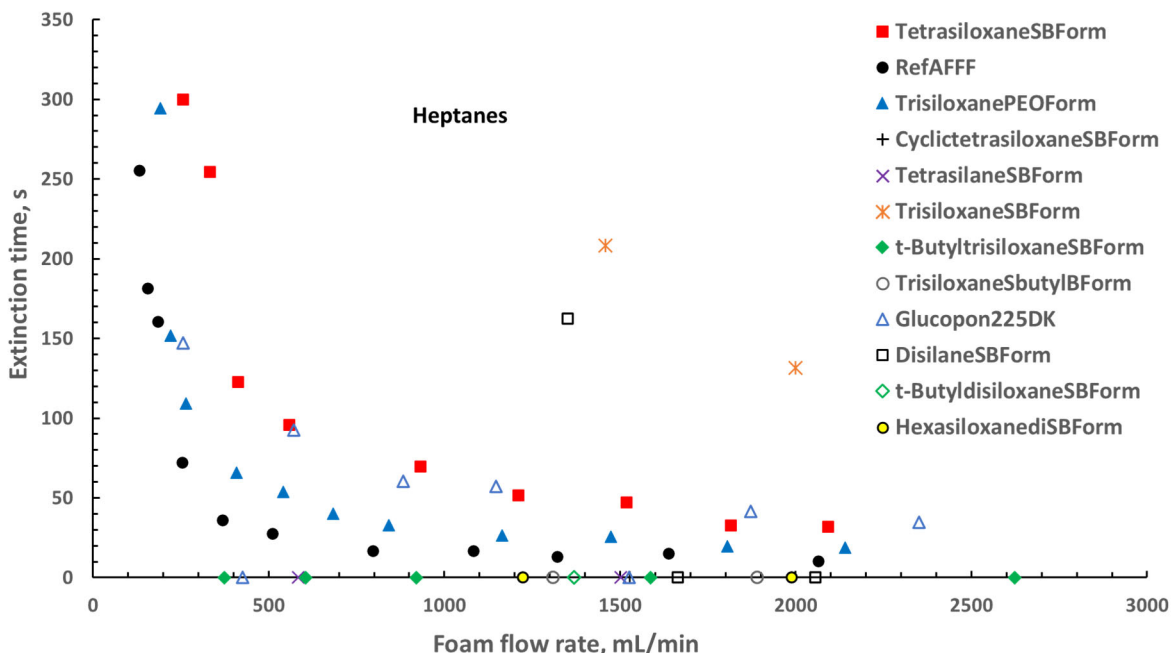


Figure 39. Heptane fire extinction time versus foam application rate onto the edge of a 19-cm diameter heptane pool for the sulfobetaine formulations. Data points along the x-axis represent no fire extinction in 5 min.

Hydrophobic and hydrophilic interactions among surfactants, water, and air were discussed in explaining gasoline fire extinction in Figure 38; gasoline contains aromatic components. Changing fuel from gasoline to heptane brings surfactant interactions with an aliphatic fuel and synergistic effects into the discussion. To begin with, trisiloxane-PEO exhibited shorter extinction times for heptane fires than for gasoline due to synergistic effects, which are not well understood. Also, because of lack of synergistic effects, the heptane fire extinction profiles for the sulfobetaine formulations exhibited longer fire extinction times than trisiloxane-PEO and RefAFFF unlike those for gasoline. However, the trends exhibited by varying the head and tail structures on heptane fire extinction times are similar to that of gasoline fire extinction times as explained below.

Changing the head from PEO to sulfobetaine increased the extinction times for heptane similar to that observed for gasoline and changing it to SbutylB head worsened. Again, this could be because the ionic head increases the hydrophilicity without increasing the hydrophobicity of the tail causing imbalance in amphiphilicity. Changing the tail from trisiloxane to t-butyltrisiloxane tail with the same SB head has unclear effect on fire extinction time because of overflow of the foam from the burn vessel but changing to tetrasiloxane tail reduced the extinction times significantly for heptane similar to the effects observed for gasoline fires. This could be because they increase the hydrophobicity of the tail balancing it with the increased hydrophilicity of the SB head. The heptane fire extinction profile for tetrasiloxaneSB is similar to that of

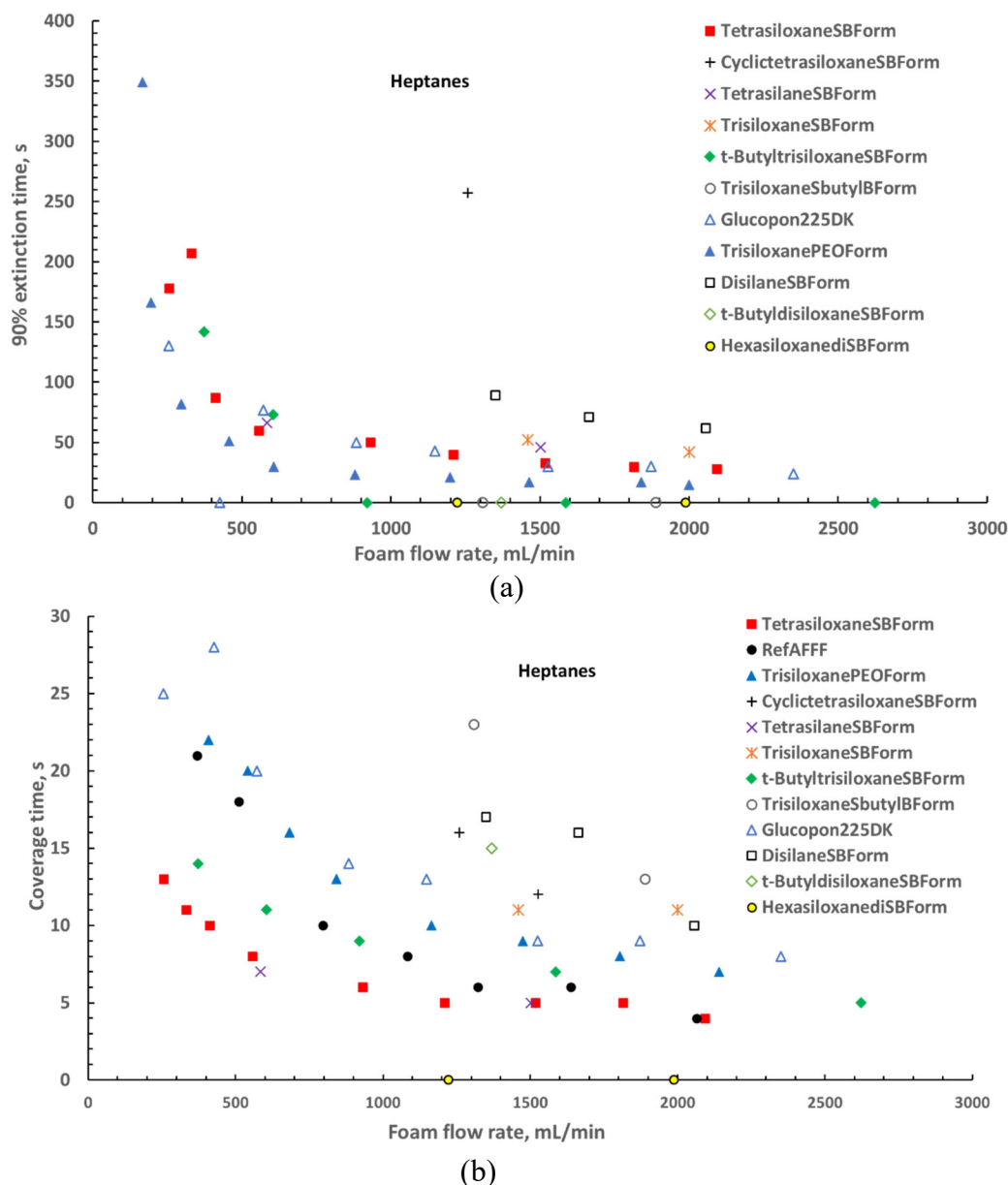


Figure 40. Heptane fire performances (a) 90% fire extinction time and (b) pool coverage time versus foam application rate onto the edge of a 19-cm diameter gasoline pool fire for the sulfobetaine formulations. Data points along the x-axis represent no fire extinction in 5 min.

Glucopon225DK individually showing lack of synergism unlike the gasoline case. Removing the oxygen from the tetrasiloxane tail with tetrasilane tail resulted in no extinction. This could be because it further increases hydrophobicity of the tail causing an overshoot and slight imbalance with the hydrophilicity of the SB head. Even more surprisingly, changing conformation of the tail from branched tetrasiloxane to cyclic tail potentially increased the tail's hydrophobicity and fire extinction times (no extinction at 1526 mL/min foam flow rate) dramatically. The precise reasons for this effect of tail's conformation on fire extinction is unclear. The heptane fire extinction times seem to correlate with the trends in expansion ratio shown in Figure 38b and to those for gasoline fire extinction in Figure 37a. Figure 40a shows that 90% extinction times follow

the trends exhibited by the extinction times shown in Figure 39 as the surfactant molecular structure is changed. Very long edge flames were observed for TrisiloxaneSB and CyclicTetrasiloxaneSB foams as indicated by 90% extinction times are about 30% of the times for complete fire extinction. Figure 40b shows all sulfobetaine foams cover heptane pool very quickly but some of them take slightly longer than the gasoline pool.

5.4.3. Jet Fuel Fire

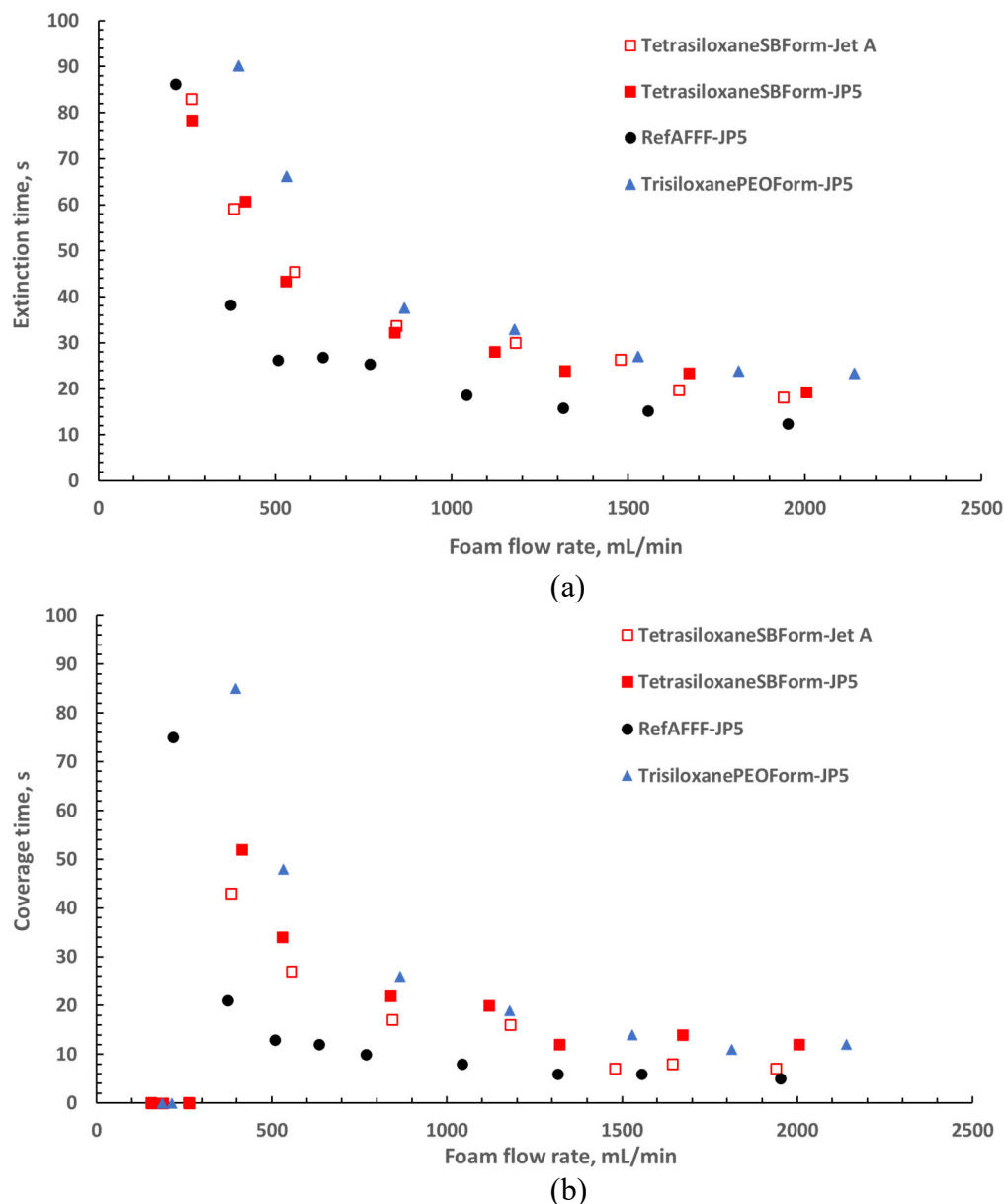


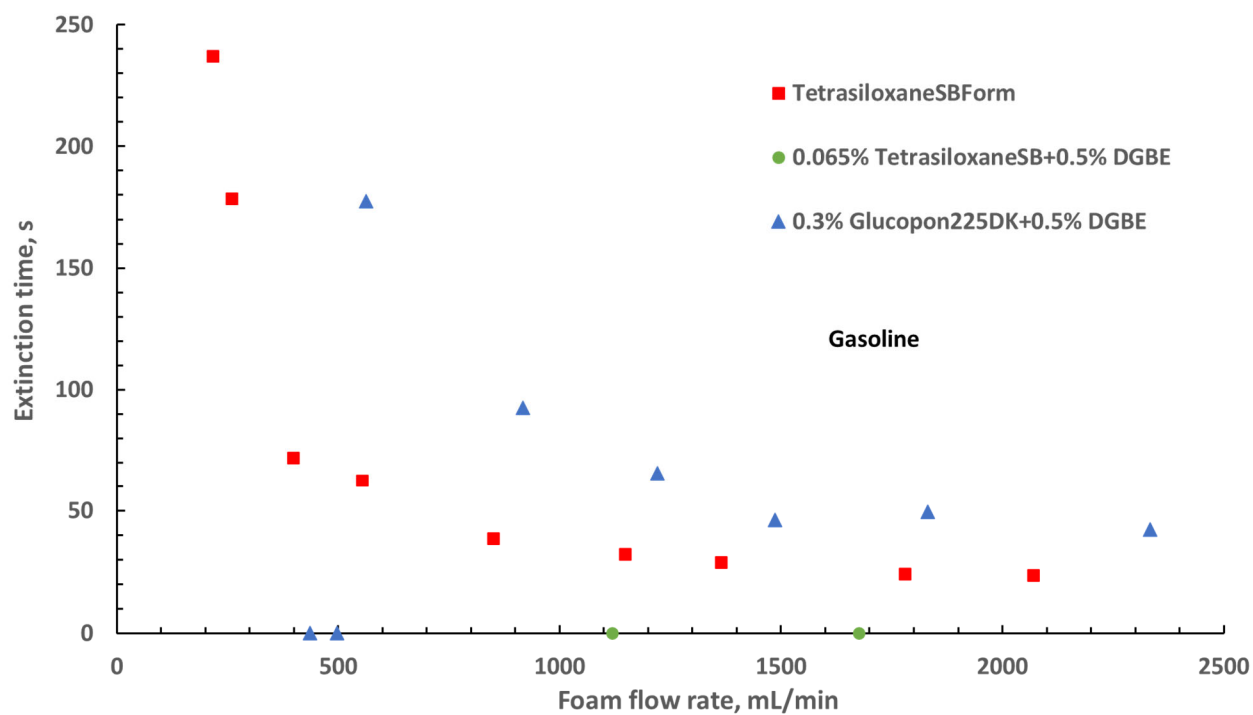
Figure 41. Jet fuel fire performances (a) extinction time and (b) pool coverage time versus foam application rate onto the edge of a 19-cm diameter gasoline pool fire for the sulfobetaine formulations. Data points along the x-axis represent no fire extinction in 5 min.

Jet fuels contain aromatic components like gasoline. We have performed a limited experiments on jet fuels with tetrasiloxanesulfobetaine formulation. Figure 41a shows that the sulfobetaines extinguish jet fuel fires faster than gasoline fires and much faster than heptane fires at a fixed foam application rate. Like in the case of gasoline and heptane, the sulfobetaine formulation is still slower than RefAFFF. Also, as the trisiloxane-PEO is changed to tetrasiloxaneSB, the extinction time decreases significantly following the trend observed with gasoline fires. Pool coverage times are shown in Figure 41b. Interestingly, the coverage times are comparable to fire extinction times at low foam flow rates and they decrease to about 40 to 60% of the extinction time as the foam flow rate is increased. In comparison, the coverage times are a small percent of the extinction times for heptane and gasoline fires.

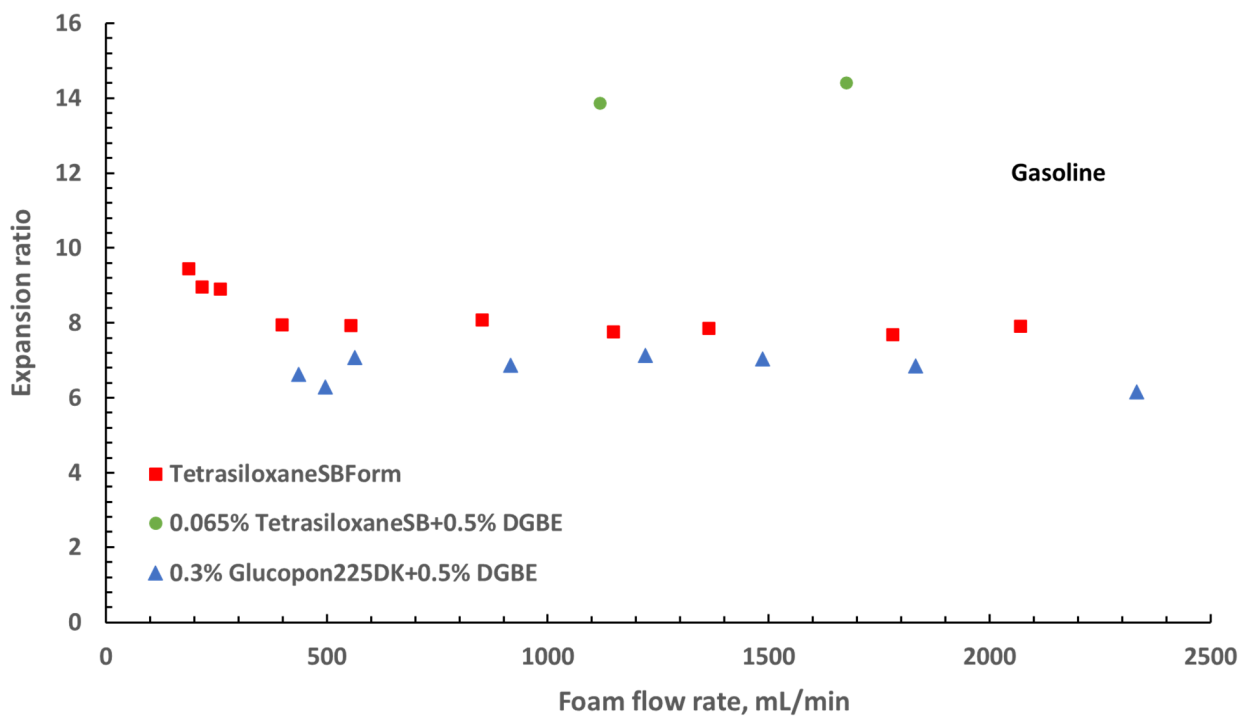
5.4.4. Synergistic Effects for Gasoline Fires

Previously, we showed that heptane pool fire suppression is enhanced when trisiloxane-PEO is mixed with Glucopon225DK in a formulation shown in Table 1 (row 11) compared to the siloxane (0.1 % trisiloxane-PEO with 0.5 % DGBE) or glucopon (0.5 % Glucopon225DK with 0.5 % DGBE) surfactants used individually to generate foams, exhibiting significant synergistic effects [9]. By synthesizing homologous series of trisiloxanepolyoxyethylene surfactants, we also showed that the degree of synergism for heptane fire varies with varying oxyethylene head of the trisiloxane and with varying head and tail sizes of the alkyl polyglucosides [26]. In contrast, the synergistic effects are not seen with the trisiloxanePEOForm for gasoline fires. In Figure 36a, the gasoline fire extinction times for trisiloxane-PEO formulation (solid triangles) are only slightly below the Glucopon225DK individual surfactant's fire suppression (open triangles) at foam flow rates below 500 mL/min. At higher foam flow rates, the trisiloxane formulation exhibits fire extinction time comparable or slightly above those for the Glucopon225DK individually. This shows much reduced synergism between trisiloxanePEO and Glucopon225DK on gasoline compared to that on heptane pool fire.

For tetrasiloxaneSB formulation, Figures 39 and 40a show that the heptane fire extinction and 90% extinction times are comparable or slightly worse than those for Glucopon225DK (0.3 % Glucopon225DK with 0.5 % DGBE) individually. This indicates lack of synergism in heptane fire suppression for the tetrasiloxaneSB in sharp contrast to the trisiloxane-PEO formulation because the mixture's fire suppression profile is not an improvement over the individual surfactant Glucopon225DK. However, the tetrasiloxaneSB formulation does exhibit significant synergistic fire suppression for gasoline fires as shown in Figures 42 and 43. Figures 42a and 43a show that the 0.065 % tetrasiloxane with 0.5% DGBE did not extinguish the gasoline fire even at large foam flow rates as indicated by the data points along the x-axis. In fact, the foam could not even cover the pool as shown in Figure 43b. Figures 42a and 43a also show that 0.3% Glucopon225DK with 0.5% DGBE could extinguish the gasoline fire but took more than twice the time than the mixture containing both siloxane and glucopon (tetrasiloxaneSB formulation). So, the mixture formulation clearly demonstrates the synergistic fire suppression effects on gasoline fires in sharp contrast to the heptane fire. Figure 42b shows that the sulfobetaine individually generates very dry foam with an expansion ratio of 14 and while Glucopon225DK individually generates a wetter foam with expansion ratio between 6 and 7. The tetrasiloxane-sulfobetaine formulation has an expansion ratio closer the that of Glucopon225DK foam and might help spread the foam more quickly on the pool surface as indicated in Figure 43b.

