Surfactants with Organosilicate Nanostructures for Use as Fire-Fighting Foam (F^3)

SERDP Exploratory Development (SEED) Project # WP18–1519

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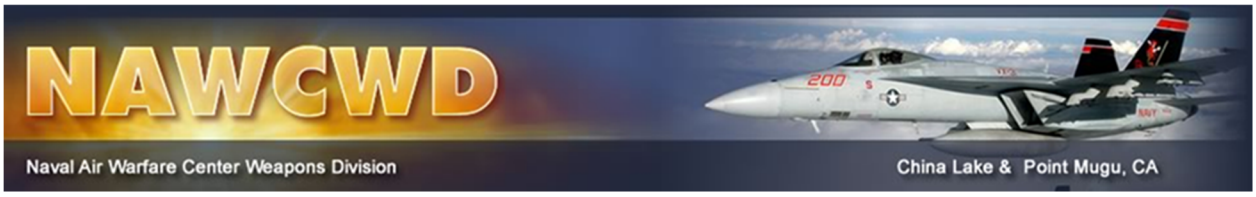
16 July 2019



REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*	2. REPORT TYPE	3. DATES COVERED *(From - To)*
03/26/2019	Technical Report	03-13-2018 - 09-30-2019

4. TITLE AND SUBTITLE
Surfactants with organosilicate nanostructures for use as fire-fighting foam (F3)

5a. CONTRACT NUMBER
W74RDV80725748

5b. GRANT NUMBER
none available

5c. PROGRAM ELEMENT NUMBER
3060716D8Z

6. AUTHOR(S)
Matthew C Davis, M. Joseph Roberts, Erik D Tolmachoff, Eric S Sievert, Ramagopal Ananth and Arthur W Snow

5d. PROJECT NUMBER
WP18-1519

5e. TASK NUMBER
none available

5f. WORK UNIT NUMBER
none available

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
NAWCWD, Code 4F0000D, 1900 N. Knox Rd., Stop 6303
China Lake, CA 93555-6106

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Strategic Environmental Research and Development Program (SERDP)
4800 Mark Center Drive
Suite 16F16
Alexandria, Virginia 22350-3605

10. SPONSOR/MONITOR'S ACRONYM(S)
SERDP

11. SPONSOR/MONITOR'S REPORT NUMBER(S)
none available

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release distribution is unlimited

13. SUPPLEMENTARY NOTES
none available

14. ABSTRACT
The objective of this project was to synthesize and/or identify fluorine-free materials to replace perfluoroalkyl surfactants in fire-fighting foams. Polyhedral oligosilsesquioxanes are thermally stable silicate materials that could be made into surfactants by asymmetric attachment of poly(ethylene)glycol 'tails' to increase water solubility. Aminopropylsiloxanes were another platform that could be chemically modified by salt formation or quaternization to create fluorine-free surfactants. The surfactant properties of these new silicon-containing materials will be measured such as surface and interfacial tensions against cyclohexane, specified by MIL-F-24385F.

15. SUBJECT TERMS
AFFF, siloxane, surfactants, foam, surface tension, fire-fighting, silicon, amines, carboxylic acids, perfluorooctanesulfonate, organic synthesis, physical chemistry, optical tensiometry, NMR

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			Matthew C Davis
					19b. TELEPHONE NUMBER *(Include area code)*
U	U	U	SAR	75	760-939-0196

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List of Acronyms

AA	L-ascorbic acid
AFFF	aqueous film forming foam
APG	alkylpolyglycoside
APS	3-aminopropylmethylbis(trimethylsiloxy)silane
APS4	3-aminopropyltris(trimethylsiloxy)silane
CMC	critical micelle concentration
DoD	Department of Defense
F^3	fire-fighting foams
mN/m	millinewtons per meter
NAWCWD	Naval Air Warfare Center Weapons Division
NMR	nuclear magnetic resonance spectroscopy
NRL	Naval Research Laboratory
OTMAP	octa(tetramethylammonium)polyhedral oligomeric silsequioxane
PEG	polyethyleneglycol
PFAS	perfluorooctanesulfonate
PFOA	perfluorooctanoic acid
POSS	polyhedral oligomeric silsequioxanes
σ	surface tension
S	spreading coefficient
T	temperature
TBPOH	tetrabutylphosphonium hydroxide
THMPCl	tetrakis(hydroxymethyl)phosphonium chloride