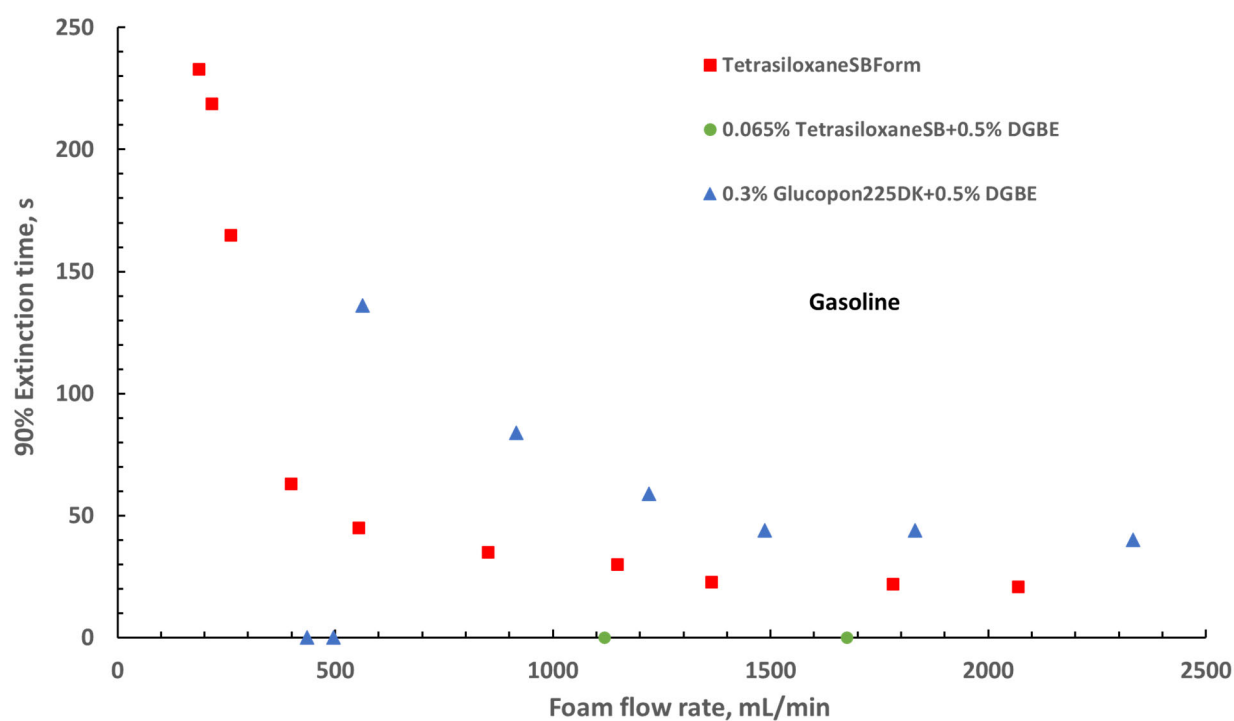


(a)

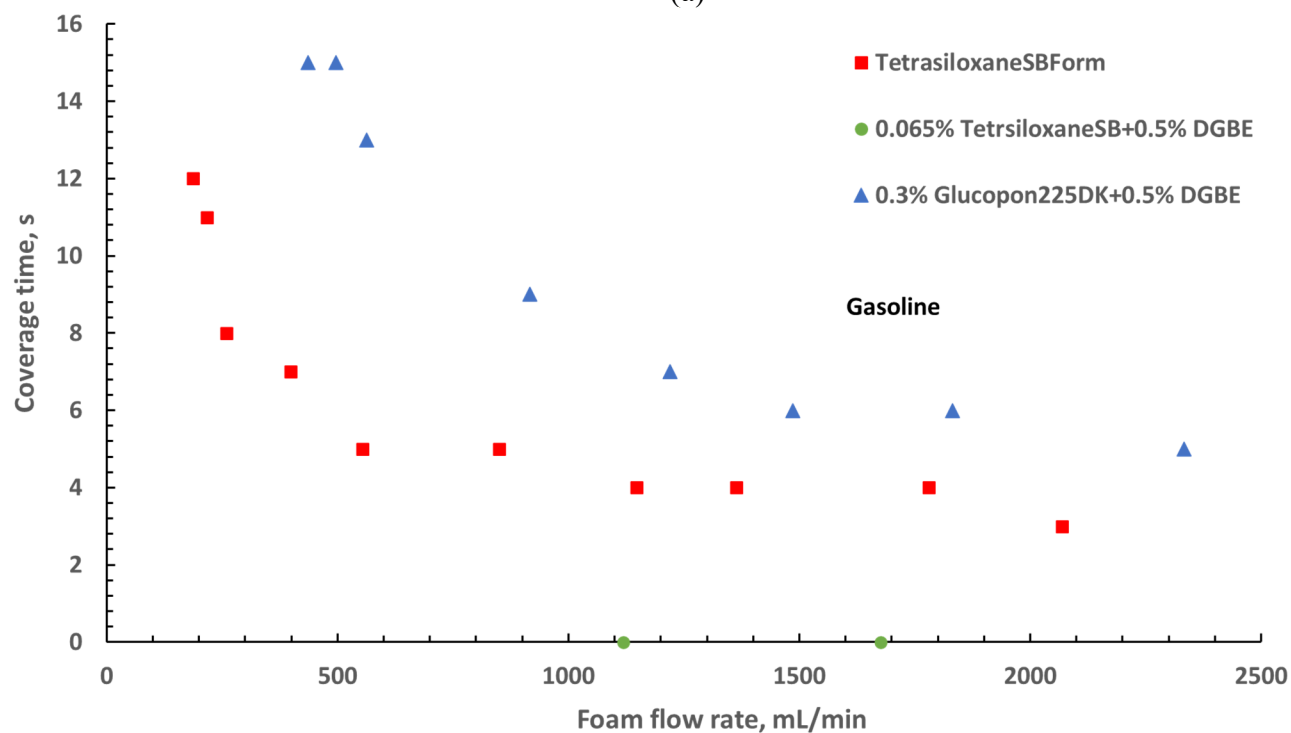


(b)

Figure 42. Comparison of individual surfactants versus mixture (formulation) showing synergistic fire suppression (a) extinction time and (b) foam expansion ratio versus foam application rate onto the edge of a 19-cm diameter gasoline pool fire for the sulfobetaine formulations. Data points along the x-axis represent no fire extinction in 5 min.



(a)



(b)

Figure 43. Comparison of individual surfactants versus mixture (formulation) showing synergistic fire suppression (a) 90% extinction time and (b) pool coverage time versus foam application rate onto the edge of a 19-cm diameter gasoline pool fire for the sulfobetaine formulations. Data points along the x-axis represent no fire extinction in 5 min.

5.4.5. Effects of Siloxane to Glucopon Ratio on Gasoline Fires

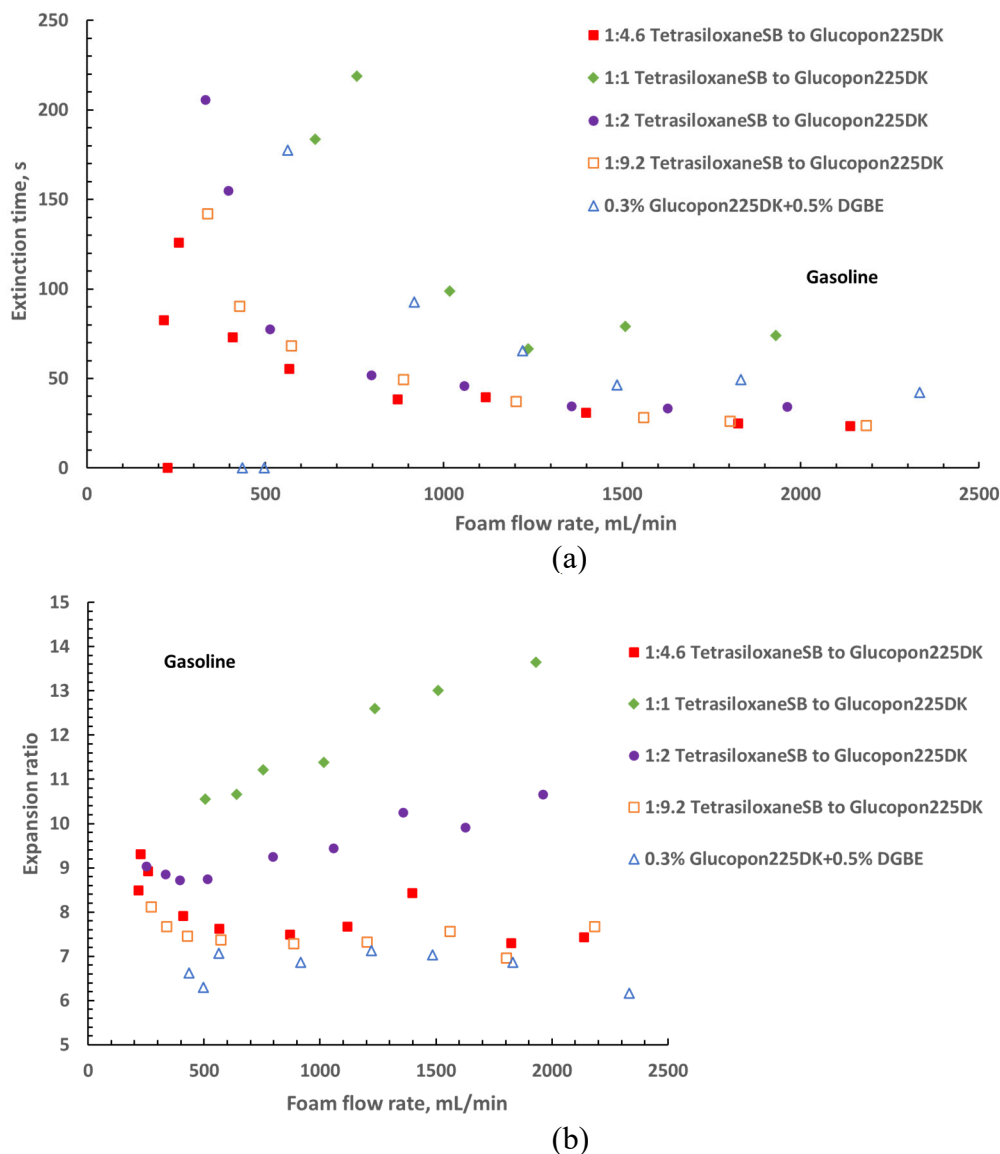


Figure 44. Effects of varying siloxane to glucopon ratio on (a) extinction time and (b) foam expansion ratio versus foam application rate onto the edge of a 19-cm diameter gasoline pool fire for the sulfobetaine formulations. Data points along the x-axis represent no fire extinction in 5 min.

The siloxane to glucopon ratio is varied from 1:1 to 1:4.6 by increasing the Glucopon225DK amount in the mixture relative to the tetrasiloxaneSB, which is fixed at 0.065 %. It is increased further to 1:9.2 by fixing the glucopon concentration at 0.3 % and reducing the siloxane concentration to 0.033 %. Figure 44a shows that the extinction times are longer than the extinction times for glucopon when used individually at 1:1 ratio. It indicates that the synergistic effects are severely reduced at 1:1 ratio. As the glucopon amount is increased, the synergistic effects are dramatically enhanced resulting in reduced extinction times compared to that of foams

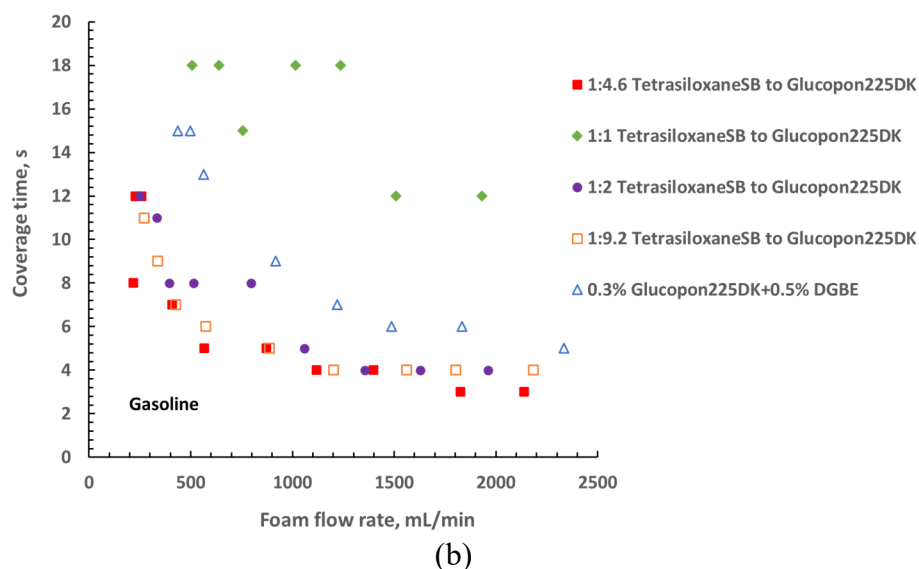
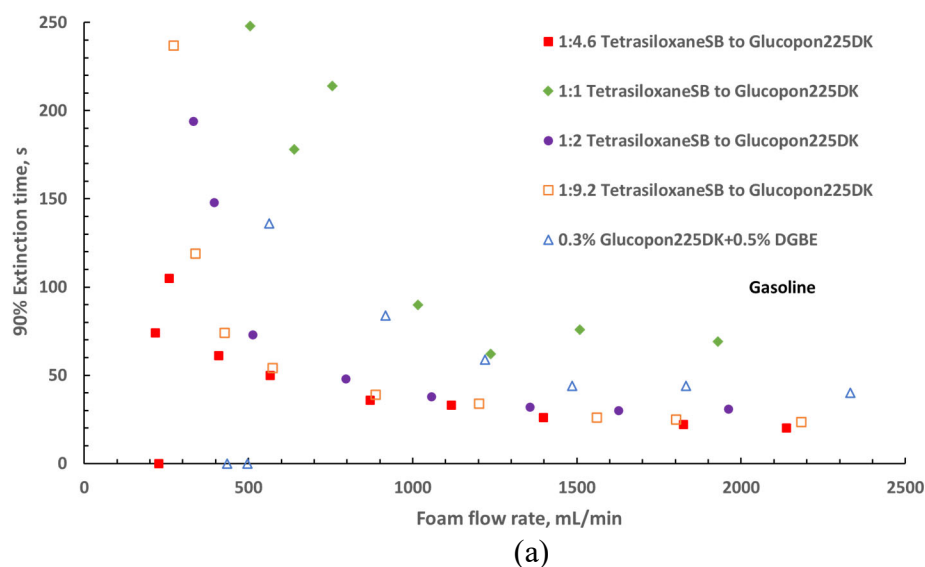


Figure 45. Effects of varying siloxane to glucopon ratio on (a) 90% extinction time and (b) pool coverage time versus foam application rate onto the edge of a 19-cm diameter gasoline pool fire for the sulfobetaine formulations. Data points along the x-axis represent no fire extinction in 5 min.

generated with glucopon individually. Interestingly, Figure 45b shows significant reduction in foam expansion ratio as the glucopon amount is increased in the mixture. At a ratio of 1:4.6, the expansion ratio approaches that of glucopon used individually indicated by the open blue triangles. Figures 44a and b suggest an apparent correlation between expansion ratio and extinction times. When the ratio is increased to 1:9.2, Figures 44a and b show slight effects on the extinction times and expansion ratio profiles towards the profile for glucopon used individually as one might expect. Figures 45a and b exhibit trends similar to the extinction time profiles in Figure 44a. Figure 45b shows synergistic effects in coverage time similar to that seen in extinction time. As the glucopon amount is increased relative to the siloxane, the reduced expansion ratio shown in Figure 44b may have contributed to faster foam spread.

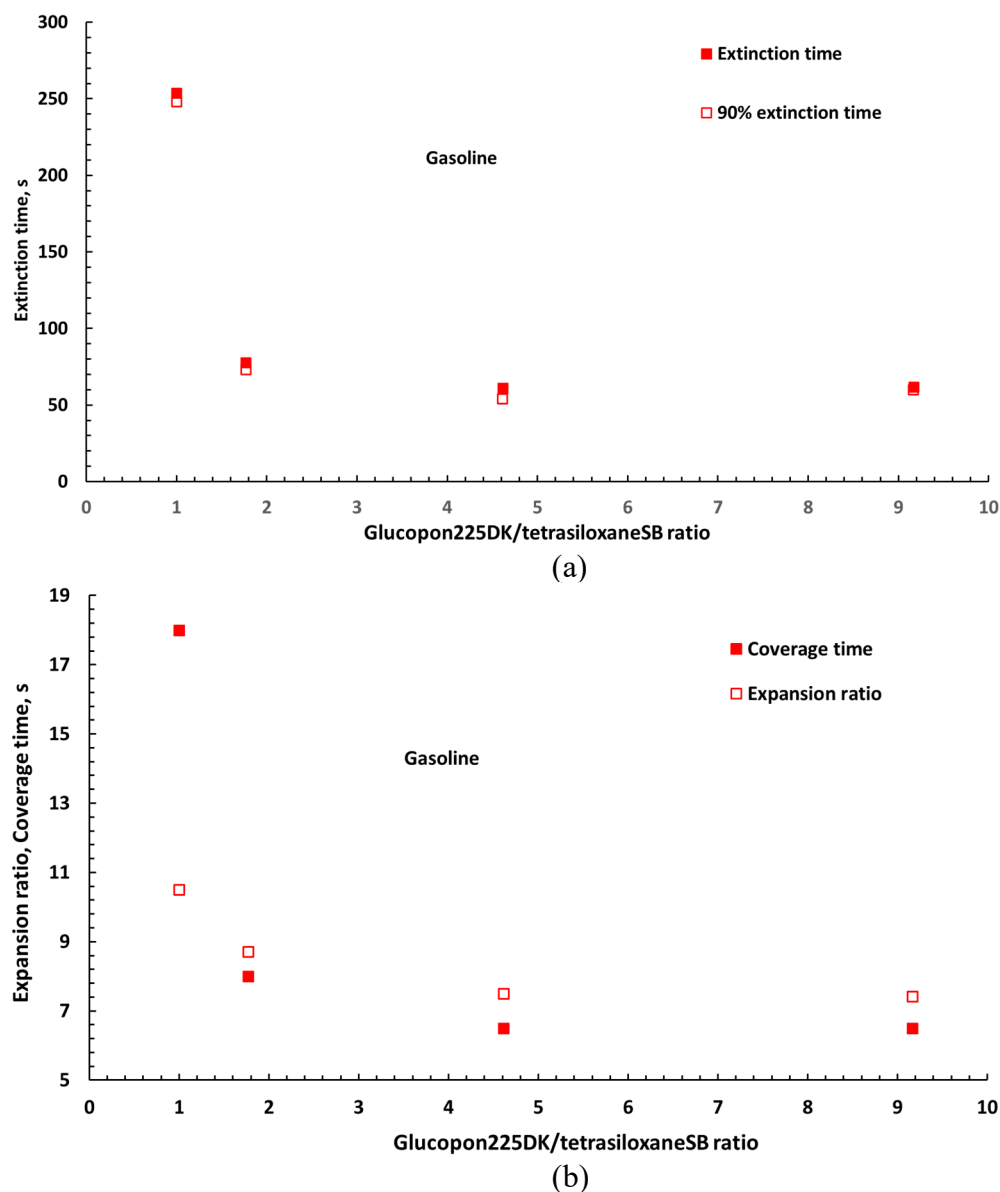


Figure 46. Effects of varying siloxane to glucopon ratio in a mixture on (a) 100% and 90% extinction times (no fire extinction is observed for siloxane and Glucopon surfactants individually), and (b) pool coverage time and foam expansion ratio for the sulfobetaine formulations at 500 mL/min foam flow rate. Data points along the x-axis represent no fire extinction in 5 min.

Figures 46a and b show quantitatively the effects of siloxane to glucopon ratio taken from Figures 44 and 45 at 500 mL/min foam flow rate. As the siloxane to glucopon ratio is increased, the extinction times decrease by roughly a factor of 4 and coverage times decrease by a factor of 3. The expansion ratio decreases by a factor of 1.4.

5.5. Task 7 – 28 ft² MILSPEC fire extinction and burnback testing

Solutions for large scale testing are prepared by dissolving the necessary quantities of glucopon225DK and DGBE into distilled water in 400 mL flasks. On the day of testing, the buckets

and 400 mL flask were transported to Chesapeake Bay Detachment in Maryland where the testing was performed. A required quantity of the siloxane surfactant was dissolved into the glucopon/DGBE mixture in the 400 mL flask. Then, the flask contents were poured into the 5-gallon containers with distilled water. The contents in the 5-gallon buckets were stirred at a moderate speed using a hand-held power stirrer placed deep in the buckets to minimize foaming. We measured expansion ratio by filling a 5-gallon bucket with foam generated from the MilSpec nozzle and measuring the foam weight and also by the standard method described in MIL-PRF-24385SH document. Additional data collection included DFA measured drainage with time, bubble coarsening with time, and initial bubble size as shown in Figures 30 to 32.

We conducted 28 ft² pool fire MilSpec testing on tetrasiloxaneSB formulation shown in Table 1. It included fire extinction tests on unleaded, alcohol-free, gasoline followed by a burnback test with a total of 90 seconds foam deposition including the extinction time. We also conducted a cold burnback test, where fresh fuel is used in the burnpan, and foam is deposited for a fixed 60 s at 2 gallon per minute solution flow rate with a MilSpec aspirated nozzle. The fire extinction test was also conducted for Jet A pool fires. Table 15 lists the fire extinction and burnback times. The tetrasiloxaneSBForm is a clear improvement over the trisiloxanePEOForm in extinguishing a gasoline pool fire in 62 s while the trisiloxanePEOForm could not. The cold burnback times are also much longer for the tetrasiloxaneSBForm. The tetrasiloxaneSBForm also extinguishes Jet-A fire faster than compared to the trisiloxanePEOForm.

Table 15. 28 ft² 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

5.6. Task 5.3. - Stability and shelf life

Surfactants composed of a zwitterionic sulfobetaine hydrophile coupled to a siloxane hydrophobe represent a class of surfactants with exceptional properties, particularly with respect to aqueous surface activity and range of critical micelle concentration (CMC). An unexpected and striking feature of this surfactant class is a degradation of the siloxane tail caused by the sulfobetaine head in aqueous solution. There is a significant susceptibility of this class of surfactants to hydrolysis and an interesting dependence on the siloxane tail structure. We investigate the origin of the hydrolysis issue, its correlation with structure and possible methods for surfactant stabilization. The hydrolysis appears to be generated by a sheath of water molecules tightly bonded to the surfactant head which become acidic as a result of this bonding and large aggregate formation. New insight described below in detail involves documentation of a strongly

bound hydration layer (4.3 to 8.6 water molecules based on measured pKa values) to the sulfobetaine moiety which is speculated to serve as a nucleation site for formation of an aqueous exclusion zone at a surfactant aggregate – water interface. The somewhat unique tendency of ionic siloxane surfactants to form large bilayer and/or vesicle aggregates [37] appears to be an enabling feature for an exclusion zone formation. Adjacent to the negatively charged exclusion zone is an acidic outer region [38] which is speculated to cause acceleration of the hydrolysis rate of siloxane tail of a sulfobetaine-siloxane surfactant. Protective measures investigated include use of a pH7 buffer and of an alkyl polyglucoside co-surfactant. Both of these were very significant in slowing the hydrolysis rate.

5.6.1. Siloxane surfactants studied for hydrolytic stability

Figure 47 shows the siloxane structures subjected to hydrolysis and the abbreviations used to identify the surfactants.

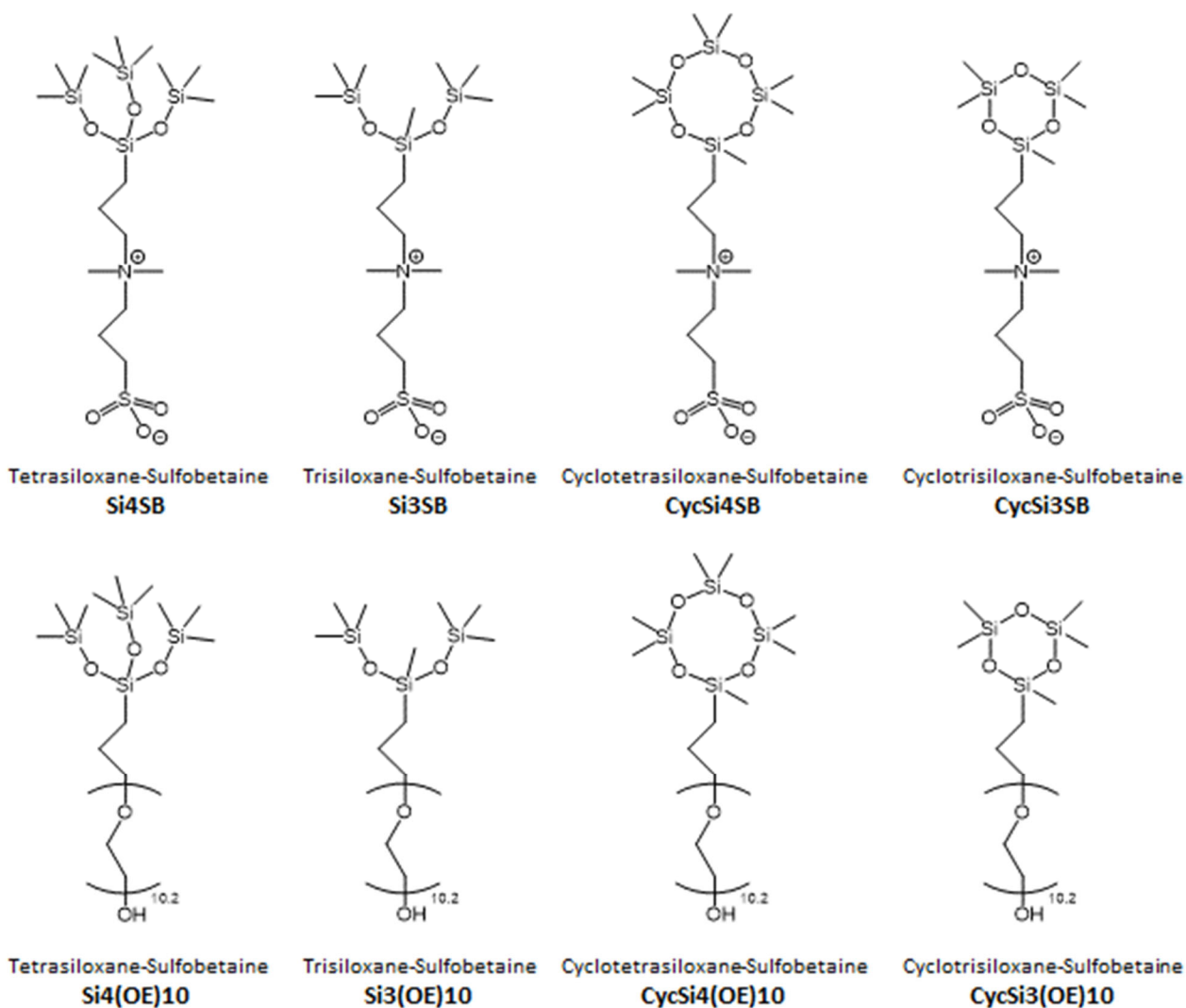


Figure 47. Siloxane surfactants subjected to hydrolysis.

5.6.2. Preparation of model compounds used for studying hydrolysis

HO-Si(CH₃)₂-OH, dimethylsilanediol. N10478-128 This compound was prepared by modified literature procedure [39]. A solution of 1.50g (11.6 mmol) (CH₃)₂SiCl₂ in 15ml dry Et₂O was added dropwise to a stirred solution of 2.40g (23.7 mmol) Et₃N and 0.45g (25.3 mmol) H₂O in 35 ml Et₂O at 0 °C over a 1.25 hr period. The precipitated Et₃NH⁺Cl⁻ salt was filtered, and filtrate concentrated by rotary evaporation to yield 1.925g. This concentrate was dissolved in 33ml pentane/Et₂O (3:1 v/v) from which the pure product crystallized on standing to yield 0.40g (37%). mp 99 °C (lit. 98-100 °C). See APPENDIX I for NMR spectrum.

HO-Si(CH₃)₂-O-Si(CH₃)₂-OH, tetramethyldisilanediol. N10478-138 This compound was prepared by modified literature procedure [39]. A solution of 10.00g (49.2 mmol) (Cl(CH₃)₂Si)₂O in 100ml dry Et₂O was added dropwise to a stirred solution of 10.19g (100.7 mmol) Et₃N and 1.93g (107.2 mmol) H₂O in 194 ml acetone/Et₂O (7:1) at 0 °C over a 1.5 hr period. The precipitated Et₃NH⁺Cl⁻ salt was filtered, and filtrate concentrated by rotary evaporation followed by addition of 80 ml pentane and further rotary evaporation of about half of the added pentane when spontaneous crystallization was observed. The mixture was cooled to 0 °C to complete crystallization, filtered and washed 2x with 20 ml of 0 °C pentane. The crystals were vacuum dried to yield 6.61g (81%). Mp collected by filtration and filtrate was seeded to yield 1.925g. This concentrate was dissolved in 33ml pentane/Et₂O (3:1 v/v) from which the pure product crystallized on standing to yield 0.40g (37%). mp 63 °C (lit. 63-64 °C). See APPENDIX I for NMR spectrum.

5.6.3. Hydrolysis measurement methods

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Advance 300 NMR system operating at 300 MHz using 5mm diameter cells. Chemical shifts are referenced to deuterated solvent resonances except when D₂O is used as solvent with surfactant hydrolysis protocol described below. Fourier Transform infrared (FTIR) spectra were recorded on a Nicolet Magna 750 FTIR spectrometer from thin film samples on a NaCl window. Surface tension measurements of surfactants at the air-water interface were conducted with a platinum Wilhelmy plate (dimensions: 0.038 cm thickness x 0.988 cm width) connected to a NIMA PS4 surface pressure sensor calibrated with a 100.0 mg weight. After the initial wetting of the Wilhelmy plate by the solution, four successive measurements each with a 60 sec equilibration time were made and the average of these measurements used in data workup. Potentiometric titrations and pH measurements were conducted with a Thermo Scientific Orion Versa Star Pro electrochemistry meter and Ross 8172BNWP pH electrode.

NMR protocol for surfactant hydrolysis monitoring consisted of a solution of each surfactant to be analyzed and recordings its ¹H NMR spectra over a 2 wk period. Solutions were prepared by addition of 3mg siloxane surfactant to 2.00g D₂O, stirring for two min, a 30 sec addition of 1.0 ml tetramethylsilane (TMS) vapor (from headspace of a TMS vial via gas-tight syringe with needle below the solution surface) and transfer to a 5 mm NMR cell. ¹H NMR spectra were recorded with sufficient number of scans for a good signal to noise resolution of the TMS resonance.

Complementary NMR and surface tension measurements for correlation with the hydrolysis of the **Si4SB** surfactant and with the effects of an added pH 7 buffer and of alkylpolyglycoside (APG) co-surfactant + diethyleneglycol monobutyl ether (DGBE) were conducted over a 12 day period. The pH 7 phosphate buffer is composed of a 1.6:1.0 wt/wt

K₂HPO₄:KH₂PO₄ ratio [40] used in a 10:1 wt/wt buffer: **Si4SB** surfactant quantity. The pH 7 buffer - **Si4SB** solution for NMR measurement was prepared by dissolution of 3mg **Si4SB** in 2.00 g D₂O followed by addition of 21 mg K₂HPO₄, 10 mg KH₂PO₄ and the 1 ml TMS vapor. The APG+DGBE - **Si4SB** NMR solution was prepared by the addition of 6mg Glucopon® 225DK (an APG concentrate [30, 41]) +10 mg DGBE in place of the phosphate buffer in the previous sentence. The solution for NMR measurement were prepared by dissolution of 6 mg **Si4SB** in 4.00 g D₂O followed by addition of 12 mg APG+20 mg DGBE and 2.0 ml TMS vapor. Solutions for the surface tension measurements were prepared from an initial saturated stock solution consisting of 60 mg **Si4SB** added to 100.00 g deionized water stirred for 1 hr and allowed to settle for 1 hr. Four solutions were then prepared from this saturated **Si4SB**/water stock solution: (1) 20 ml stock solution + 105 mg K₂HPO₄ + 10 mg KH₂PO₄; (2) 20 ml stock solution + 60 mg APG co-surfactant + 100 mg DGBE; (3) 20 ml stock solution + 105 mg K₂HPO₄ + 10 mg KH₂PO₄ + 60 mg APG co-surfactant + 100 mg DGBE; and (4) control of 20 ml stock solution only. Two additional control solutions of 60 mg APG co-surfactant + 100 mg DGBE in 20 g deionized water and 60 mg APG co-surfactant + 100 mg DGBE + 105 mg K₂HPO₄ + 10 mg KH₂PO₄ + 60 mg in deionized water were also prepared.

5.6.4. Interfacial properties

Plots of the equilibrium surface tension versus log of the molar concentration for the series of sulfobetaine-siloxane and polyoxyethylene-siloxane surfactants are presented in Figure 48. The curves in these plots correlate with the head and tail structures of these surfactants and can be analyzed by the Gibbs equation. The critical micelle concentration, CMC, and surface tension at CMC, γ_{CMC} , are derived from the break points in the plots defined by linear extrapolation of the curves above and below the CMC. The surfactant parameters corresponding to the surface excess concentration at the air-water interface, Γ_1 , and area per surfactant molecule at the interface, A_1 , are obtained from the slopes of the plots below the CMC via the Gibbs adsorption equation.

$$\Gamma_1 = \frac{-1}{2.303RT} \left(\frac{d\gamma}{d\log C} \right) \quad A_1 = \frac{10^{16}}{N\Gamma_1}$$

where R is the gas constant, T is absolute temperature and C is the molar concentration. The results of this characterization for these surfactants are summarized in Table 16.

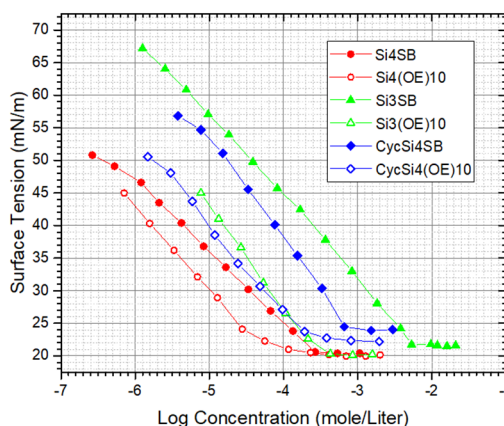


Figure 48. Equilibrium surface tension of aqueous solutions of the sulfobetaine- and poly(oxyethylene)-surfactants vs log molar concentrations.

The correlations of surfactant structure with property are very interesting. With respect to surface tension, the surfactant tail structure is the main contributor as comparisons of **Si4SB** vs **Si4(OE)10**, **Si3SB** vs **Si3(OE)10** and **CycSi4SB** vs **CycSi4(OE)10** reveal small differences. When the effects of tail structure variation are compared, the sulfobetaine and polyoxyethylene series of surfactants show similar trends with larger surface tension variation.

Table 16. Surface tension based surfactant characterization parameters.

Surfactant	Si4SB	Si3SB	CycSi4SB	Si4(OE)10	Si3(OE)10	CycSi4(OE)10
MW (g/mole)	504	430	490	804	730	790
γ_{CMC} (mN/m)	20.6	21.7	24.0	19.9	20.0	22.8
CMC (g/Kg)	0.135	2.30	0.363	0.0462	0.210	0.166
CMC (mM)	0.27	5.32	0.74	0.058	0.29	0.18
Γ_1 (mole/cm ²)x10 ¹⁰	1.8	2.4	2.6	2.3	2.8	2.6
A_1 (Å ² /molecule)	82	68	64	72	60	63

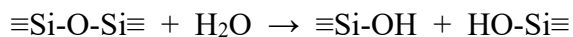
γ_{CMC} : **Si4SB < Si3SB < CycSi4SB** **Si4(OE)10 < Si3(OE)10 < CycSi4(OE)10**

The branched tri- and tetrasiloxane tail structures are both more effective than the cyclic siloxane in reducing γ_{CMC} . For the CMC property both head structure and tail structure make a significant contribution as similar comparisons of head structure variation **Si4SB** vs **Si4(OE)10**, **Si3SB** vs **Si3(OE)10** and **CycSi4SB** vs **CycSi4(OE)10** and tail structure variation below indicate: **CMC: Si4SB < CycSi4SB < Si3SB** **Si4SB(OE)10 < CycSi4(OE)10 < Si3SB(OE)10**

The sulfobetaine head group promotes more water solubility than the polyoxyethylene group, and the trisiloxane tail correlates with a higher water solubility than either of the tetrasiloxane tail structures. With respect to the surfactant packing density at the air-water interface, both head and tail structures play a role. The size and branching in the tetrasiloxane structure give its surfactants the lowest Γ_1 and highest A_1 values, while the more compact cyclotetrasiloxane structure confers intermediate Γ_1 and A_1 values. The smaller branched trisiloxane head structure confers a parallel trend in Γ_1 and A_1 to that for the branched tetrasiloxane but with larger and smaller numbers for the respective Γ_1 and A_1 values reflection the trisiloxane's smaller size.

5.6.5. Siloxane surfactant hydrolysis

The hydrolytic susceptibility of silicone surfactants with its dependence on pH and CMC has been known for some time [42]. It is catalyzed by acid or base and is generally represented by the following reversible reaction wherein a Si-O-Si siloxane structure is converted two Si-OH silanol structures:



It is a very slow process in the pH range of 6-8 but accelerates markedly by acid or base catalysis outside of this range. Techniques for investigating siloxane hydrolysis reactions are vary with objective of the work and type of surfactant. A detailed hydrolysis study on the commercial nonionic trisiloxane-polyoxyethylene surfactant Silwet® L-77, where the effects of concentration, pH and temperature were investigated, uses measurements of wetting, surface tension, turbidity and gas chromatography [43]. Another excellent study on zwitterionic sulfobetaine-siloxane surfactants uses surface tension measurements for surfactant degradation and gas chromatography to identify decomposition products to study hydrolytic decomposition over a pH range of 2-10 [32]. Several more current siloxane surfactant studies report hydrolysis issues with most using surface tension and/or spreading measurements [44, 45, 46, 47, 48] but some using chromatographic and/or spectroscopic methods [49, 50]. While hydrolysis assessment based on surface tension and spreading measurements has important practical implications, it is helpful to complement this knowledge with fundamental insight from a chemical structure based analysis of the surfactant in bulk aqueous solution. Specifically, a spectroscopic diagnostic coupled if need be/possible with quantitative chromatographic identification of undecomposed surfactant and products is very useful. A nonionic polyoxyethylene-siloxane was analyzed in this manner by way of size exclusion chromatography and nuclear magnetic resonance (NMR) [49] with the finding of no polyoxyethylene degradation and significant siloxane degradation which was quantified by ^1H NMR. Surfactant chromatography can be particularly challenging particularly when ionic species are involved. However, obtaining NMR data is relatively facile and can be used to monitor initial decomposition and signature hydrolysis products. This work develops a relatively simple ^1H NMR protocol to monitor siloxane surfactant hydrolysis.

The initial design of this ^1H NMR protocol focuses on the Si-CH₃ spectral region from a relatively dilute single surfactant in D₂O. Typically 3 mg surfactant is mixed into 2g D₂O followed by addition of a trace of tetramethylsilane (TMS) for chemical shift reference. Spectra are then recorded at intervals from several hours to a couple of weeks depending on magnitude of spectral changes. The Si-CH₃ region (0.25 to -0.02 ppm) of spectra recorded over a duration of 13 days are presented in Figure 49.

Figure 49 contains several spectroscopic features of silicone surfactants dissolved in D₂O: a broadening of some Si-CH₃ resonances; the appearance and growth of new Si-CH₃ resonances coupled with decline of initial Si-CH₃ resonances with increasing hydrolysis time. The (OE)10 head structures correlate with a broadening of the Si-CH₃ resonances as compared with the SB head structures bonded to analogous silicone tails. Contributing to this effect is the larger molecular size of the of the (OE)10 surfactant molecules. Also their lower CMC values (Table 16) correlate with a larger population in the micelle environment. In APPENDIX I the micelle effect and resolution of nonequivalent SiCH₃ resonances are examined, but conditions for these data acquisitions deviate significantly from the simple protocol designed to make comparative assessments of surfactant hydrolytic stability under practical conditions. This hydrolytic stability is monitored by examining the spectra of each surfactant for systematic changes over a time of 0 to 13 days. When each of the three sulfobetaine-siloxane surfactants is compared with the polyoxyethylene-siloxane analog surfactant, it is clear that the sulfobetaine surfactant undergoes a

much more rapid hydrolysis. For the first four surfactants in Figure 49, the order of hydrolytic susceptibility is:

Si4SB > Si3SB >> Si4(OE)10 > Si3(OE)10

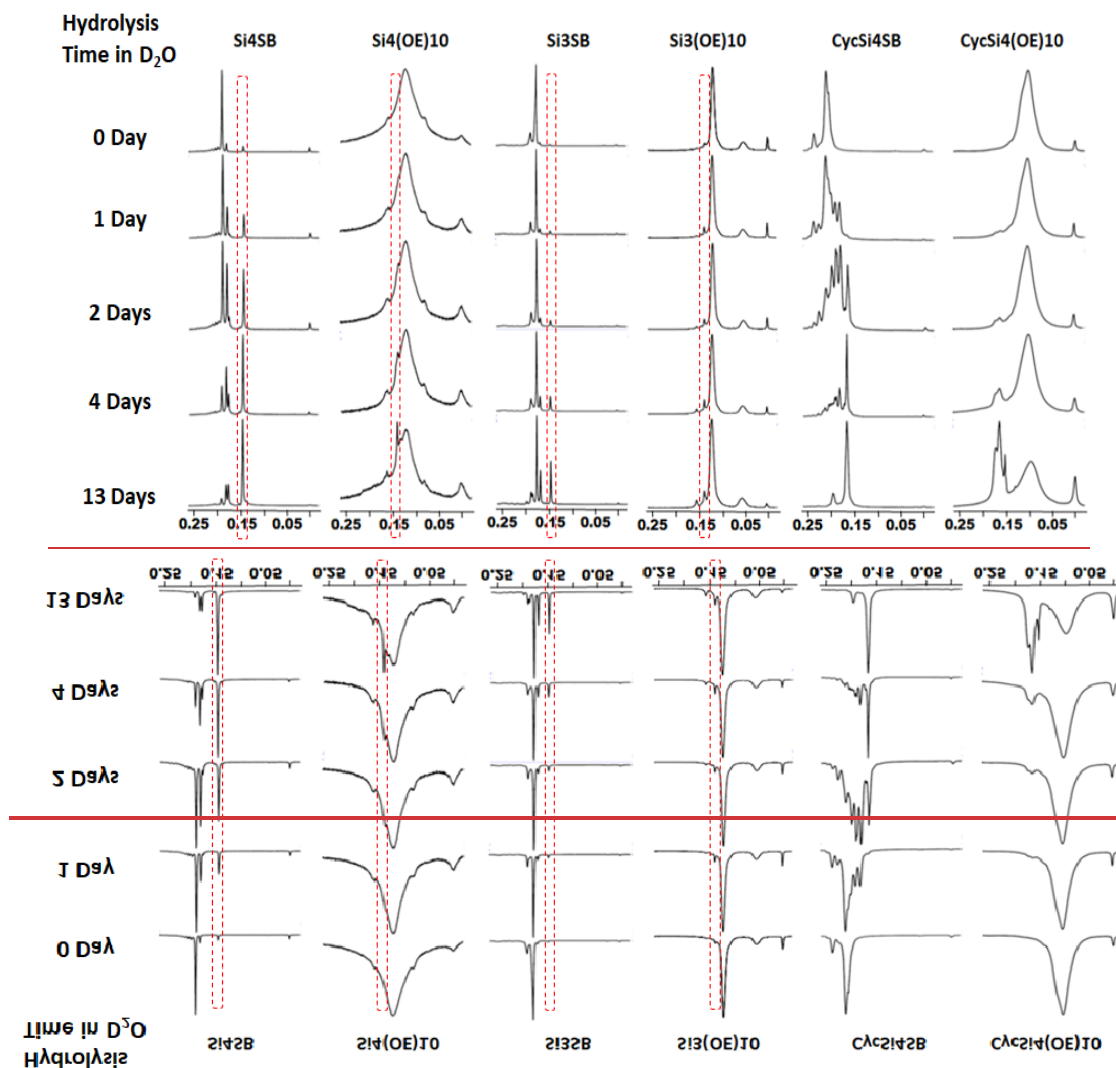


Figure 49. ^1H NMR spectra of the Si-CH₃ region for six surfactants in dilute D₂O solution depicting the effects of hydrolysis over a 13 day period. The dashed line encircles a resonance at 0.147 ppm assigned to either of both the (CH₃)₃Si-OH and (CH₃)₃Si-O-Si(CH₃)₃ hydrolysis products. The small resonance at 0.00 ppm is from the trace of TMS reference added to the D₂O solution.

Also noted in the spectra of these four surfactants is the growth of a major hydrolysis product with a resonance at 0.147 ppm. Since this hydrolysis involves cleavage of a Si-O-Si bond structure by H₂O in these surfactant tail structures, two simple product possibilities are CH₃Si-OH and CH₃Si-O-SiCH₃. The latter has been reported by gas chromatography to be a hydrolytic decomposition product of sulfobetaine-siloxane surfactants [32]. These two compounds were synthesized and found to have Si-CH₃ resonances at chemical shifts of 0.149 and 0.144

respectively under conditions corresponding to the protocol of Figure 49 as presented in APPENDIX I. Finally, the two cyclotetrasiloxane surfactants in the right columns of Figure 49 exhibit a similar hydrolytic instability with the sulfobetaine being more rapidly hydrolyzed than its **Si4(OE)10** analog. This hydrolysis appears to be more complex with multiple resonances of these hydrolysis products range from 0.15 to 0.25 ppm. Obvious products from the cyclotetrasiloxane head structure would be hydroxyl terminated dimethylsiloxane compounds of which HO-Si(CH₃)₂-OH and HO-Si(CH₃)₂-O-Si(CH₃)₂-OH were synthesized, and their spectra were found to have Si-CH₃ resonances at chemical shifts of 0.000 and 0.150 ppm under above protocol conditions as also presented in supporting information. The issue of particular importance is the correlation is the correlation of siloxane hydrolytic and presence of the sulfobetaine surfactant head group structure.

To obtain more definitive information, a simple sulfobetaine compound, (CH₃)₃N⁺(CH₂)₃SO₃⁻, was synthesized and added in 1:1 and 0.5:1 molar ratios to a D₂O solution of the most hydrolytically stable siloxane surfactant in Figure 49, **Si3(OE)10**. Hydrolysis was monitored, and results presented in Figure 50.

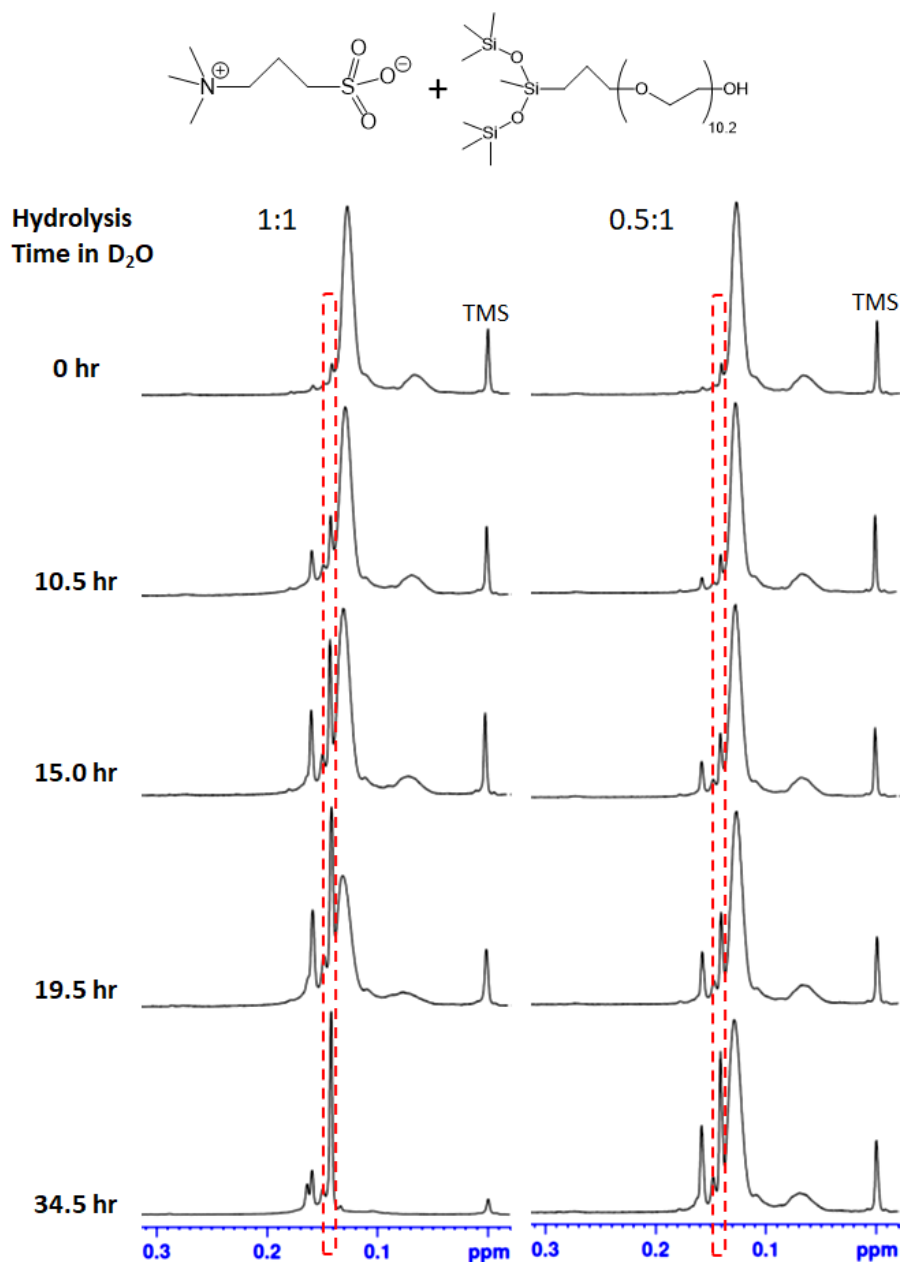


Figure 50. ^1H NMR spectra of the Si-CH₃ region for 1:1 and 0.5:1 mixtures of $(\text{CH}_3)_3\text{N}^+(\text{CH}_2)_3\text{SO}_3^-:\text{Si}_3(\text{OE})_{10}$ in D_2O solution for hydrolysis monitoring according to protocol. The dashed line encircles a resonance at 0.147 ppm assigned to either of both the $(\text{CH}_3)_3\text{Si-OH}$ and $(\text{CH}_3)_3\text{Si-O-Si}(\text{CH}_3)_3$ hydrolysis products.

The hydrolysis proceeds quite rapidly compared with the data presented in Figure 49. It is dependent on the concentration of sulfobetaine, and major product(s) are $(\text{CH}_3)_3\text{Si-OH}$ and $(\text{CH}_3)_3\text{Si-O-Si}(\text{CH}_3)_3$ as indicated by the growth of resonance at 0.147 ppm. This clearly indicates that sulfobetaine functionality is responsible for the hydrolysis, and intermolecular reactivity is as effective or more effective than intramolecular reactivity. The next question to address is why the sulfobetaine functionality exhibits hydrolytic activity toward the siloxane structure.