Keywords

AFFF, siloxane, surfactants, foam, hydrocarbons, fuel, surface tension, fire, fire-fighting, silicon, silicate, amines, carboxylic acids, perfluorooctanesulfonate, organic synthesis, physical chemistry, optical tensiometry, NMR

Disclaimer

The work reported in this document was funded by the Strategic Environmental Research and Development Program (SERDP) under Weapons Systems and Platforms Project WP-2523 to the Naval Air Warfare Center China Lake. It has been subjected to the SERDP's peer and administrative reviews, including Standard Form 298, and has been approved for publication as a SERDP document. Any opinions expressed in this report are those of the project lead and do not, necessarily, reflect the official positions and policies of SERDP. Any mention of commercial products or trade names does not constitute either discouragement or recommendation of said products by SERDP.

Acknowledgements

I'd like to thank my collaborators, Joe, Erik, Eric, Gopal and Art, for their assistance in conducting experiments and collecting the various data during the project. Thanks to: Alfred Baca (NAWCWD) for use of the Attension Theta instrument, Braxton Lewis and Jeff Houff (both of Noblis) for making a poster slot available for the 2018 SERDP Symposium after the deadline was past due, Tom Groshens (NAWCWD) for assistance with the X-ray crystal structure of the APS salt, Lawrence Baldwin (NAWCWD) for maintaining our aging NMR instrument so all of the reaction products and intermediates could be characterized, Katie Hinnant (NRL) for collecting surface tension and interfacial tension measurements of APS/AA surfactant on heptane, Michelle Wade and Tom Czibovic (both of NAWCWD) for assistance in purchasing and receiving supplies and chemicals throughout the project, Dawn Frazier (NAWCWD) for managing the financial accounts of the project and Rick Raessler (Chemours) for samples of the AFFF ingredients.

Abstract

Introduction and Objectives: Perfluoroalkyl surfactants are the key ingredients in aqueous film forming foams (AFFF) which are used by the Department of Defense and others to fight hydrocarbon pool (Class B) fires. Perfluoroalkyl surfactants work extremely well for this application, however there are growing concerns about these materials because they are highly persistent in the environment and may be toxic to plants and animals or increase their risk to certain diseases. The objective of this project was to synthesize and/or identify fluorine-free materials to replace perfluoroalkyl surfactants in fire-fighting foams. The new materials will be made to operate equally well to quickly extinguish hydrocarbon pool fires. The new materials could become drop-in replacements to existing fire-fighting technology to allow the Department of Defense to continue its mission with less ecosystem impact and maintain a high degree of environmental stewardship.

Technical Approach: Silicon is the second most abundant element in the Earth's crust and so new surfactants made from this element might be environmentally-friendly materials. Polyhedral oligosilsesquioxanes are thermally stable silicate materials that could be made into surfactants by asymmetric attachment of poly(ethylene)glycol 'tails' to increase water solubility. Aminopropylsiloxanes were another platform that could be chemically modified by salt formation or quaternization to create fluorine-free surfactants. The surfactant properties of these new silicon-containing materials will be measured such as surface and interfacial tensions against cyclohexane, specified by MIL-F-24385F. Silicon-based surfactants with spreading coefficient > +3 mN/m will be tested for extinguishing small-scale hydrocarbon pool fires.