5.6.6. Sulfobetaine surfactant hydration and acidity

As indicated at the beginning of this section, silicone surfactants in general have a susceptibility to hydrolysis that is relatively slow in the pH range of 6-8 but accelerates markedly by acid or base catalysis outside of this range. A screening experiment was conducted where 6 mg of each surfactant and of the $(\text{CH}_3)_3\text{N}^+(\text{CH}_2)_3\text{SO}_3^-$ were dissolved in 40 ml quantities of deionized water followed by a pH measurement. Unexpectedly, those solutions containing a sulfobetaine moiety all exhibited pH values between 3.1 and 3.8 units. The three polyoxyethylene-siloxane surfactant solutions had pH values ranging from 5.6 to 5.9 while that for the deionized water ranged from 5.9 to 6.0.

This result indicates that the sulfobetaine moiety is behaving as an acid strong enough to effect accelerated hydrolysis of a siloxane surfactant's tail structure or perhaps that there may be a strong acid byproduct from the synthesis of the sulfobetaine surfactants. For the latter possibility unreacted 1,3-propanesultone reagent from the synthesis in Figure 47 is an obvious candidate. It is used in slight excess, and its contact with water could produce 3-hydroxypropylsulfonic acid. To examine this the hydrolytic susceptibility of 1,3-propanesultone and acidity of its hydrolysis product, two control experiments were conducted: a NMR and pH monitoring of pH monitoring of the propanesultone dissolved in water (see APPENDIX I). Both experiments showed a clean conversion to the 3-hydroxypropylsulfonic acid over a 50 hr period (Figures SA and SB). The traces of the signature resonances of 3-hydroxypropylsulfonic acid are not found in the spectra of the sulfobetaine surfactants. The pH of the propanesultone solution quickly falls below a value of 2 and levels off at a value of 1.3. For 3-hydroxypropylsulfonic acid a pKa value of 1.69 has been reported [51]. Small quantities of 3-hydroxypropylsulfonic acid in aqueous solutions produce pH well below 3 described in the preceding paragraph, and the sulfobetaine surfactant titrations (Figure 51) and pKa measurements (Table 17) also indicate that 3-hydroxypropylsulfonic acid does not have a meaningful presence.

To quantify this acidic behavior, titrations of the sulfobetaine surfactants and $(\text{CH}_3)_3\text{N}^+(\text{CH}_2)_3\text{SO}_3^-$ compound were conducted. The titration curves are depicted in Figure 51. From these curves equivalent weights were determined and compared with molecular weights. In each case the equivalent weight was significantly greater than the molecular weight. As discussed in more detail below, this difference is attributable to a sheath of water molecules tightly bonded to the sulfobetaine structure. The number of water molecules in the sheath can be determined by dividing this equivalent weight – molecular weight difference by the molecular weight of water. These results are presented in Table 17. The pKa values for these sulfobetaine compounds were determined from the titration half equivalence point according to the Henderson-Hasselbalch equation [52].

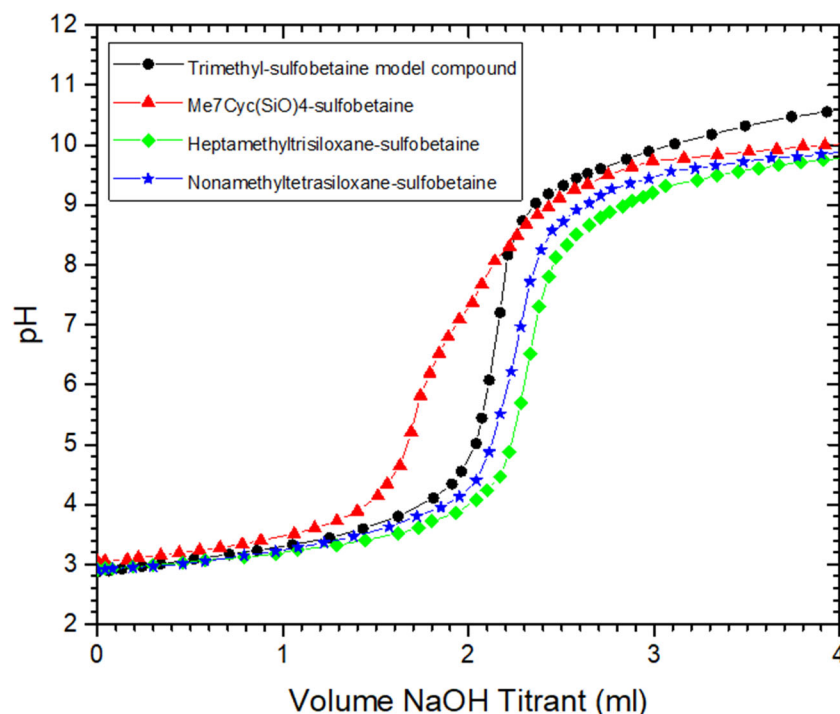


Figure 51. Potentiometric titration of $(\text{CH}_3)_3\text{N}^+(\text{CH}_2)_3\text{SO}_3^-$ model sulfobetaine compound and CycSi4(OE10, Si3SB and Si4SB) sulfobetaine surfactants.

Table 17. Titration results for sulfobetaine compound and siloxane surfactants.

Property	$(\text{CH}_3)_3\text{N}^+(\text{CH}_2)_3\text{SO}_3^-$	CycSi4SB	Si4SB	Si3SB
MW (g/mole)	181	490	504	430
Eq Wt (g/equivalent)	336	612	582	519
$(\text{Eq Wt} - \text{MW})/\text{MW}_{\text{H}_2\text{O}}$	8.6	6.8	4.3	5.0
pKa	3.4	3.4	3.3	3.3

The two remarkable features in Table 17 results are that the excess mass in the sulfobetaine equivalent weights corresponds to tightly bonded water molecules ranging from 4.3 to 8.6 units and that associated with the sulfobetaine moiety is a strong acidity with pKa ranging from 3.3 to 3.4. As to the rationale for such properties, a broader review of sulfobetaine research provides interesting insight. For almost two decades polysulfobetaines have been investigated for a water hydration layer that is strongly bonded to its zwitterionic structural feature [14, 15, 16, 17, 18] which has an associated application as marine antifouling or fouling-release coatings [21, 22, 23, 24, 25]. The positive and negative charges held in close proximity but spaced apart generate a very strong electrostatic interaction with water molecules bonding them tightly to this region. This phenomenon is sometimes referred to as a superhydrophilicity [53], and for coatings has a water contact angle metric of $<10^\circ$ [54]. Analyses of this tightly bound water hydration layer to a polysulfobetaine structure have been conducted via Raman spectroscopy [15], attenuated total

reflection infrared spectroscopy [55], molecular dynamic simulation [16, 25], sum frequency generation vibrational spectroscopy [20], nuclear magnetic resonance (NMR) and differential scanning calorimetry (DSC) [18], and by neutron diffraction [56]. Within these various studies, reports of the amounts of water in this hydration layer vary considerably ranging from 1.6-2.3 to 7-8 to 25-26 water molecules per sulfobetaine functional group. The result in Table 17 of 4.3-8.6 water molecules per sulfobetaine unit is most closely in agreement with the 7-8 range reported by Wu et al. [18] in which a depiction of the water molecules in the hydration layer involves a hydrostatic bonding eight water molecules to the two ionic centers.

With respect to the acidity associated with the hydrated sulfobetaine indicated in Table 17, no report of this property was mentioned in the literature cited in the preceding paragraph. A broader search for acidity associated with hydration layers strongly bonded to ionic substrates located an interesting concept for water association referred to as an aqueous “exclusion zone” (EZ). It is largely derived from the research of Gerald H. Pollack and is also referred to as “the fourth phase of water” [38]. This EZ is nucleated at a hydrophilic surface (e.g. polyacrylic acid hydrogel, mercapto-undecanoic acid self-assembled monolayer, Nafion film, ion exchange beads and biological tissue) extends to a microscopic thickness (10 to >100 microns) and excludes water-dissolved solutes from its domain [57]. In the EZ the water molecules form a planar hexagonal arrangement but without the strong interplanar bonding of hexagonal structures characteristic of ice [38]. The planar layers more resemble the graphite ability to laterally shift somewhat resembling a liquid crystal with a high viscosity. The EZ composition was found to be H_3O_2 resulting in a negatively charged interior and a positively charged region at and beyond the EZ interface with liquid water. The acid character of this liquid water interface has been confirmed by pH measurement [58] and by mechanical sensor measurement [59].

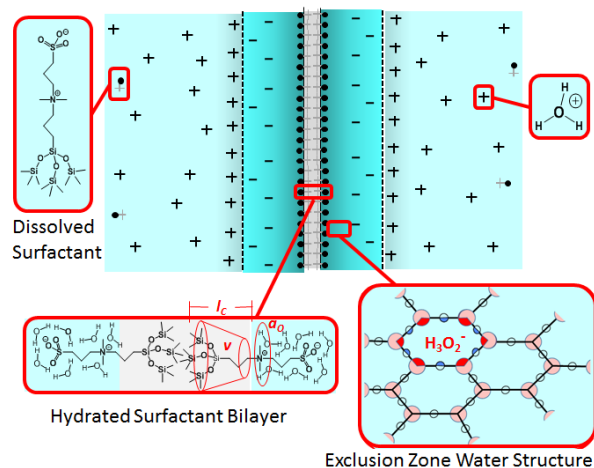


Figure 52. Illustration of a hypothetical planar Si₄SB surfactant bilayer aggregate in aqueous medium with an anionic exclusion zone (darker blue region) formed at the aqueous interface on both sides and a proton counter ion domain (light blue region) beyond the exclusion zone. These latter two features are adapted from figures in G.H. Pollack’s book about the fourth phase of water [38]. Surfactant packing parameter variables v , a_o and l_c are represented in the hydrated surfactant bilayer sketch.

To speculate how a sulfobetaine-siloxane surfactant in aqueous medium can generate an acidity approaching a $\text{pH} \approx 3$ that causes a gradual hydrolysis of its siloxane tail, a depiction in Figure 52 is utilized. This figure illustrates macroscopic and microscopic features that combine to generate a large planar bilayer aggregate of sulfobetaine-siloxane surfactant molecules interfaced with aqueous EZ. In aqueous solution above its CMC the sulfobetaine-siloxane surfactant is depicted having formed a large bilayer aggregate. The EZ is nucleated at the sulfobetaine-water interface and expands a short distance into the aqueous phase with its internal negative charge. Beyond the EZ the aqueous phase develops a positive charge in the form of hydronium ions to balance the negative charge of the EZ. Above the CMC there is an equilibrium between dissolved surfactant molecules and those within the laminar aggregate. It is the dissolved surfactant whose siloxane tail is attacked and hydrolyzed by the hydronium ion. More detail is provided about this speculation is discussed in the following two paragraphs.

Depicting the sulfobetaine-siloxane surfactant as forming a planar bilayer aggregate at concentrations above its CMC correlates with a packing factor assessment and with related behavior by other siloxane surfactants. A packing parameter concept was developed Israelachvili, Mitchell and Ninham [60] to relate surfactant molecular structures to aqueous surfactant aggregate shapes and sizes. The packing parameter is defined as $P = v/a_0l_c$ where: v is volume of the surfactant tail; a_0 is surface area of surfactant head at the interface to hydrophobic tail region in a micelle/aggregate; and l_c is extended chain length of surfactant tail. It was initially applied to linear chain hydrocarbon surfactants with values of $1/3$, $1/2$ and 1 being indicative of respective spherical micelles, cylindrical micelles and planar bilayers [60] and later to surfactants in general [61] and specifically to silicone surfactants [62, 37] with a parameter value ranges and corresponding aggregate shape correlation of: $P = 0$ to $1/3$, spherical micelle; $P = 1/3$ to $1/2$, cylindrical micelle; $P = 1/2$ to 1 , lamellar micelle. While specific examples of sulfobetaine-trisiloxane or –tetrasiloxane surfactants with reported packing factors were not found in the literature, those with carbohydrate-derived head groups were found, and all reported packing factors between 0.9 and 1.0 [63, 64, 65]. To calculate a packing factor for the **Si4SB** surfactant values for the v , a_0 and l_c parameters are obtained as follows. The molecular volume of the tetrasiloxane tail is calculated from the density and molecular weight of the $((\text{CH}_3)_3\text{SiO})_3\text{SiH}$ reagent plus the volume of the trimethylene linking structure ($578 \text{ \AA}^3 + 81 \text{ \AA}^3 = 659 \text{ \AA}^3$). The extended chain length of the tetrasiloxane tail is calculated from the C-C-C, C-C-Si, C-Si-O, Si-O-Si, O-Si-O, Si-O-C, O-C-H bond lengths and angles for a single chain as $8.2 \text{ \AA}$. The surface area of surfactant head is equated to the A_1 surfactant interface area for **Si4SB** surfactant ($82 \text{ \AA}^2$, Table 16). A packing parameter of 0.98 is calculated from these values of v , a_0 and l_c and is consistent with a planar bilayer surfactant aggregate geometry.

Illustration of the EZ in Figure 52 is derived from G.H. Pollack as briefly described above [38]. Its formation is nucleated on the planar macroscopic sulfobetaine surface. After nucleation, a micron-scale thin layer of water molecules hexagonally ordered in coplanar sheets expands into the aqueous phase excluding solute molecules. An accumulation of negative charge associated with the H_3O_2 composition of each hexagonal unit in the EZ is counterbalanced by a gradient of hydronium ions diminishing in concentration into the aqueous phase with distance from the EZ. With the sulfobetaine-siloxane surfactant above its CMC, it is proposed that the acidity associated

with the hydronium ions causes a hydrolysis to the tail of molecularly dissolved surfactant molecules.

5.6.7. Sulfobetaine-siloxane surfactant hydrolysis protection

Of all of the siloxane surfactants in Figure 47, the **Si4SB** surfactant is the most hydrolytically sensitive, is also a good candidate for testing. Two approaches were evaluated: the use of a buffer; and the inclusion in a formulation with a micelle-forming co-surfactant.

The simpler approach involved adding buffer in sufficient quantity to maintain a neutral pH while maintaining dissolution of the surfactant. A pH 7 $\text{K}_2\text{HPO}_4:\text{KH}_2\text{PO}_4$ (1.6:1.0) buffer [40] was prepared in D_2O followed by **Si4SB** addition. The quantity of buffer used was a 10:1 buffer:**Si4SB** weight ratio, and a pH of 7 was measured before and after the experiment. Analogous to the procedure used to generate the ^1H NMR monitored hydrolysis data in Figure 49, the hydrolysis of this surfactant's tail in the Si- CH_3 region (0.25 to 0.05 ppm) over a duration of 133 hr at room temperature. These spectra along with those for a non-buffered control are presented in the left and center columns of Figure 53. These results show that the hydrolysis reaction is not altered by the buffer, and, while its rate is significantly reduced by the buffer, the hydrolysis is far from eliminated.

The second approach is more directed at the firefighting foam application. A formulation has been developed that adds a candidate siloxane surfactant to an optimized mixture of an alkyl polyglycoside (APG) co-surfactant, diethyleneglycol monobutyl ether (DGBE) and water for fire suppression evaluation [9]. Currently, our highest performing formulation uses the **Si4SB** surfactant in a 2:3:5 weight ratio of **Si4SB**:APG:DGBE [66]. This formulation with D_2O in place of H_2O is used for the NMR-based hydrolysis evaluation as depicted in the right column of Figure 53.

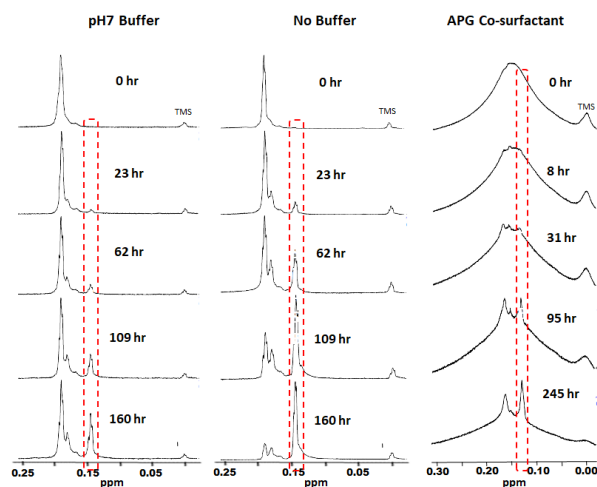


Figure 53. ^1H NMR spectra of the Si- CH_3 region depicting hydrolysis effects for **Si4SB** in pH7 buffered and unbuffered D_2O during a 160 hr period and in a formulation with an alkyl polyethylene glucoside surfactant and diethylene glycol monobutyl ether in D_2O . The dashed line encircles a resonance chemical shift regions assigned to either of both the $(\text{CH}_3)_3\text{Si-OH}$ and $(\text{CH}_3)_3\text{Si-O-Si}(\text{CH}_3)_3$ hydrolysis products.

In the NMR spectrum an extensive broadening of the Si-CH₃ resonance as shown in the 0 hr spectrum in the right column of Figure 53. This broadening is attributed to incorporation of **Si4SB** into a large APG micelle, and it is a hypothesis that this APG micelle may afford hydrolysis protection. Over a 245 hr monitoring period small narrow resonances begin to slowly emerge, one of which correlates the trisiloxane hydrolysis products indicated by encircling dashed line in the series of spectra. The bulk of the area of this group of resonances is associated with the initial broad indicating that the degree of hydrolysis is significantly less than that for the non-buffered control and also less than that for the pH 7 buffer which have durations of 160 hr. However, the hydrolysis was not completely suppressed.

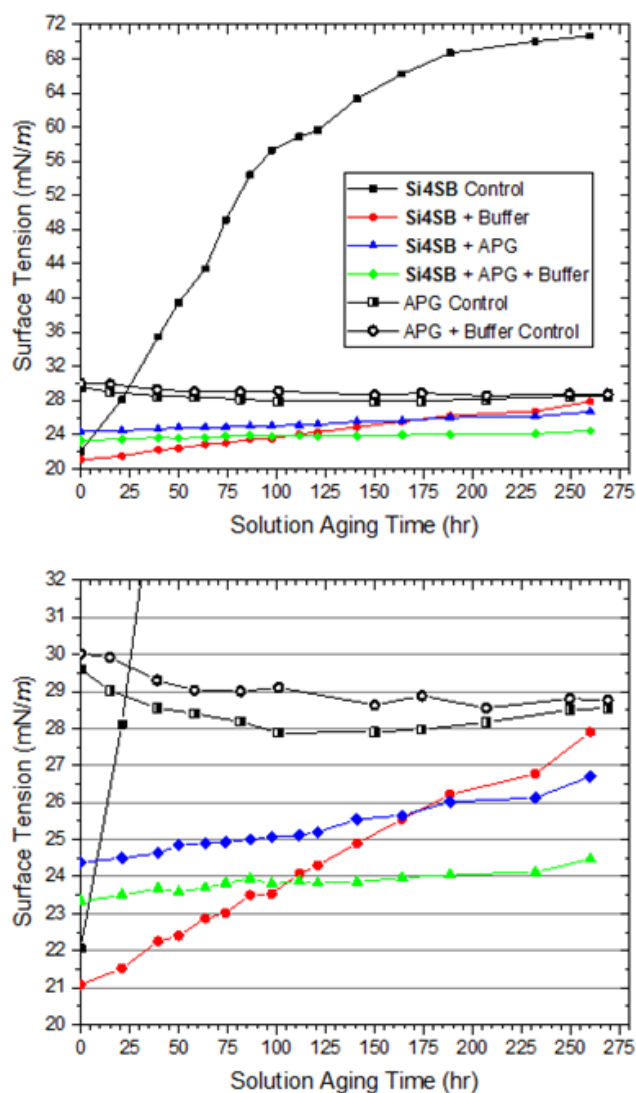


Figure 54. Surface tension monitoring for hydrolysis of **Si4SB** in presence of pH 7 buffer, APG co-surfactant and both buffer and co-surfactant compared with controls of **Si4SB** alone, APG co-surfactant alone and APG + pH 7 buffer. The lower plot is an expansion of the upper plot.

To complement the NMR hydrolysis assessment comparable surface tension monitoring of **Si4SB** solutions with pH 7 buffer, APG co-surfactant and combined buffer and APG was conducted along with control experiments as depicted in Figure 54. The **Si4SB** control solution displays a very rapid surface tension increase with the surface tension of water being approached at the end of the experiment. This is consistent with the NMR experiment of a complete hydrolysis. Addition of the pH 7 buffer significantly lowers the rate of surface tension increase, but, after 250 hr, the surface tension is approaching 30 mN/m characteristic of hydrocarbon surfactants. The APG co-surfactant provided much better siloxane protection although it did elevate the initial surface tension by 3 or 4 mN/m. The combination of both APG and buffer provided the best protection over the 275 hr duration of the experiment although the surface tension did increase by a couple of units. It is also of interest to note that the addition of the APG or/and the buffer does increase the surface tension a few units.

For siloxane hydrolysis assessment both the NMR and surface tension monitoring methods complement each other quite well. The former confirms the degradation of the siloxane structure in bulk solution, and the latter indicates that the loss of surface activity is gradual during the hydrolysis rather than being unaffected until a minimal threshold surfactant quantity, e.g. CMC, is approached. This latter observation is somewhat unintuitive. The surface tension method also is more facile to conduct and yields a direct numerical metric.

5.7. Task 8 – Submit Technical Reports to SERDP

Submitted.

6. Conclusions

An environmentally-friendly, fluorine-free, drop-in replacement to AFFF is being developed based on siloxane surfactant chemistry. If successful in improving the fire suppression on gasoline and heptane, a siloxane based formulation has the potential to be a drop-in replacement for AFFF because of low viscosity of the 3% concentrate, unlike many of today's commercial fluorine-free formulations, which include polymers. A true fluorine-free replacement should have fire suppression and burnback performance matching that of AFFF with the performance less sensitive to fuels, physical properties amenable to existing hardware, and low impact on the environment and human health.

Previously, we identified a pair of nonionic commercial silicone (trisiloxane-polyoxyethylene or Dowsil 502W additive of Dow Silicones Co.) and hydrocarbon (alkylpolyglycoside or Glucopon225DK of BASF) surfactants from a number of commercial hydrocarbon and silicone surfactants of various types. We also showed that the surfactant pair in NRL developed formulation (Table 1, column 1, row 11) suppressed heptane pool fires reasonably well, but less so on gasoline fires. The fuel sensitivity is due to extraction of the silicone surfactant by the aromatic components in gasoline. To improve the fire performance on gasoline, we designed and synthesized novel siliconesulfobetaine surfactants.

We synthesized several closely related surfactant molecular structures that transition from trisiloxanePEO to tetrasiloxaneSB in a stepwise manner as shown in Figure 1. This gradually varies the hydrophilicity of the head with tail fixed and hydrophobicity of the tail with the head fixed. If we begin with trisiloxanePEO as reference point for a balanced amphiphilicity, increasing

hydrophilicity of the head or hydrophobicity of the tail, one at a time, reduces the amphiphilic balance unless both head and tail are changed to preserve the balance. The reduced amphiphilicity can affect the degree of surfactant activity at an interface and in a micelle. The manifestation of these effects is seen on surface and interfacial tensions, and critical micelle concentrations. As the amphiphilic balance is decreased, a significant increase in interfacial tension and CMC is observed for the siloxane surfactant solution and as the balance is restored with tetrasiloxaneSB the interfacial tension and CMC also decrease significantly as shown in Table 13. For a solution of surfactant mixture containing siloxane and glucoside, CMC is affected significantly by the structural variation and amphiphilicity but not the interfacial tension potentially because glucoside adsorbs predominantly at a fuel-water interface unlike the air-water interface and changes to siloxane surfactant have a minimal effect.

We used the same methods and conditions for all of the surfactant solutions to generate foams, characterize foams, and conduct fire suppression. Therefore, any differences seen among siloxane surfactants can ultimately be attributable to differences in their molecular structure in Figure 1. We find that foam quality in terms of bubble size distribution, bubble coarsening, and liquid drainage, are not affected by the siloxane structure significantly at the bench scale but are affected at the large scale, where the average bubble sizes are as much as six times smaller as shown in Figures 30 to 32. Changing the head from PEO to SB and the tail from trisiloxane to tetrasiloxane appears to reduce the average bubble size by a factor of 3 at the large scale. All of the SB foams degrade more rapidly than the trisiloxanePEO foams as shown in Figure 33 and reasons are unclear. Despite this rapid foam degradation, the heptane vapor permeation rate through the foam layer is significantly slower for the tetrasiloxaneSB foam relative to trisiloxanePEO foam shown in Figure 36. These results suggest that the diffusion rate is suppressed by chemical interactions between heptane vapor and siloxane surfactant adsorbed at air-water interface rather than due to significant differences in foam bubble structure.

As the amphiphilic balance is decreased by the changes to the trisiloxanePEO molecular structure, the fire extinction time and foam expansion ratio increase and as the balance is restored with tetrasiloxaneSB, the fire extinction time and foam expansion ratio decrease significantly in Figure 37 similar to the effects on CMC. For most other siloxaneSB surfactants, the fire extinction times and expansion ratios are longer than for the tetrasiloxaneSB due to the decreased amphiphilicity. Foam degradation and fuel permeation do not appear to correlate with trends in fire extinction time. But applying the degradation and fuel transport results to fire suppression is complicated by the foam application dynamics, where foam layer spreads and its thickness increases with time unlike the conditions used in the above bench scale measurements. Even though the expansion ratio appear to follow the effect of changes in amphiphilic balance, the relationship between expansion ratio and fire extinction times is somewhat unclear because Glucopon225DK foam has a small expansion ratio and yet has one of the longest fire extinction times as shown in Figure 37. Large scale testing confirms bench scale result that tetrasiloxaneSB formulation could extinguish a 28 ft² gasoline fire in 62 s compared to no extinction with trisiloxanePEO formulation, and 26 s extinction with RefAFFF as shown in Table 15.

Eventhough fire extinction times follow the trends with siloxane amphiphilicity for a given fuel, the role of fuel and the differences in extinction times among different fuels remain unexplained. One reason is that tetrasiloxaneSB shows synergism with Glucopon225DK on gasoline fire as shown in Figure 42 but not on heptane fire while the opposite is true for

trisiloxanePEO [9]. The degree of synergism depends on the ratio of glucopon to siloxane surfactant concentration as shown in Figure 46. In addition, it is possible that the zwitterionic head might have prevented the surfactant dissolving into the aromatic components of gasoline unlike trisiloxanePEO, which has been shown to diffuse from the fuel-water interface into gasoline phase over time [26]. However, the fire extinction time for gasoline is smaller than for heptane for tetrasiloxaneSB while the opposite is true for the trisiloxanePEO [26]. So, questions remain unanswered regarding basic mechanisms responsible for the differences in fire extinction times for different fuels.

Observation of a rapid, self-inflicted hydrolysis for a series of sulfobetaine-siloxane surfactants is described. An understanding of this hydrolysis phenomenon coupled with preventative measures for further development is needed. New insight involves documentation of a strongly bound hydration layer to the sulfobetaine moiety which is speculated to serve as a nucleation site for formation of an aqueous exclusion zone at a surfactant aggregate – water interface. The somewhat unique tendency of ionic siloxane surfactants to form large bilayer and/or vesicle aggregates [37] appears to be an enabling feature for an exclusion zone formation. Adjacent to the negatively charged exclusion zone is an acidic outer region [38] which is speculated to cause acceleration of the siloxane tail of a sulfobetaine-siloxane surfactant. Protective measures investigated include use of a pH 7 buffer and of a polyethylene glucoside co-surfactant. While these measures were very significant, a greater depth of mechanistic understanding and more effective hydrolysis prevention are needed.

The results presented show that surprisingly small changes to a surfactant molecular structure can result in dramatic changes in CMC, foam expansion ratio, foam degradation, fuel permeation through foam, and improvements in fire suppression. They appear to have only small effects on foam bubble size distributions and liquid drainage for foams generated by sparging method at bench and large scales. Many of these changes could largely be explained by the changes to amphiphilic balance of the surfactants involved and we show that the effects of surfactant's amphiphilicity permeates from CMC and foam stability to fire suppression. But, the degree of improvement in fire suppression are fuel specific because fuels affect the degree synergism between the surfactants. The sulfobetaine formulations are more effective on alcohol-free gasoline than on heptane. Foams cover the pool surface very quickly relative to fire extinction on gasoline and heptane, while they are comparable for Jet A. The degree of synergism arise from molecular interactions among surfactants, water, and fuel at an air-water interface and future work is needed to better understand the interactions and the role of fuels. The novel siloxane formulations presented in this study can provide insights to developers of fluorine-free alternatives to AFFF, and have low bulk viscosity unlike most commercial fluorine-free formulations, which contain polysaccharides or other polymeric additives that dramatically increase concentrate's bulk viscosity limiting their shipboard firefighting application [36, 67].

We quantified acute and chronic toxicities of individual siloxane, hydrocarbon, fluorocarbon surfactants and RefAFFF using *P. promelas* and *C. dubia* species following standard methods (U.S. Environmental Protection Agency, 2002. EPA/821/R/012. U.S. Environmental Protection Agency, Office of Water, Washington, DC and U.S. Environmental Protection Agency, 2002. Short-term methods for estimating the chronic toxicity of effluents and receiving waters to freshwater organisms. Fourth Edition. EPA/821/R-02/013). Based on these results the least toxic

of the compounds/formulations evaluated included DGBE, 502W sulfate, NRL 502, MD2062-124 and MD2086-1, which generally fell in the slightly toxic to practically nontoxic range (i.e., >10 mg/L). Conversely the most toxic compounds/formulations evaluated included the Capstone mix, HMTS, N10477-09, and Silwett-77, which generally fell in the highly to moderately toxic range (i.e., 0-10 mg/L) for the test species and endpoints evaluated. Based on results of the most complete data set (*C. dubia*) the relative order of toxicity of the tested compounds from least toxic to most toxic for acute survival (Figure 24, Table 8) is as follows: Capstone 1157, 502W Sulfate < NRL502W, MD2062-124, MD-2086-1< DGBE<502W<Glucopon 225DK, Glucopon 215UP<Silwett-77<<N10477-09<HMTS<<Capstone mix. The order of relative toxicity was similar in chronic tests with *C. dubia* was similar with the exception of Capstone which was comparatively more toxic in relation to the other compounds/formulation evaluated with a reproductive IC50 value of 5.28 mg/L (Table 9). The relative order of toxicity for the common set of compounds/formulation (Capstone 1157, DGBE, and NRL502W) tested across all species and endpoints was similar though there were pronounced differences in toxicity between species for some compounds (e.g., DGBE LC50 for an LC50's of 75mg/L for survival in acute tests with *C. dubia* survival vs. and LC50 of 2092 mg/L for *P. promelas*) (Tables 8 & 10).

7. Acknowledgements

We like to thank Mr. Felix Kummerlen (ESP scientist), Dr. Dennis Kim (ASEE Post Doc) for help in conduction bench scale fire suppression experiments and Dr. Paige Sudol (NRC Post Doc) for help in obtaining large scale DFA measurements. We also thank Dr. John La Scala of SERDP for supporting this work under WP22-3391 program.

8. Productivity

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APPENDIX I

I. ¹H NMR spectra of reaction and purification of synthesized surfactants described in section 5.1.2.

This section describes the use of ¹H NMR to monitor synthesis reactions and purifications of the surfactants presented in Figure 47 with the exception of **CycSi3SB** and **CycSi3(OE)10**. The hydrosilylation reaction used to connect the head and tail of these surfactants has many variations that couple its usefulness and complexity with an unpredictability. This reaction dates back to the 1950's, and a particularly useful review is that edited by Bogdan Marciniec [Marciniec 2009]. Applying this reaction to specific synthesis involves decisions about procedural issues. These include selection of a specific catalyst and reaction conditions to be used. The usual approaches involve copying a well-documented procedure in the literature and adopting such a procedure to similar reagents. In this work the latter procedure is followed. Silicone surfactant reviews are very helpful in identifying specific catalysts (Speier's catalyst, Karstedt's catalyst), describing side reactions (olefin isomerization, alkoxysilane formation) [LeGrow and Petroff 1999]. For the sulfobetaine-siloxane and polyoxyethylene-siloxane subclasses of silicone surfactants, reviews and articles of particular interest are respectively [Snow et al 1990, 1991; Fenton 1990] and [Kanner et al 1967; Maki et al 1969; Cartis 1979].

For the syntheses reported this work decisions involving catalyst selection, reaction conditions, reaction monitoring and product isolation were made as follows. The initial catalyst selection was Speier's catalyst prepared as a 1.0 wt% solution of H₂PtCl₆·6H₂O in 2-propanol. The hydrosilylation reaction is very exothermic ($-\Delta H = 32.82$ kcal/mol) and an unpredictable induction period precedes this reaction [Speier 1979]. This catalyst worked well with the trisiloxane-hydride and allyl-polyoxyethylene reagents, but the more active Karstedt's catalyst, platinum-divinyl tetramethyl disiloxane complex 5.0 wt% in xylenes [Nakajima and Shimada 2015], was found to be needed when the tetrasiloxane-hydride and allyl-amine were involved. Development of reaction conditions involved initial small 1-2g scale reactions with a 10% molar excess of allyl reagent from a 1:1 molar ratio of siloxane-hydride:allyl compound. A small quantity of catalyst was added (about 1:10000 molar ratio catalyst:siloxane-hydride), and this reaction mixture was monitored by temperature to detect an exotherm and by NMR to monitor the relative quantities of allyl and silyl-hydride consumed as well as products and any byproducts. The temperature was gradually increased with an oil bath from 20 to 100 °C over a period of several hours while monitoring for the exotherm via a reaction mixture – oil bath positive temperature differential. The reaction was also monitored for color development. Key observations are: that the exotherm occur at a moderate temperature (<50 °C) and not significantly exceed the bath temperature; the Si-H resonance disappear indicating reaction completion; quantity of remaining allyl resonances and observation of other vinyl resonances indicative of allyl isomerization; transition of Si-CH₃ resonances from that for reagent to that for product; reaction mixture color development indicative of degradation. If an observed exotherm temperature exceeds the oil bath temperature by 30 °C, the quantity of catalyst was reduced. If, after overnight at 100 °C, the CH₂=CH-CH₂- resonances (5.8, 5.1, 3.1 ppm) and Si-H resonance (4.6 ppm), were not significantly reduced with commensurate growth of the –CH₂-CH₂-CH₂-Si resonances (see Figures SI-1 – SI-5), the more active Karstedt's catalyst or/and a higher reaction temperature was used.

For product isolation its physical properties are the determinant of methods used, and NMR is particularly helpful in assessing a level of purification. For the distillable N,N-dimethylaminopropyl-siloxane intermediates the isolation was readily achieved as is indicated by the corresponding spectra in Figure SI-1. Expansions of the Si-CH₃ region are particularly useful for confirmation of structure and observation of any methyl-siloxane byproducts. The isolation of the **Si4SB**, **Si3SB** and **CycSi4SB** sulfobetaine surfactant products was more challenging as solubility was the property used for separation. The protocol developed was to use CH₂Cl₂ for the reaction then wash the precipitated product with Et₂O until NMR indicated the product to be relatively free of reagents and byproducts. In Figure SI-2, SI-3, SI-4 spectra for the respective **Si4SB**, **Si3SB** and **CycSi4SB** surfactants are depicted along with those for the residue from the CH₂Cl₂ reaction solvent filtrate and from the Et₂O wash filtrate. As can be readily seen, the expanded Si-CH₃ region of the NMR spectra are particularly useful for diagnosing presence methyl-siloxane components that are not part of the siloxane surfactant product. Also note that the choice of deuterated solvent can have a significant effect on the chemical shift and resolution of the various Si-CH₃ resonances. CD₃OD was used in sample preparation of **Si4SB**, **Si3SB** and **CycSi4SB** for spectra in Figures SI-2, SI-3 SI-4, while CDCl₃ was used the N,N-dimethylaminopropyl-siloxane intermediate samples in Figure SI-1. The tetrasiloxane structure has one group of equivalent Si-CH₃ units, while the trisiloxane has two nonequivalent Si-CH₃ groups and the cyclotetrasiloxane has four nonequivalent Si-CH₃ groups. The CD₃OD solvent enables resolution of all four Si-CH₃ groups. A comparison of the **CycSi4SB** spectrum from a D₂O solution with that from a CD₃OD solution is made in Figure SI-5 which shows a broadening of resonances and loss of resolution in the D₂O solution. This could be correlated with micelle formation. In confirmation of this micelle formation correlation a series of **CycSi4(OE)10** over a concentration range of 1.5 to 0.047 g/Kg were recorded to show the emergence individual resonance resolution as the concentration is decreased below the CMC (see Figure SI-6). In Figure SI-7 are spectra of the **Si4(OE)10**, **Si3(OE)10** and **CycSi4(OE)10** surfactant solutions in CDCl₃. The four nonequivalent Si-CH₃ groups of **CycSi4(OE)10** are not resolved similar to that observed in Figure SI-1 for the corresponding amine intermediate.

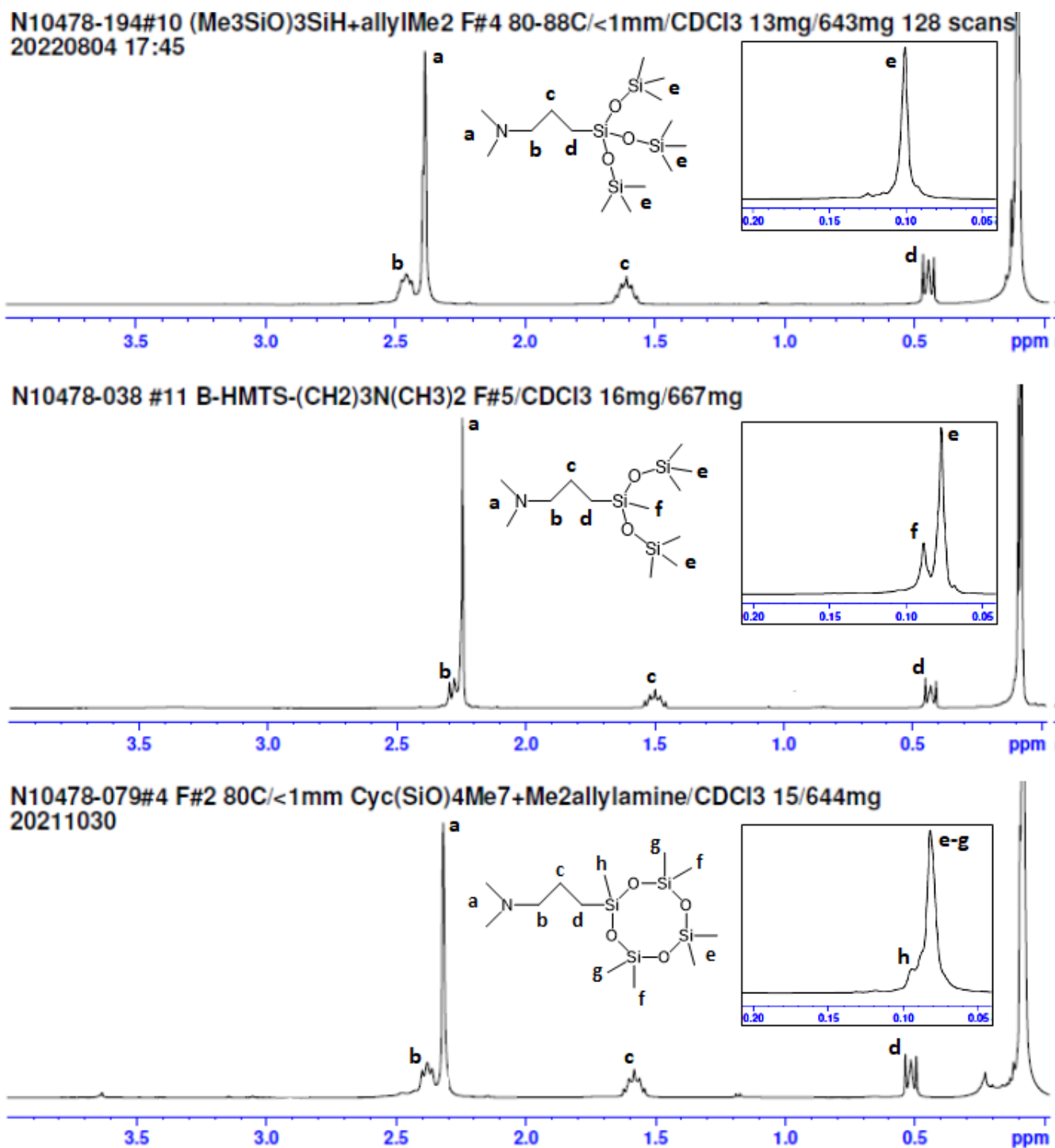
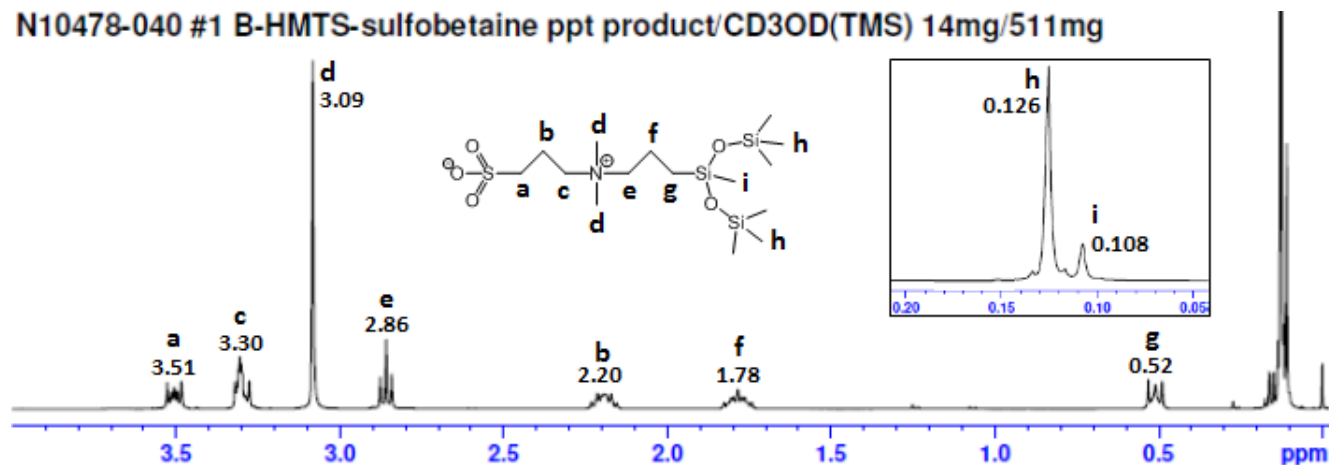
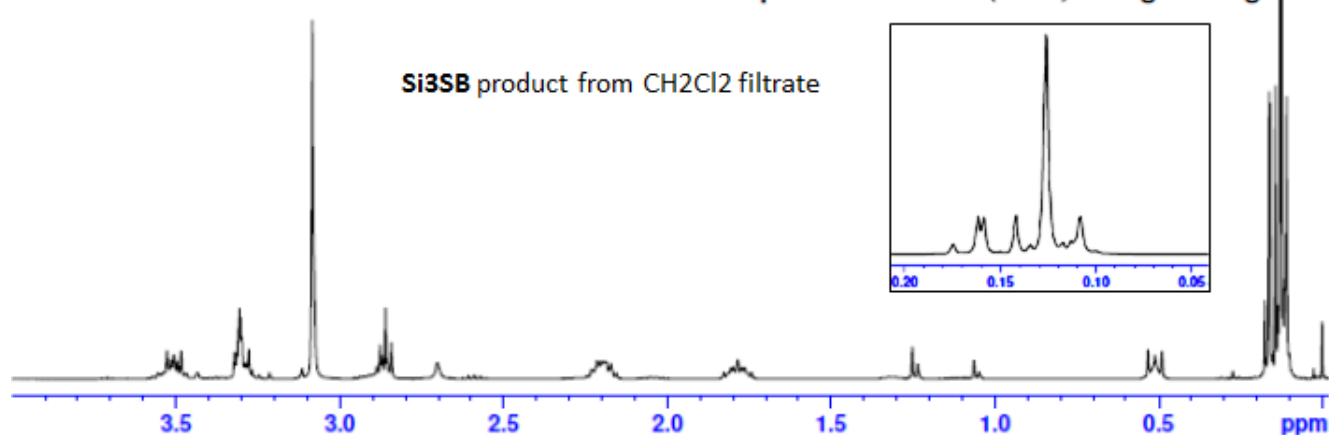


Figure SI-1. ¹H NMR spectra of synthesized dimethylaminopropyl-siloxane intermediates in preparation of Si₄SB, Si₃SB and CycSi₄SB surfactants.

N10478-040 #1 B-HMTS-sulfobetaine ppt product/CD₃OD(TMS) 14mg/511mg



N10478-040 #2 B-HMTS-sulfobetaine CH₂Cl₂ filtrate product/CD₃OD(TMS) 17mg/506mg



N10478-040 #3 B-HMTS-sulfobetaine Et₂O filtrate product/CD₃OD(TMS) 14mg/502mg

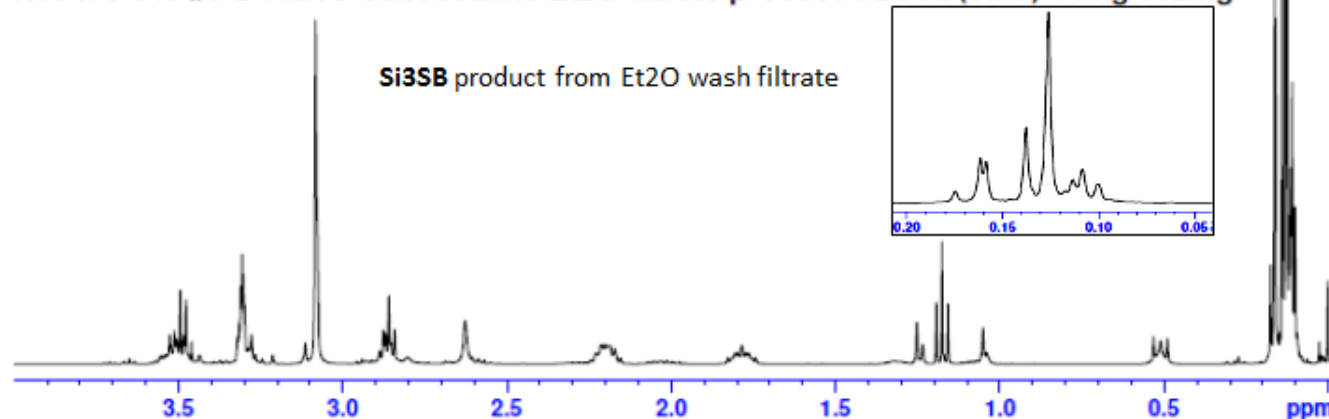


Figure SI-3. ¹H NMR spectra of **Si3SB** synthesis/CD₃OD: top – purified **Si3SB** product; middle – **Si3SB** isolated from CH₂Cl₂ filtrate; **Si3SB** isolated from Et₂O wash filtrate. Insert is expansion of the Si-CH₃ region.

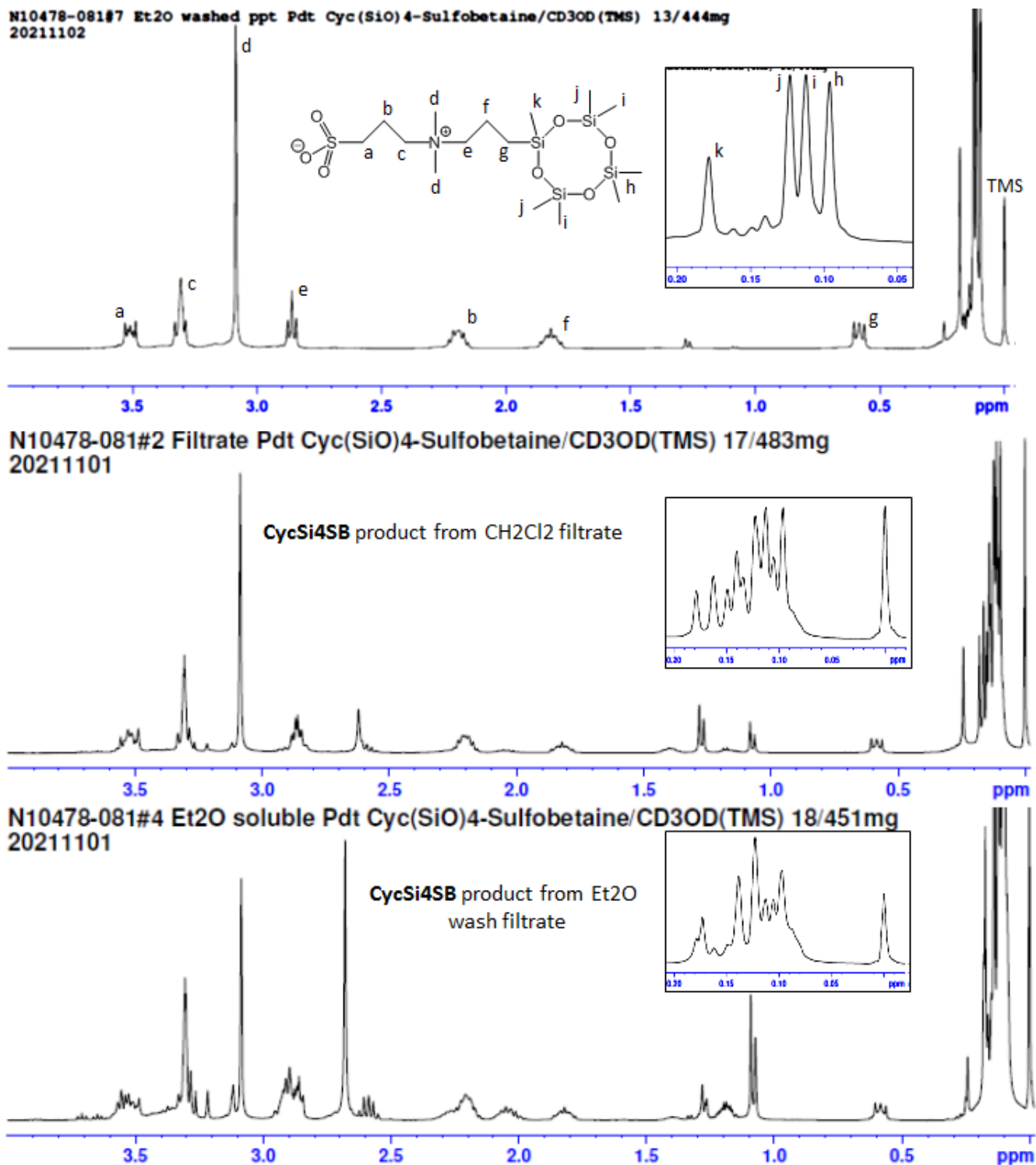


Figure SI-4. ^1H NMR spectra of **CycSi4SB** synthesis/ CD_3OD : top – purified **CycSi4SB** product; middle – **CycSi4SB** isolated from CH_2Cl_2 filtrate; **Si3SB** isolated from Et_2O wash filtrate. Insert is expansion of the Si- CH_3 region.

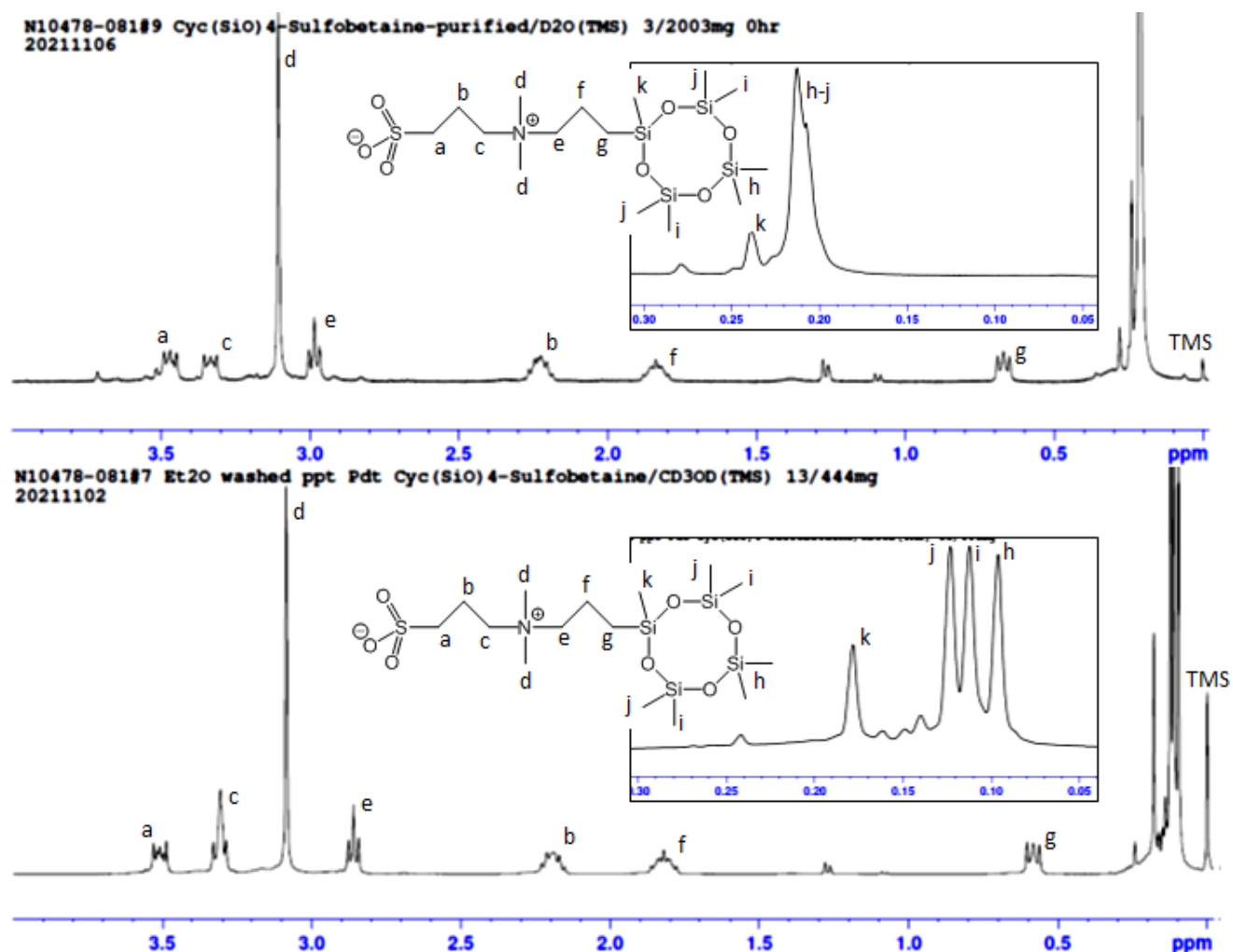


Figure SI-5. ¹H NMR spectra of CycSi₄SB in D₂O (top) and in CD₃OD (bottom) illustrating the effect of solvent and micelle formation on the Si-CH₃ resonances.

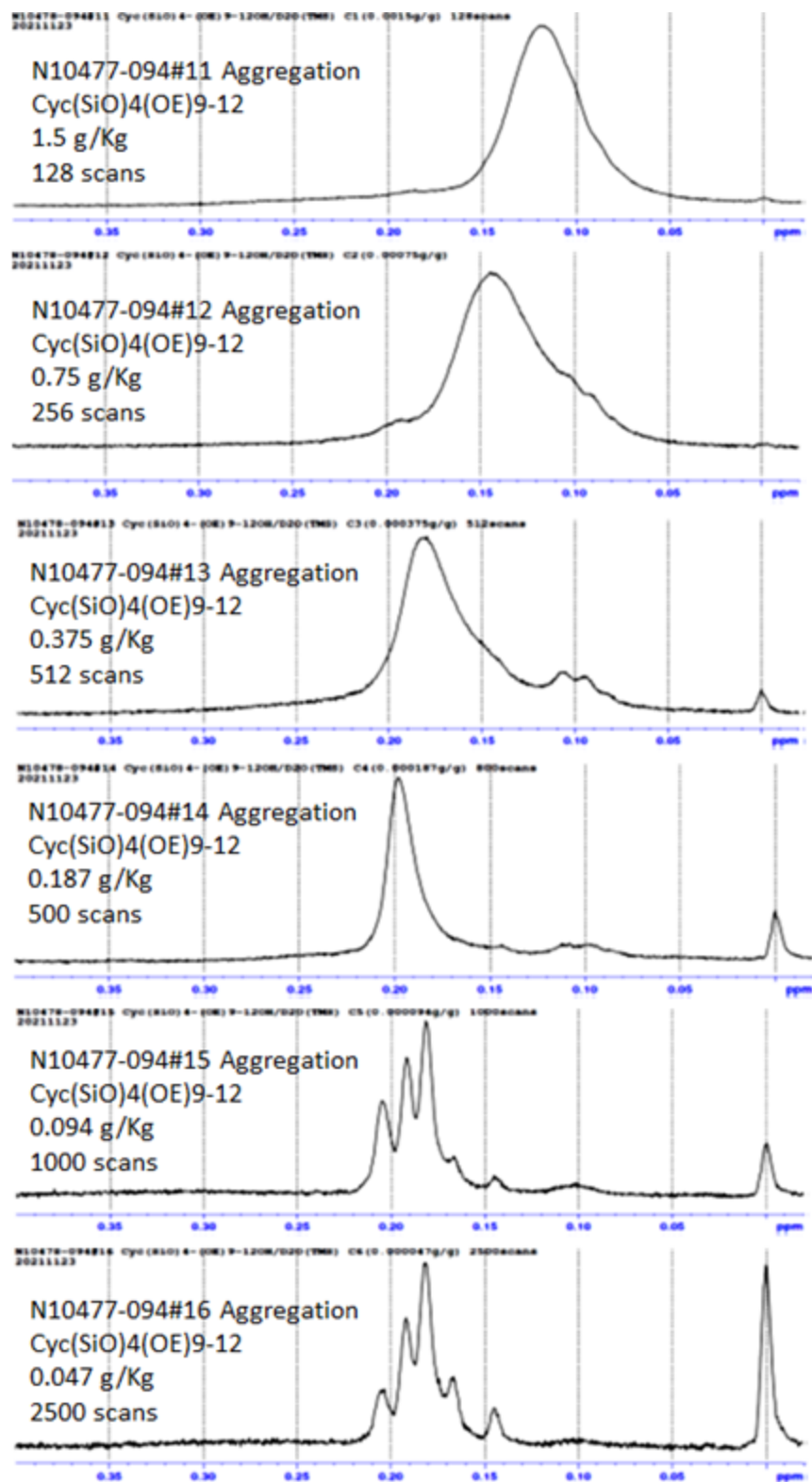


Figure SI-6. Concentration dependence and resolution of CycSi₄(OE)₁₀ Si-CH₃ ¹H NMR resonances.

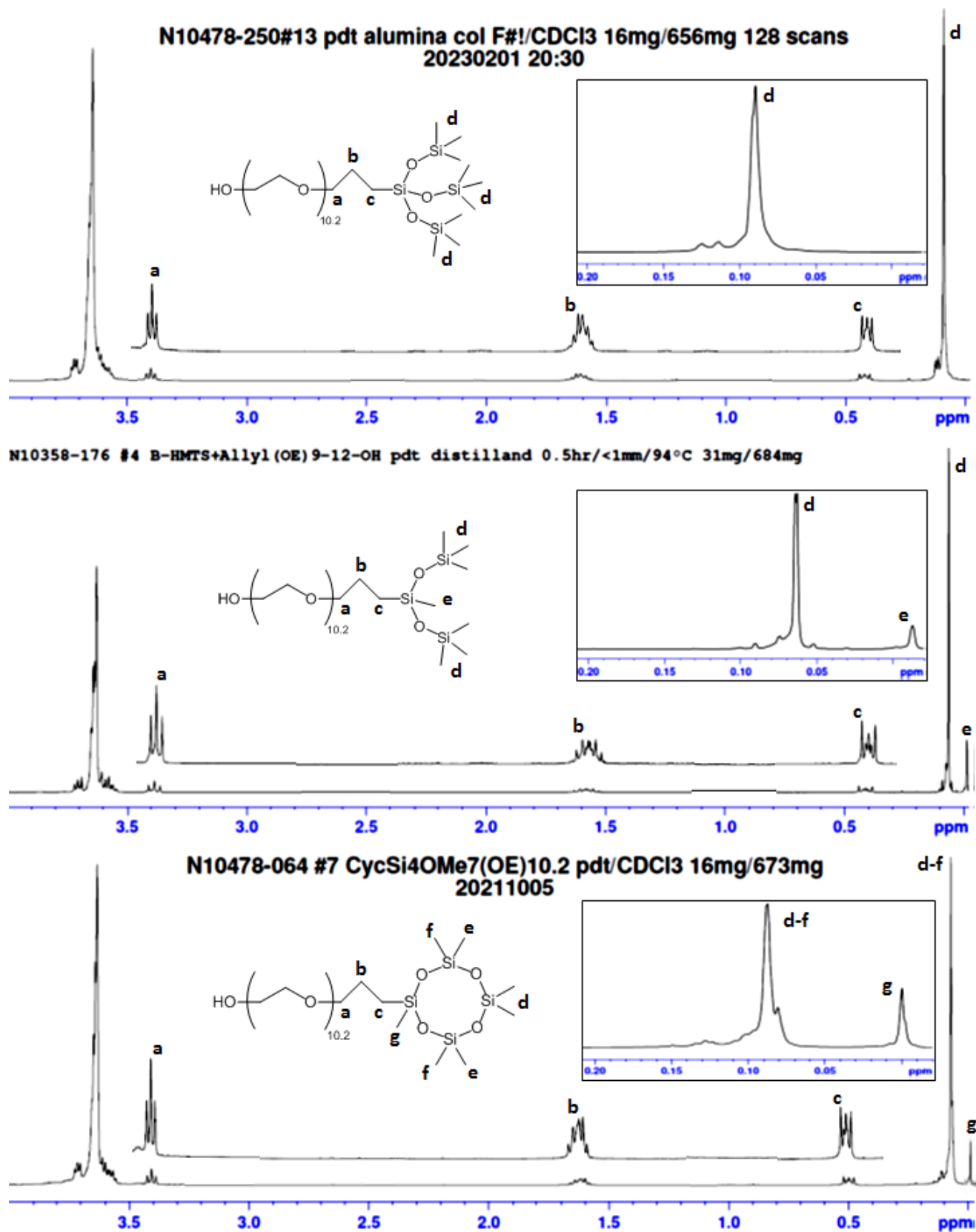


Figure SI-7. ¹H NMR spectra of synthesized and purified Si₄(OE)₁₀ (top), Si₃(OE)₁₀ (middle) and CycSi₄(OE)₁₀ (bottom) in CDCl₃.

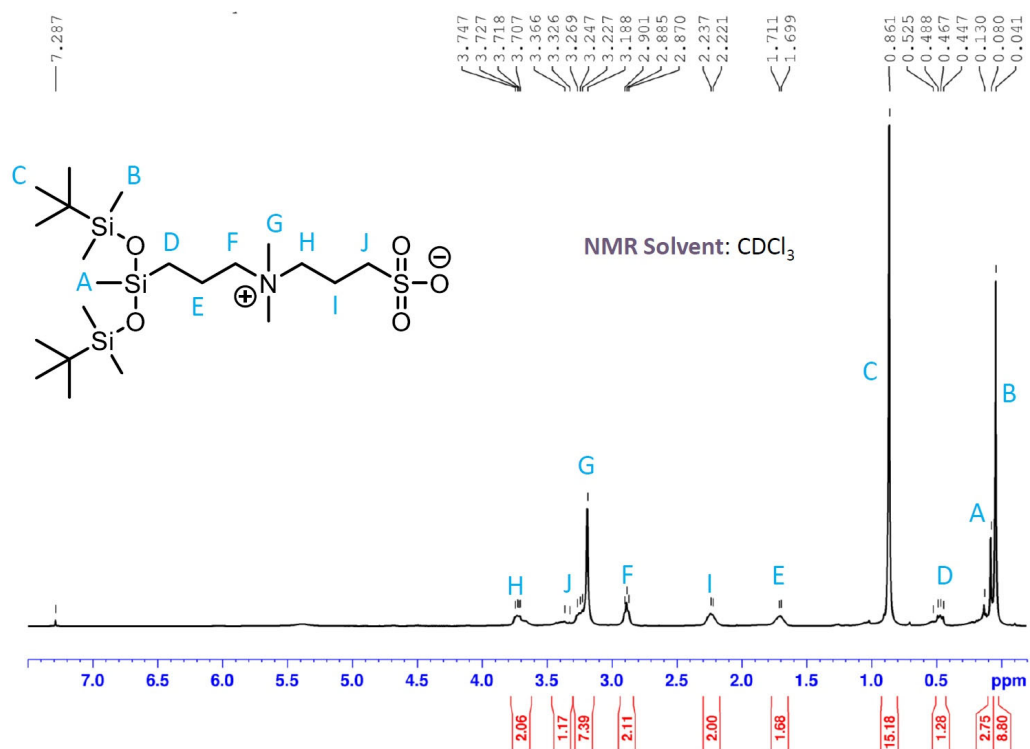


Figure SI-8. ¹H NMR spectra of synthesized and purified 3-[[3-[Di(tert-butyl)dimethylsiloxy)methylsilanyl]propyl]dimethylamino]propane-1-sulfonate (**CB-DTBTs-SB**) in CDCl₃.

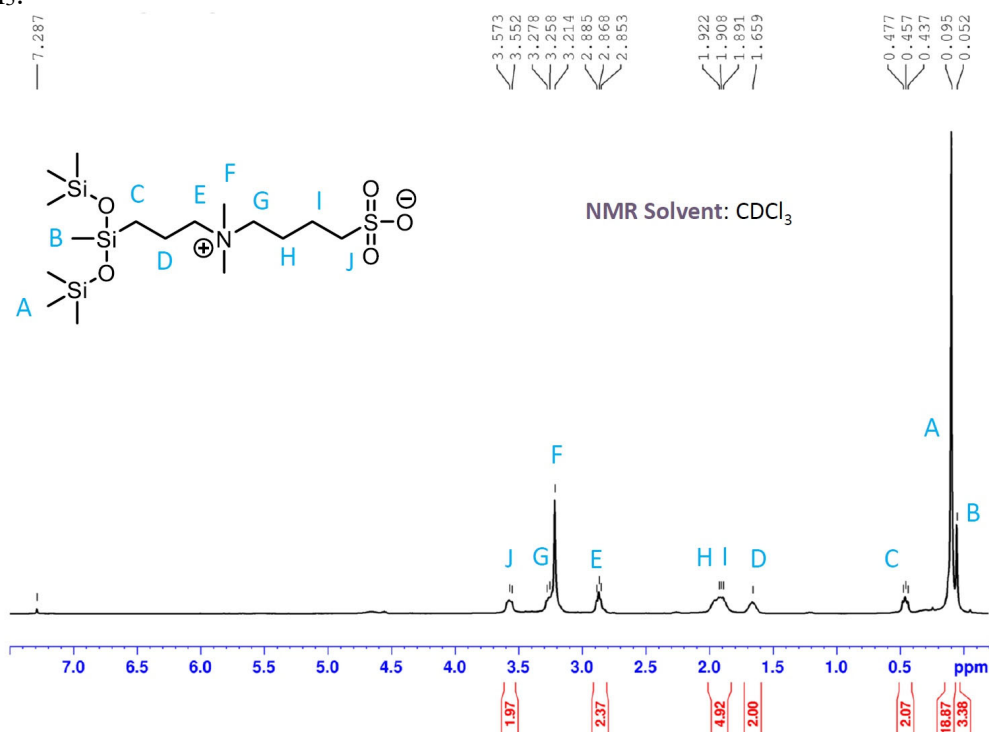
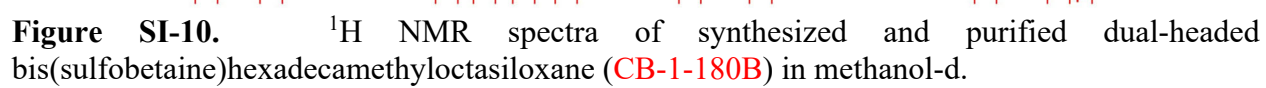


Figure SI-9. ¹H NMR spectra of synthesized and purified N,N-dimethyl-4-sulfo-N-[3-[1,3,3,3-tetramethyl-1-[(trimethylsilyl)oxy]-1-disiloxanyl]propyl]-1-butanaminium (**CB-1-123**) in CDCl₃.



II. ^1H NMR spectra of model compounds used in hydrolysis studies in section 5.6.2.

$(\text{CH}_3)_3\text{N}^+(\text{CH}_2)_3\text{SO}_3^-$, 3-(trimethylammonio)propane-1-sulfonate, was synthesized to be used as a model compound to diagnose hydrolytic susceptibility of siloxane surfactants without the sulfobetaine head group to determine if a molecularly dissolved sulfobetaine compound significantly accelerated the siloxane structure's hydrolysis. The siloxane was prepared by reacting trimethylamine with propanesultone and isolated by precipitation and Et₂O washing analogous to that used for the sulfobetaine surfactants. Reaction and ^1H NMR spectrum are depicted in Figure SI-11.

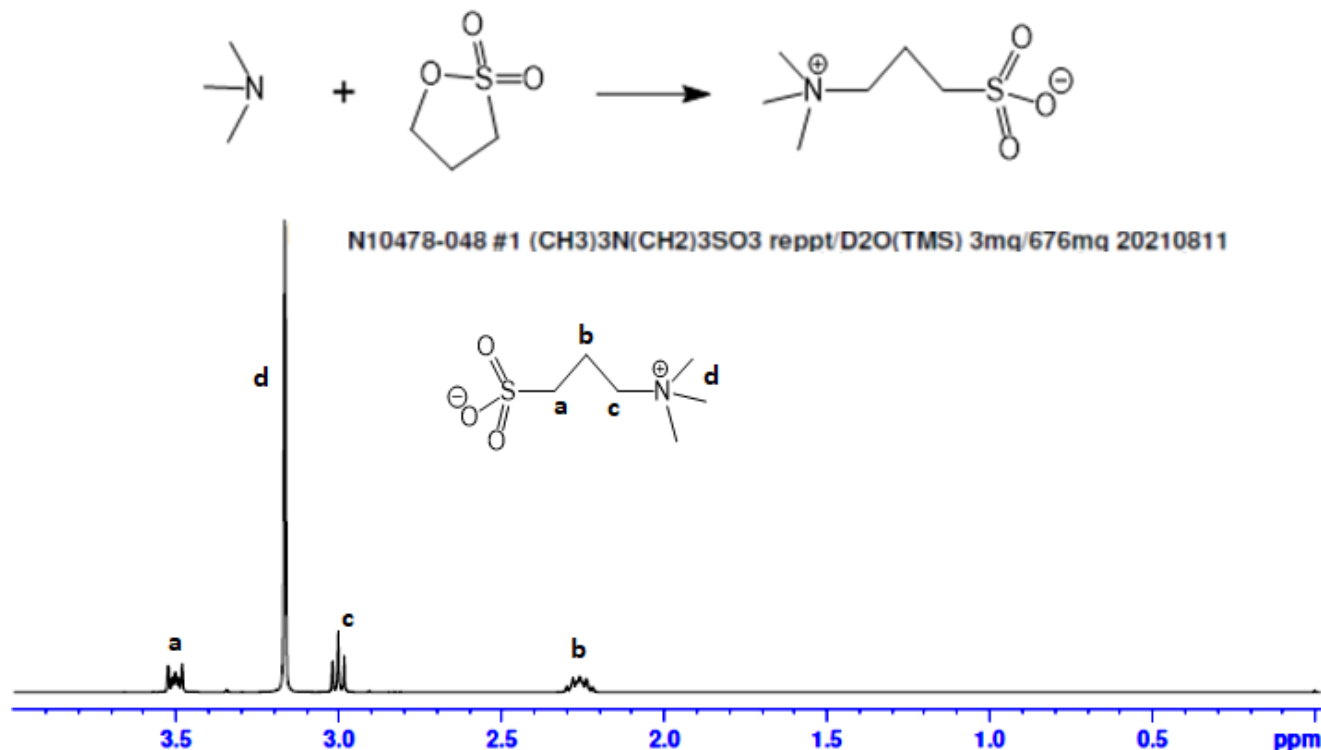


Figure SI-11. $(\text{CH}_3)_3\text{N}^+(\text{CH}_2)_3\text{SO}_3^-$ synthesis reaction and ^1H NMR spectrum.

A general chemical scheme for the hydrolysis of the siloxane structural components of the six surfactants of this study is depicted in Figure SI-12. Four simple products are envisioned as being formed (compounds 1-4). Each may potentially contribute a unique ^1H NMR signature in the Si-CH₃ region of the spectrum. Three of these model compounds were synthesized and one purchased. The NMR spectra of these model compounds in D₂O solution are presented in Figure SI-13. It is interesting to note that the chemical shifts for compounds 1, 2 and 4 are very similar, and that compound 2 has a very low water solubility nearly equal to TMS. It should also be noted that in spectra from D₂O solutions there are small chemical shift dependencies on the presence of ions (pH and presence of buffers) as well as the chemical shift reference compound selected (see Splvack and Dorn 1994 for spectra of compounds 3 and 4).

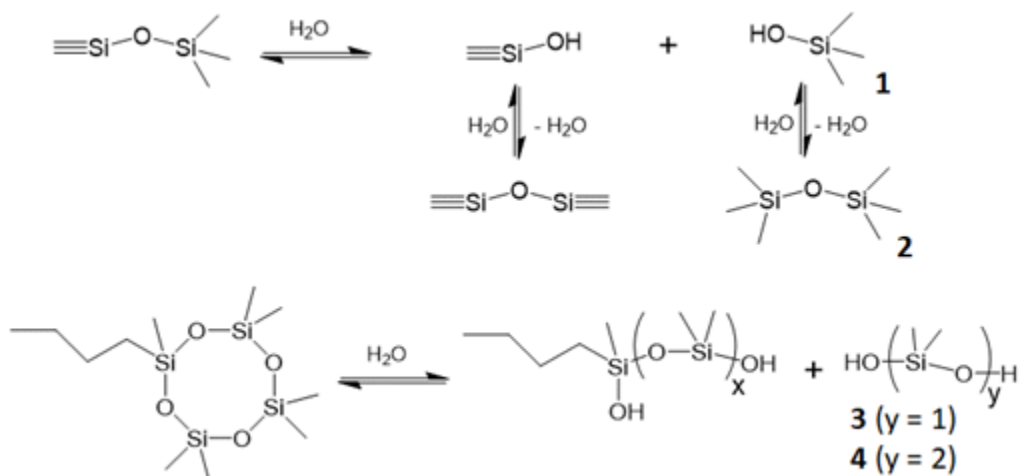


Figure SI-12. Hydrolysis reaction schemes for decomposition of **Si₄SB**, **Si₃SB**, **CycSi₄SB**, **Si₄(OE)₁₀**, **Si₃(OE)₁₀** and **CycSi₄(OE)₁₀** surfactants to four simple degradation products (compounds **1-4**).

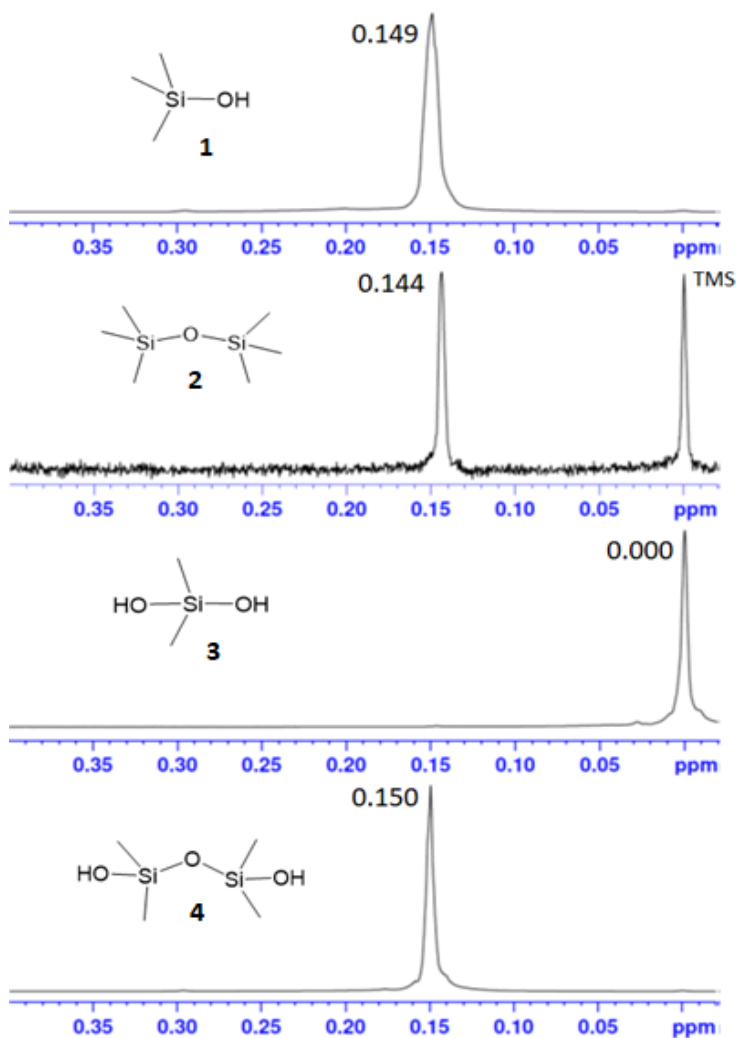


Figure SI-13. ¹H NMR spectra of Si-CH₃ region for hydrolysis model compounds **1**, **2**, **3** and **4** in D₂O solution.

III. Hydrolysis of 1,3-propanesultone to 3-hydroxypropylsulfonic acid

The unexpected finding that aqueous solutions of the **Si4SB**, **Si3SB** and **CycSi4SB** surfactants are strongly acidic (pH range 3.1-3.8) prompted suspicion of the presence of a strongly acidic impurity in these surfactants. The primary candidate for this role is propanesultone. Two control experiments are described below that examined this possibility.

The first experiment was a ^1H NMR monitoring experiment of the hydrolysis of propanesultone to 3-hydroxy-1-propylsulfonic acid. The procedure was to dissolve 30mg propanesultone in 2.00 g D_2O followed by addition of the TMS vapor reference then record NMR spectra at hourly and daily intervals. This procedure is very similar to the NMR protocol for monitoring the siloxane surfactant hydrolysis except that the propanesultone quantity was 30mg compared with the 3mg of surfactant used. The results with several representative spectra are presented in Figure SI-14. The spectrum at the top of this figure shows the reaction and resonance assignments to reactant and product structures. The series of spectra in the lower part of the figure shows the spectral changes at various hourly intervals. This hydrolysis is very simple with only one product being observed. The 3-hydroxy-1-propylsulfonic acid has three well-defined resonances at 3.70, 2.97 and 1.98 ppm. A close examination of the **Si4SB**, **Si3SB** and **CycSi4SB** surfactant spectra with expansions in these ppm regions revealed no resonances of any intensity to correlate with those of the 3-hydroxy-1-propylsulfonic acid. None of these signature resonances were observed in hydrolysis spectra of these surfactants as well.

The second experiment was a simple monitoring of pH after addition of the propanesultone to neutral water. The procedure was to add 35.00g deionized water (measured pH 6.06) to a 50ml beaker fitted with a slow moving stirring bar and a pH electrode. A 226mg quantity of propanesultone (warmed to 30 °C) was added dropwise with gentle stirring. The pH measurements were made in triplicate, and duration of this experiment was 50 hr. A plot of these data are presented in Figure SI-15a. The pH of the solution rapidly drops from 6 to 2 over a 5 hr period and levels off at a value at 1.3 as the 50 hr duration is approached. The initial concentration of the propanesultone was 0.052M and the hydrogen ion concentration corresponding to the 50hr pH measurement is 0.049M. This acidity associated with 3-hydroxy-1-propylsulfonic acid is significant lower (1.7 pH units) than that for the **Si4SB**, **Si3SB** and **CycSi4SB** surfactant solutions at the beginning of their titration in Figure 51 of the manuscript. This pH monitoring of the propanesultone hydrolysis is compared with the NMR monitoring of this reaction in Figures 15b and 15c where plots of the hydrogen ion concentration and of the growth of the 3-hydroxy-1-propylsulfonic acid resonance at 3.70 ppm as a function of time are presented. These two plots show good parallel agreement.

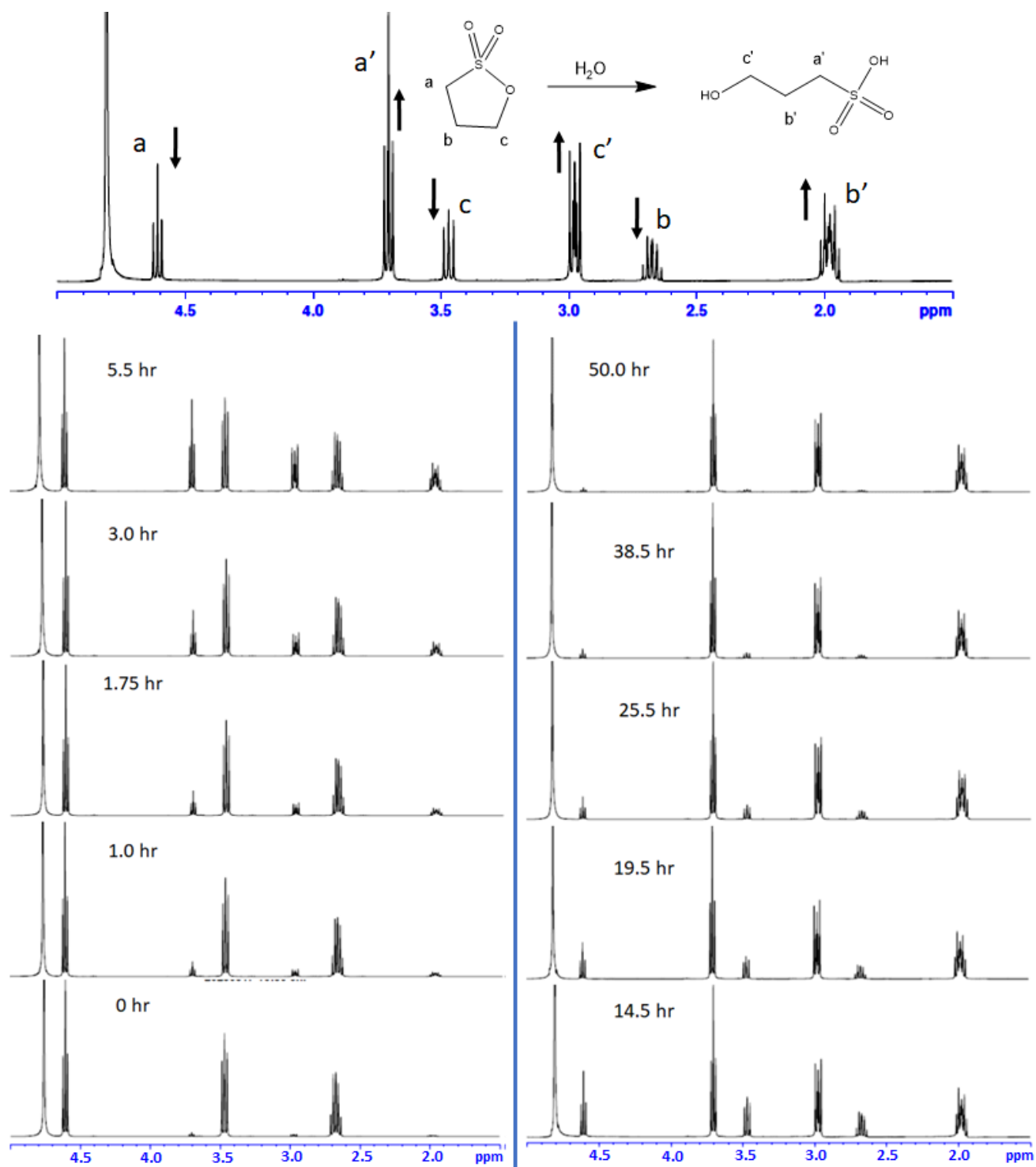


Figure SI-14. ^1H NMR monitoring of propanesultone hydrolysis to 3-hydroxy-1-propylsulfonic acid in D_2O : above – reaction and resonance assignments; below – spectral changes over 50 hr duration of reaction.

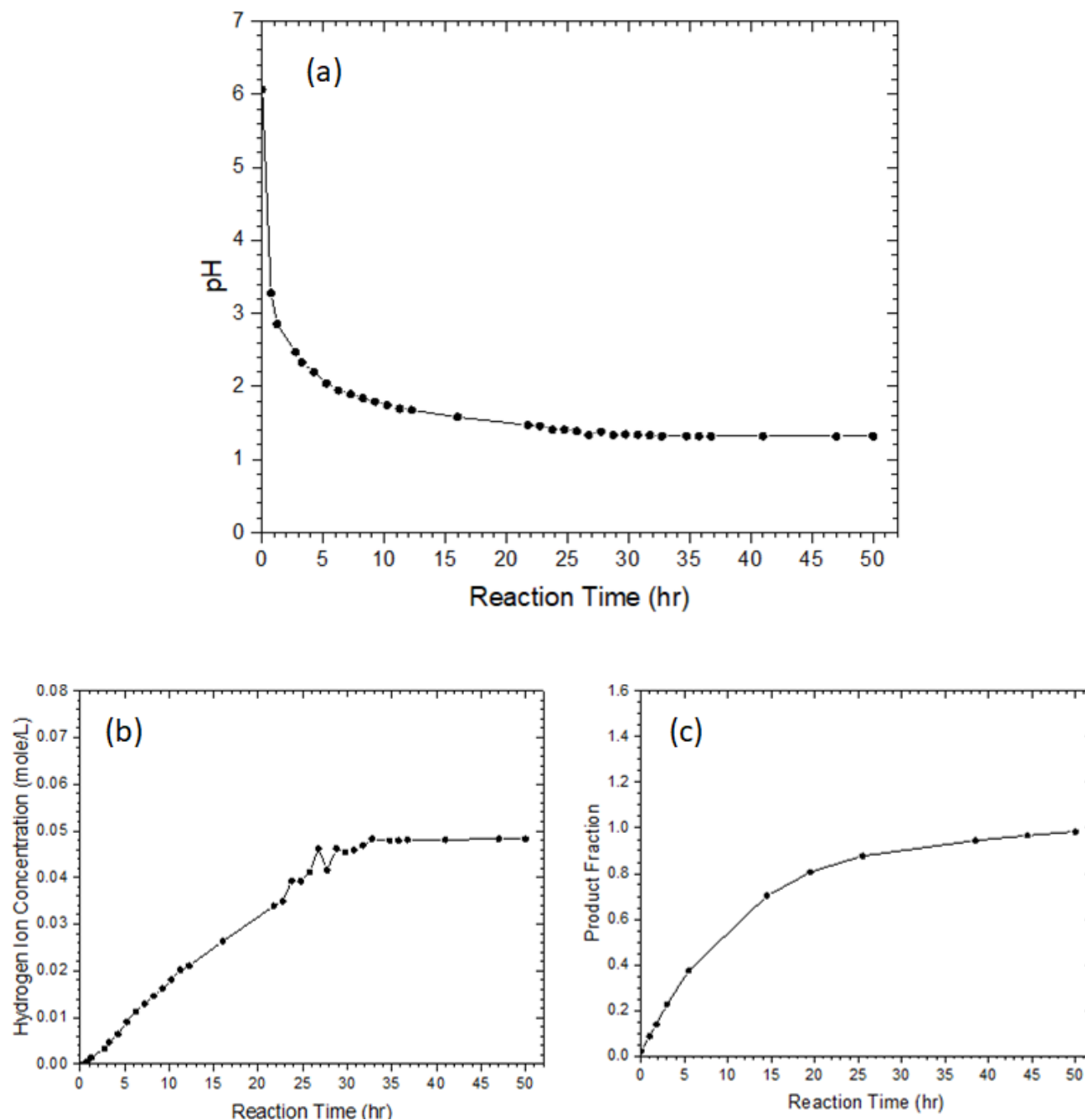


Figure SI-15. Hydrolysis monitoring plots for conversion of propanesultone to 3-hydroxy-1-propylsulfonic acid: (a) pH vs time; (b) hydrogen ion concentration vs time; (c) relative height of HO-CH₂-CH₂-CH₂-SO₃H NMR resonance (3.70 ppm) vs time.

IV. CycSi3SB and CycSi3(OE)10 synthesis attempts

The objective of this section is to provide a condensed summary of the approaches utilized and results in the attempted synthesis of the pentamethylcyclotrisiloxane intermediate to the **CycSi3SB** and **CycSi3(OE)10** surfactants depicted in Figure 47 of the manuscript with the intent that it benefits other researchers conducting related syntheses. The intended role of these surfactants was to contribute to the structure-property relationships with their analogs in Figure 47. As presented in Figure SI-16, these cyclotrisiloxane surfactants require four steps.

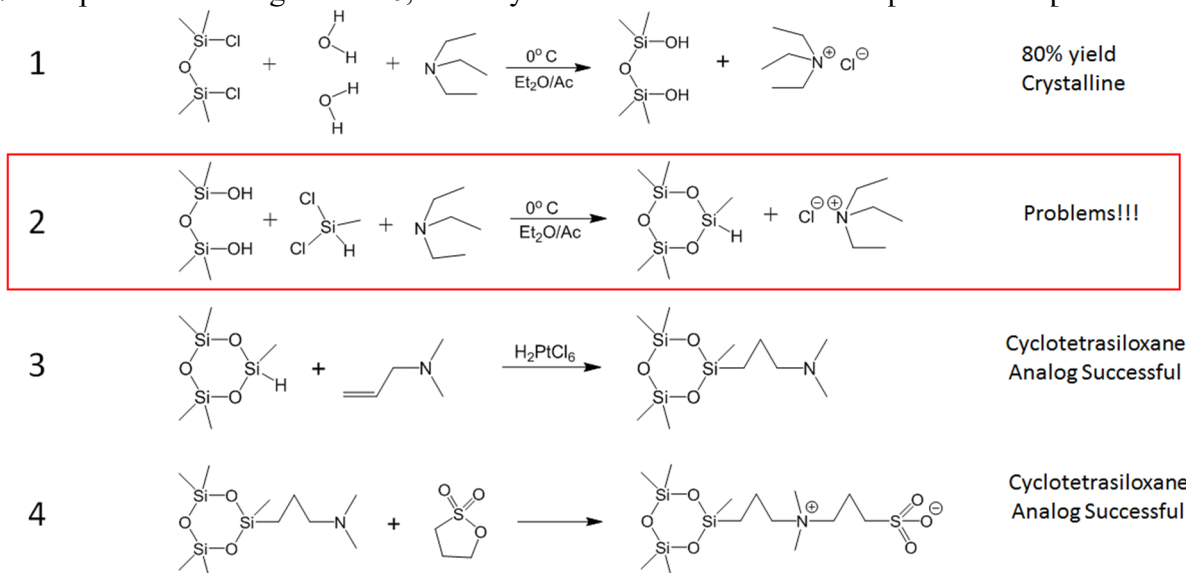
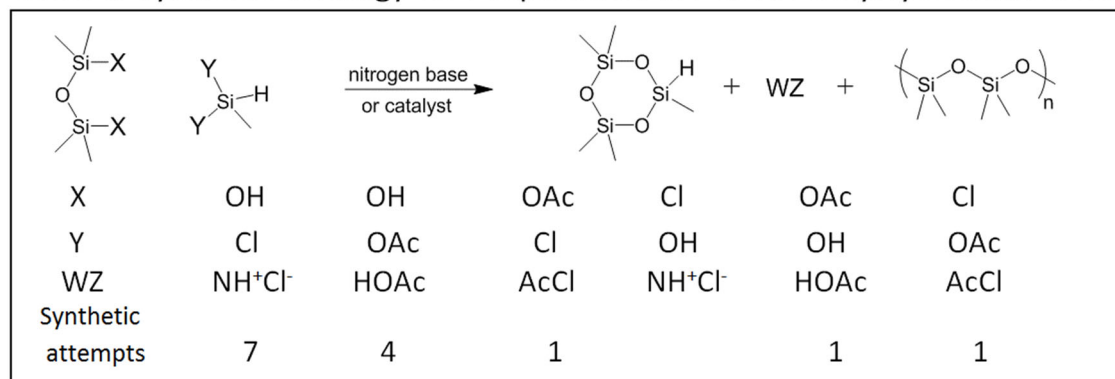


Figure SI-16. The four steps required for synthesis of the **CycSi3SB** surfactant.

Three of those steps involve transformations that work well with high yields. The product in the second step, pentamethylcyclotrisiloxane ($\text{Me}_5(\text{SiO})_3\text{H}$), is not commercially available and is the reason why this synthesis is two or three steps more than the synthesis of the other surfactants in Figure 47. There are a couple of reported syntheses for this compound in the literature, and there are a few reported syntheses for structural analogs in which different substituent structures are in the place of the peripheral hydrogen. A total of 14 attempts were made to synthesize this intermediate using both the reported procedures for this compound or adopting synthetic procedures for analogs.

Synthesis of the pentamethylcyclotrisiloxane structure with a sixth non-methyl pendant group requires a six-member ring closure reaction between disiloxane and monosiloxane reagents. The identity of reactant substituent groups to enable this ring closure reaction is a challenge. A summary of this effort is depicted in **Figure SI-17**. The dichlorosilane and dichlorodisiloxane precursors are commercially available, but the hydroxyl and acetate functionalized analog precursors must be synthesized. The synthetic routes, references, observations and reported yields for preparation of these hydroxyl and acetate analogs are presented in Figure SI-18. Also presented in this figure are observations product yields obtained in this work. The diacetoxysilane and -siloxane compounds are the more stable intermediates than the diol-analogs but are more difficult to synthesize due to an equilibrium that must be driven forward by removal of the acetyl chloride byproduct during the synthesis. As shown in Figure SI-19, this reaction is conveniently monitored by NMR. The acetyl chloride is removed by distillation, and the $\text{Cl}_2\text{SiHCH}_3$ is replenished until no further acetyl chloride is observed.

General Synthetic Strategy for Preparation of Pentamethylcyclotrisiloxane



Precursor Syntheses

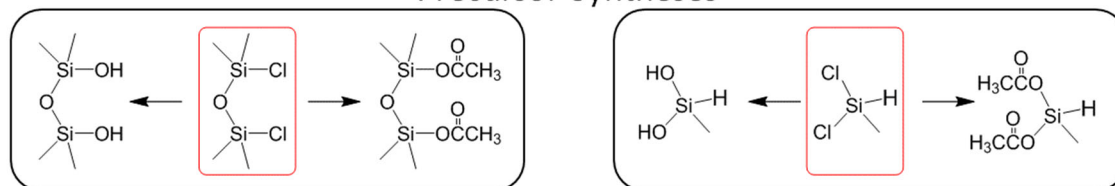


Figure SI-17. The reactions and table above show the identities and combinations of functional groups targeted for the synthesis of Me₅(SiO)₃H and of routes for precursor reagents for these synthetic attempts.

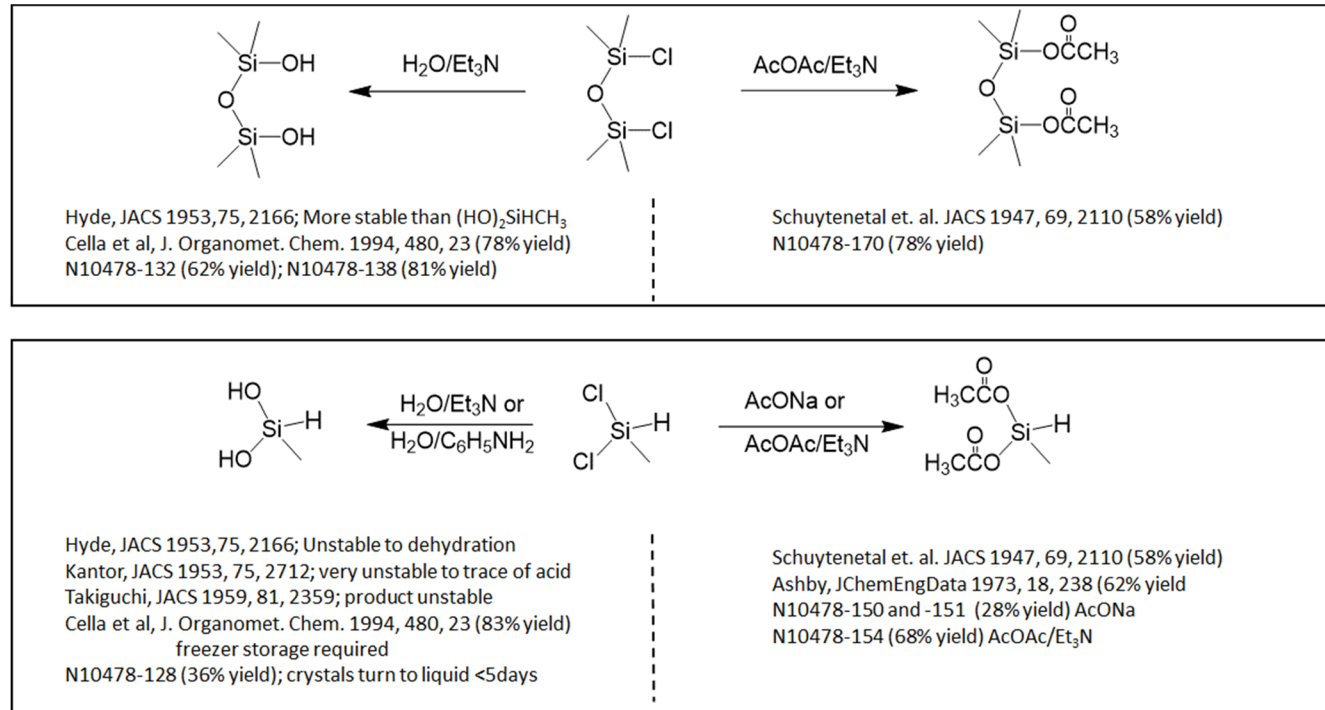


Figure SI-18. Specific preparations, references, yields and reproduced yields for precursor reagents.

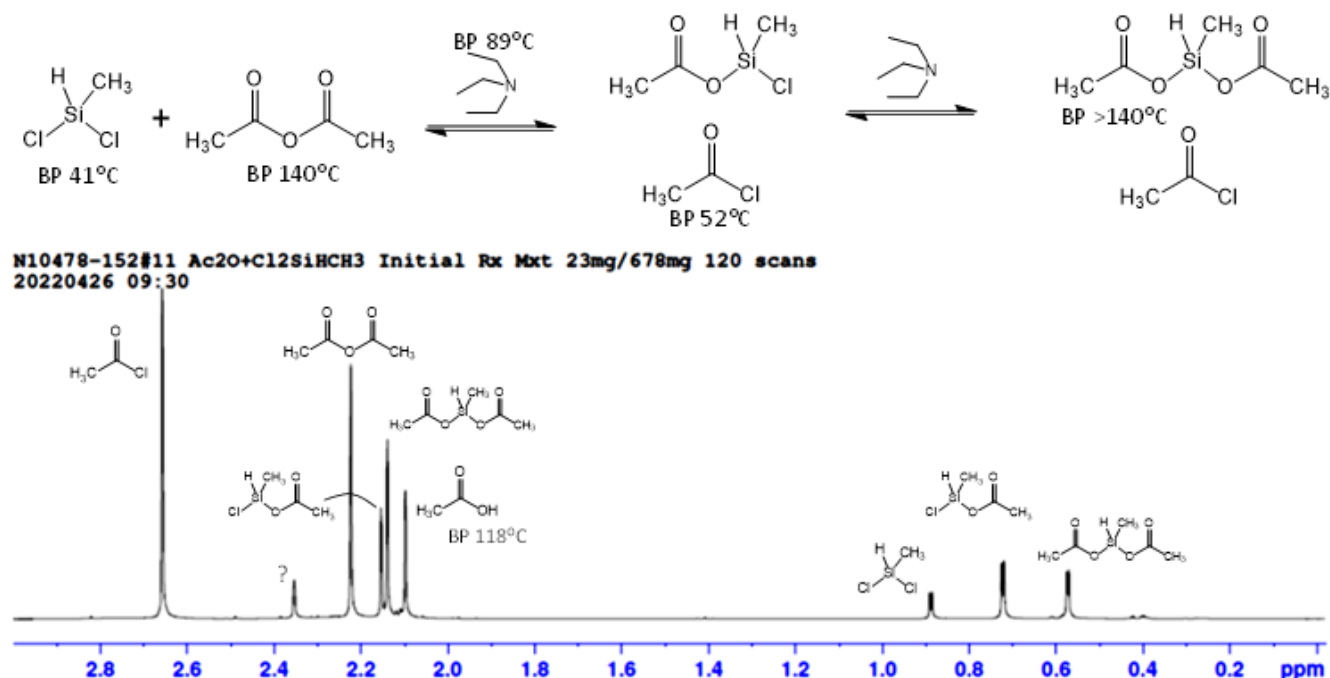
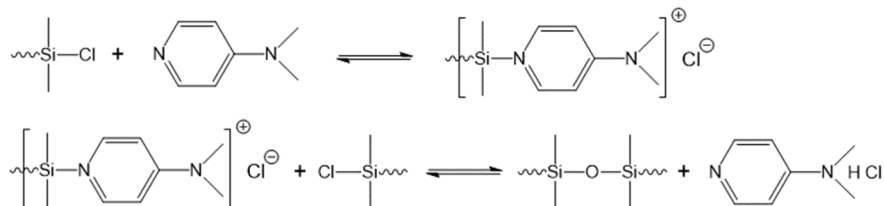


Figure SI-19. Preparation reaction for $\text{CH}_3\text{SiH}(\text{OCOCH}_3)_2$ and NMR monitoring.

With the set of chloro-, hydroxy- and acetoxy- monosilane and disiloxane reagents in Figure SI-18, a total of fourteen attempts were made toward synthesis of the $\text{Me}_5(\text{SiO})_3\text{H}$ intermediate as summarized in Figure SI-20. Seven attempts were made using the $\text{HO}(\text{Me})_2\text{SiOSi}(\text{Me})_2\text{OH} - \text{Cl}_2\text{SiHMe}$ combination. Four of the seven attempts involved the procedure specific to this compound [Paulasaar and Weber 1999; Paulasaar and Weber 2000] with the best yield obtained being 1.6% the balance being a non-volatile polymeric residue. An expanded literature search for synthesis of pentamethylcyclotrisiloxane compounds with substituent other than hydrogen located preparation of 1-vinylpentamethylcyclotrisiloxane from $\text{HO}(\text{Me})_2\text{SiOSi}(\text{Me})_2\text{OH}$ and $\text{Cl}_2\text{Si}(\text{H})\text{CH}=\text{CH}_2$ which utilized 4-*N,N*-dimethylaminopyridine (DMAP) as a catalyst in addition to NEt_3 as a base [Chojnowski and Rózga 1992; Ma and Wang 2002]. The rationale for use of DMAP in addition to NEt_3 is this nitrogen heterocycle, while having a low basicity, has a high nucleophilicity which displaces the chlorine from Si-Cl forming an activated complex which then reacts with the Si-OH to form the Si-O-Si siloxane bond [Rubinsztajn et al. 1989; Chaudhary and Hernandez 1979]. Pyridine has also been used for this purpose [Wu 1971].



Addition of the DMAP to the reaction mixture resulted in yield to 11% after three attempts. While this is an improved the yield, it is not practical for scale up. However, the 11% yield did provide an NMR signature to detect this product in future synthetic attempts (see Figure SI-21). The

colorless non-volatile liquid residue is a polysiloxane. It appears that the HCl byproduct even in the presence of the NEt₃ base may be generating significant polymer formation.

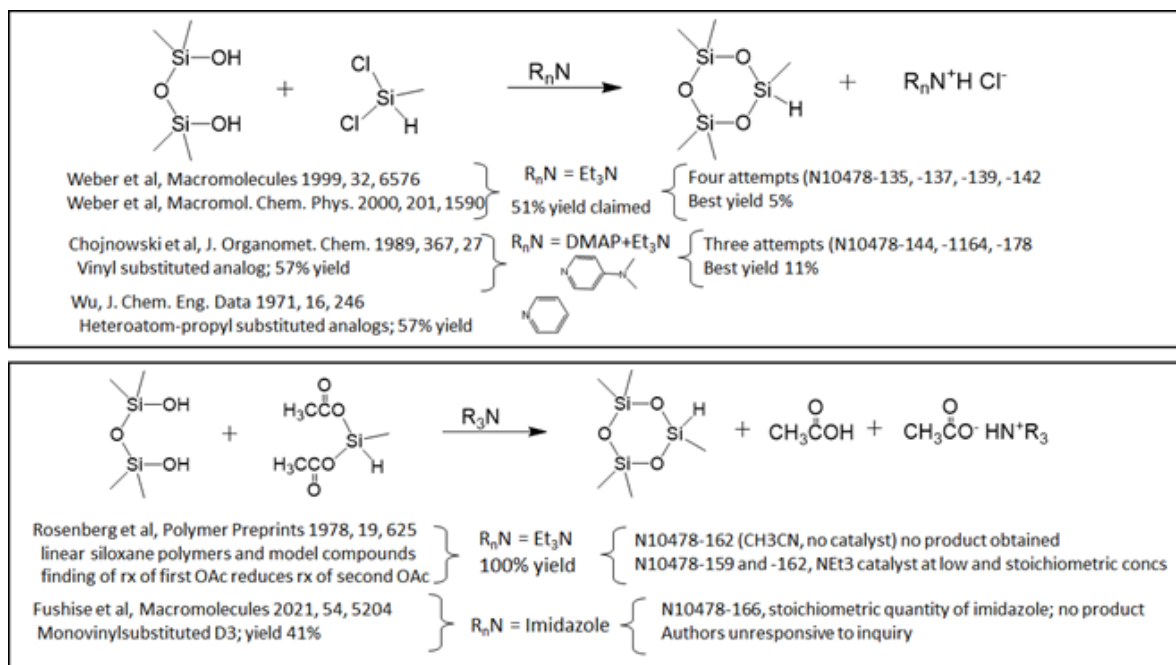


Figure SI-20. Synthetic routes toward the pentamethylcyclotrisiloxane intermediate adapted from literature.

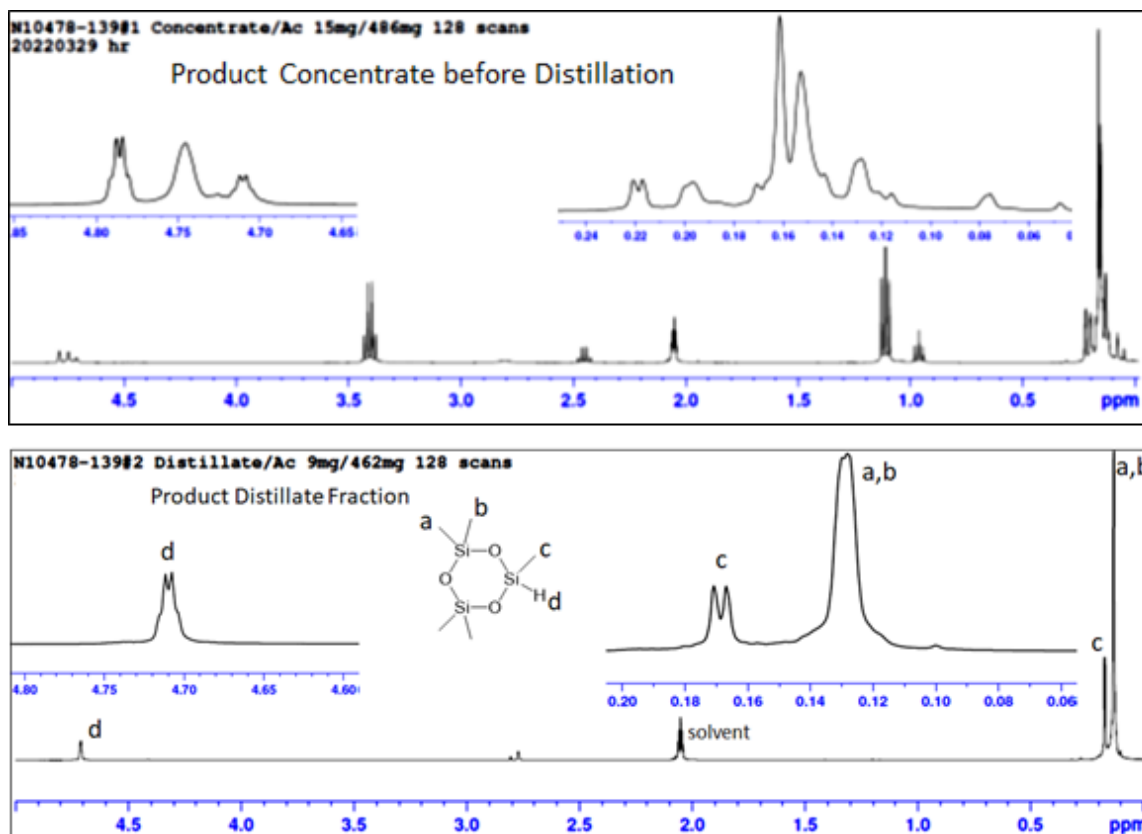
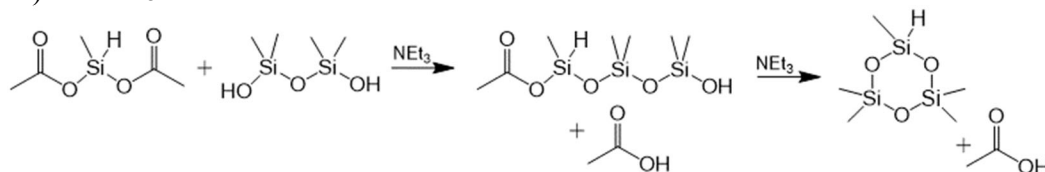


Figure SI-21. NMR spectra of product concentrate and isolated pentamethylcyclotrisiloxane product from $(\text{HOSi}(\text{CH}_3)_2)_2\text{O} + \text{Cl}_2\text{Si}(\text{H})\text{CH}_3$ reaction catalyzed by NEt_3/DMAP .

Searches undertaken for synthetic procedures to condense a Si-OH with Si-OAc functional groups to Si-O-Si with HOAc byproduct revealed some possibilities. These procedures would then be applied to the intermediates in Figure SI-18 to try to develop a synthesis of the desired pentamethylcyclotrisiloxane intermediate.

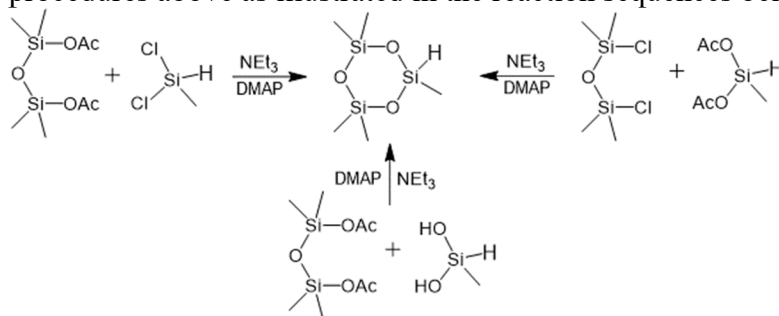
The reaction of a disiloxane-diol with silane-diacetate catalyzed by an amine appeared promising [Rosenberg and Nahlovsky 1978]. The reaction adopted to the $\text{HO}(\text{Me})_2\text{SiOSi}(\text{Me})_2\text{OH}$ and $(\text{AcO})_2\text{SiHCH}_3$ is as follows:



Two attempts were made with NMR monitoring. The reaction did not progress to ring closure. The reference states that reaction of the second acetate functionality on $(\text{AcO})_2\text{SiHCH}_3$ is significant lower after the first has reacted which would be consistent with our observation of only a small amount of non-volatile polymer residue.

Other literature references report synthesis routes to pentamethylcyclotrisiloxane analogs where the sixth substituent a different organic moiety from the desired hydrogen. A recent reference reports a synthesis route to vinyl, 3-chloropropyl and allyl functionalized pentamethylcyclotrisiloxane from reaction of the $\text{HO}(\text{Me})_2\text{SiOSi}(\text{Me})_2\text{OH}$ with $(\text{AcO})_2\text{SiRCH}_3$ ($\text{R} = \text{vinyl}$, etc.) in acetonitrile solvent with a later addition of imidazole [Fuchise et al. 2021]. Two attempts were conducted following the referenced procedure with substitution of the $(\text{AcO})_2\text{SiHCH}_3$ for the $(\text{AcO})_2\text{SiRCH}_3$ ($\text{R} = \text{vinyl}$, etc.) analog were made with an approximate yield of 2% - there being other similarly volatile byproducts to separate. The quantity of siloxane polymer residue was relatively small. A recent patent claims synthesis the condensation coupling of acyloxysilanes with silanols reagents catalyzed by zeolite (CBV780) to yield siloxane compounds in yields as high as 95% [Yamashita et al. 2018]. For the desired pentamethylcyclotrisiloxane compound in this work, this procedure with the $\text{HO}(\text{Me})_2\text{SiOSi}(\text{Me})_2\text{OH}$ with $(\text{AcO})_2\text{SiHCH}_3$ did not yield the desired product.

Three additional experiments were conducted monosilane and disiloxane roles were reversed from the procedures above as illustrated in the reaction sequences below:



The first reaction reversed the acyloxy and chloro groups on the disiloxane and monosilane reagents and the procedure of [Chojnowski and Róžga 1992] was utilized. The yield was much less than the 11% described above. The second reaction using the dichlorodisiloxane and diacyloxymethylsilane reagents did not yield detectable product, but formation of significant quantities of non-volatile polysiloxane residue were not observed. The third reaction using the somewhat unstable silanediol yielded a significant quantity of polysiloxane residue without detectable desired product.

The difficulty in synthesis of cyclotrisiloxane surfactants leads to fundamental questions as to their function stability if/when successfully synthesized. A brief examination of carbon-oxygen vs silicon-oxygen bonding and energetics is instructive. In Figure SI-22 are presented comparative bond angle and length metrics for oxygen-silicon-oxygen, oxygen-carbon-oxygen and carbon-carbon-carbon linkages followed by comparative numbers for the dimethylsiloxane structures in six-member rings, eight-membered rings and linear chains. The six-membered siloxane ring has a significant departure with respect bond angle and length compared with the eight-membered ring and linear chain. This results in significant ring strain as indicated for the trisiloxane ring and a near zero ring strain for the tetrasiloxane ring structures. The trisiloxane ring is also planar while the tetrasiloxane ring is not.

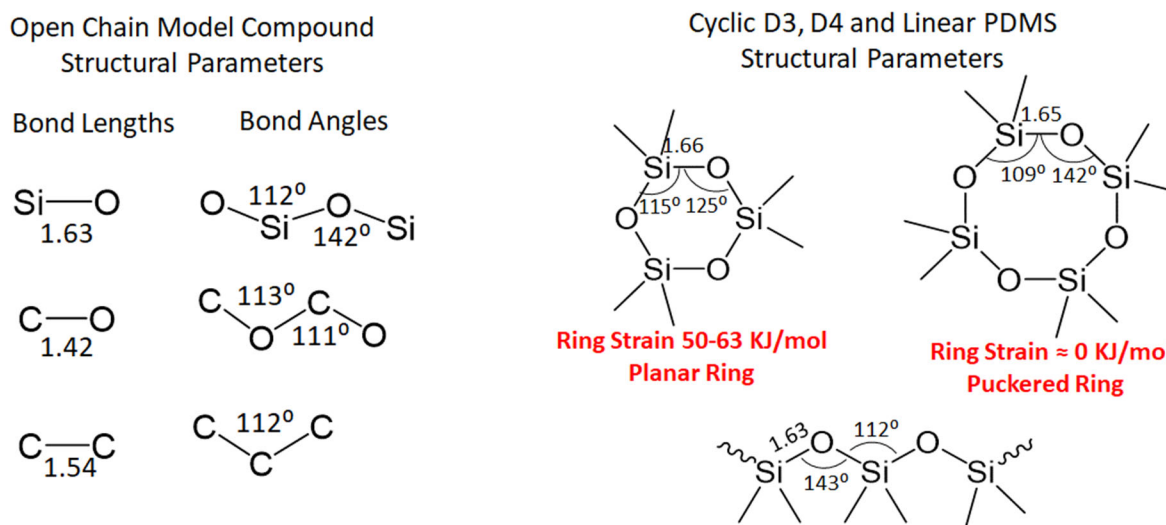


Figure SI-22. Fundamental cyclosiloxane molecular structure stability issues. Data sources: [Aggarwal and Bauer 1950; Steinfink et al. 1955; Yokoi 1957; Tashiro et al. 2007; Longenberger et al. 2017]

With respect to incorporation of these siloxane rings as tail structures in surfactants, the ring strain in the six-membered ring would be a cause of concern as to its hydrolytic stability. The hydrolysis experiment using the NMR protocol described in the experimental section of the manuscript was conducted using the hexamethylcyclotrisiloxane and the octamethylcyclotetrasiloxane as model compounds in the presence and absence the 3-(trimethylamine)propane-1-sulfonate ((CH₃)₃N⁺(CH₂)₃SO₃⁻) sulfobetaine model compound. This hydrolysis experiment is analogous to that presented for **Si3(OE)10** in Figure 50 of the manuscript. The NMR monitoring results are presented in Figure SI-23. The initial spectrum of the six membered siloxane ring compound has a single resonance at 0.150 ppm. After addition of the

$(\text{CH}_3)_3\text{N}^+(\text{CH}_2)_3\text{SO}_3^-$, this resonance is near completely diminished and three new resonances appear in less than the time needed (<0.5 hr) to obtain a spectrum following this addition. This same experiment applied to the eight membered siloxane ring compound results in the initial resonance at 0.057 ppm being shifted and broadened resonance at about 0.155 ppm and a reduction in the 0.057 ppm peak height. A new narrower resonance at 0.144 also appears, initially becomes more intense then diminishes with monitoring time. A third resonance also appears at 0.168 ppm and becomes the dominant one. These data verify that the cyclic trisiloxane structure is much more susceptible to hydrolysis, and the incorporation of such a structure in a surfactant intended for aqueous applications is not well advised. Assignment chemical structures for the hydrolysis product resonances is an item for further research. It should be noted that the water solubility of the hexamethylcyclotrisiloxane and the octamethylcyclotetrasiloxane model compounds is reported to be 1.56 ppm and 0.056 ppm respectively [Varaprath et al. 1996], and NMR protocol uses a 3mg/2g solution (1500 ppm) indicating both solutions are colloidal dispersions in the NMR experiment. The broadening of the octamethylcyclotetrasiloxane compound's resonance on addition of the ionic $(\text{CH}_3)_3\text{N}^+(\text{CH}_2)_3\text{SO}_3^-$ may correlate with this compound's lower water solubility.

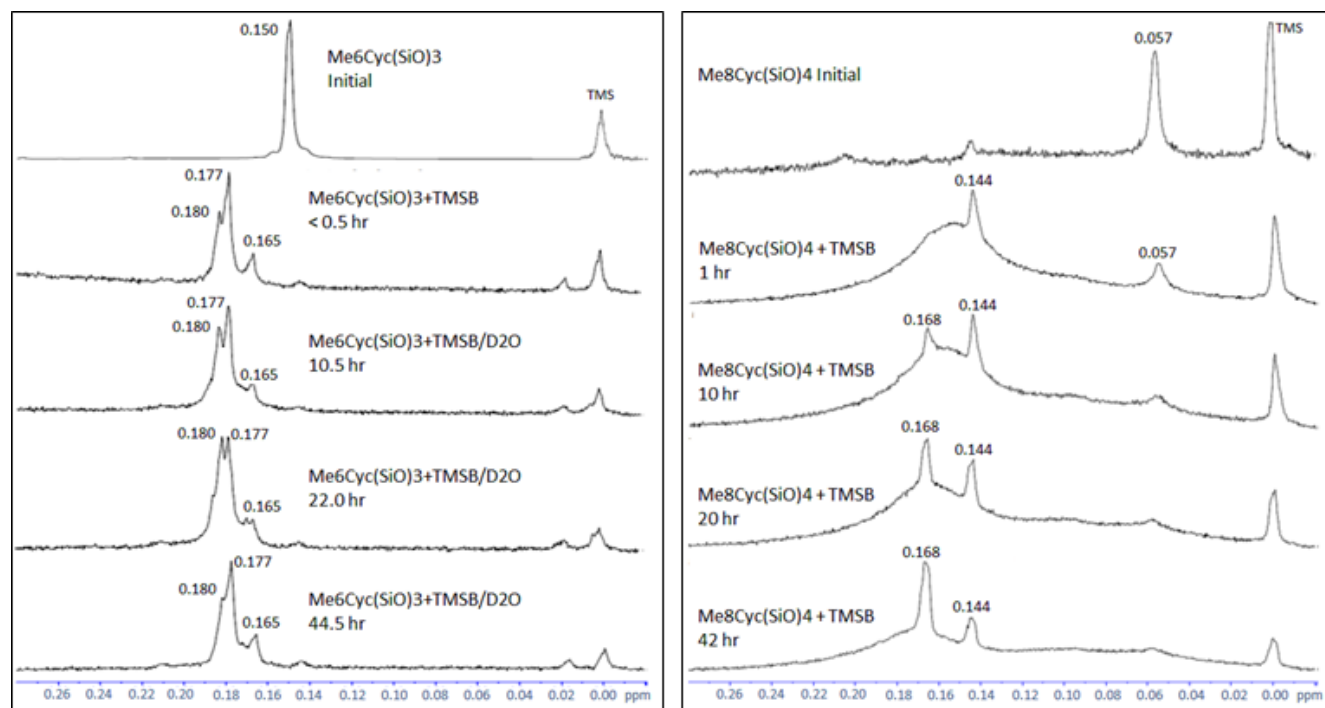


Figure SI-23. ^1H NMR spectra of the Si-CH₃ region for 1:1 weight ratio mixtures of hexamethylcyclotrisiloxane - $(\text{CH}_3)_3\text{N}^+(\text{CH}_2)_3\text{SO}_3^-$ (left) and of octamethylcyclotetrasiloxane - $(\text{CH}_3)_3\text{N}^+(\text{CH}_2)_3\text{SO}_3^-$ (right) in D_2O solution for hydrolysis monitoring according to protocol.

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