Results: An incomplete, polyhedral oligosilsesquioxane trisilanol was successfully modified with three poly(ethylene)glycol chains by a platinum-catalyzed hydrosilation reaction. The pegylated-polyhedral oligosilsesquioxane was soluble in water and its surface tension in air decreased with increasing concentration. Unfortunately, its lowest surface tension in air was only 48 mN/m at 9 weight% loading meaning it was a poor surfactant. Interfacial tension against cyclohexane was 18.5 mN/m, which calculated to a spreading coefficient of –49.8 mN/m meaning it would not spread on the surface of this hydrocarbon, and that the surfactant did not meet the mil spec requirements. The ascorbic acid salt of 3-aminopropyl-methylbis-(trimethylsiloxy)silane (APS/AA) was a better surfactant with positive spreading coefficients on both cyclohexane (+4.7 mN/m) and heptane (+0.74 mN/m). Unfortunately, foamed APS/AA was unable to extinguish a heptane pool fire even at the high delivery rate of 1500 mL/min. Quaternary ammonium salts of 3-aminopropylmethylbis(trimethylsiloxy)silane were easy to synthesize and appeared to be strong surfactants requiring further study. The derivatives of aminopropylsiloxanes are not stable in water indefinitely but decomposed fairly quickly.

Benefits: The surface tension of polyhedral oligosilsesquioxane surfactant would have to be greatly decreased to have a chance as a fire-fighting foam. This might be accomplished by decreasing the hydrocarbon content of the silicate cage. The aminopropylsiloxanes appear to be excellent lead compounds with low surface tensions. These compounds could be readily derivatized by a high throughput screen (HTS) to discover new surfactants with tailored properties for fire-fighting foams. However, favorable tensiometry measurements do not necessarily equate to a good fire-fighting foam as the aminopropylsiloxane salt demonstrated.

Executive Summary

Introduction: The triservices of the DoD use enormous quantities of highly flammable substances, particularly high vapor pressure hydrocarbon liquids (such as gasoline, diesel and jet fuel) which pose serious risks of fire. Even though personnel have excellent training with appropriate procedures and safeguards in place to minimize the risks of fire from these substances, fires can and do happen. Extinguishing such fires as fast as possible must be accomplished in order to minimize damage to infrastructure, vehicles and equipment as well as keep personnel safe from harm on ships or airfields. Fire-fighting foams (F^3) were developed to combat hydrocarbon liquid pool fires as early as 1902 and these are referred to as Class B foams. F^3 are based on surfactants (surface active agents) that can be added to water, typically at the nozzle of a hose by a mixing head inlet, which create a thick foam spray, Figure 1. The F^3 is sprayed onto the pool fire, similar to a wide blanket, and in this way the fire is covered over with a stable mass of small air-filled bubbles.

Figure 1 Navy personnel in full fire suits to fight high temperature jet fuel fire with film forming foam (AFFF).

The burning fuel is thus starved from atmospheric oxygen and is extinguished. Because the aqueous foam is composed mostly of air, it is light and able to rest on top of the hydrocarbon, for example gasoline, whose density is typically less than water (e.g. octane: d = 0.7 g / mL) but also has a very low surface tension of 20.7 mN/m, Table 1. Gasoline is a much harder fuel to form a film on than diesel on account of its lower surface tension.

Table 1 Surface tensions of various DoD hydrocarbon fuels.

FUEL	Surface tension mN/m (24 C)
Diesel	28.3
Jet	26.7
gasoline	20.7

Not all surfactants work well as F^3 and many types have been tried. The best surfactants for F^3 are the perfluorooctanesulfonate (PFOS) and perfluorooctanoic acid (PFOA) and related perfluoroalkyl brethren, whose fire-fighting applications were discovered and developed by the US Navy, Figure 2.

Figure 2 Chemical structure of perfluorooctanoic acid (PFOA), a typical ingredient that is used in AFFF concentrates that is highly effective at putting out liquid hydrocarbon fires.

These perfluoroalkyl surfactants maintain good quality foams and also have the unique property of being both hydrophobic *and* oleophobic. This means that the perfluoroalkyl surfactants are resistant to dissolve in both water and non-polar liquids such as the hydrocarbon fuels, Figure 3.

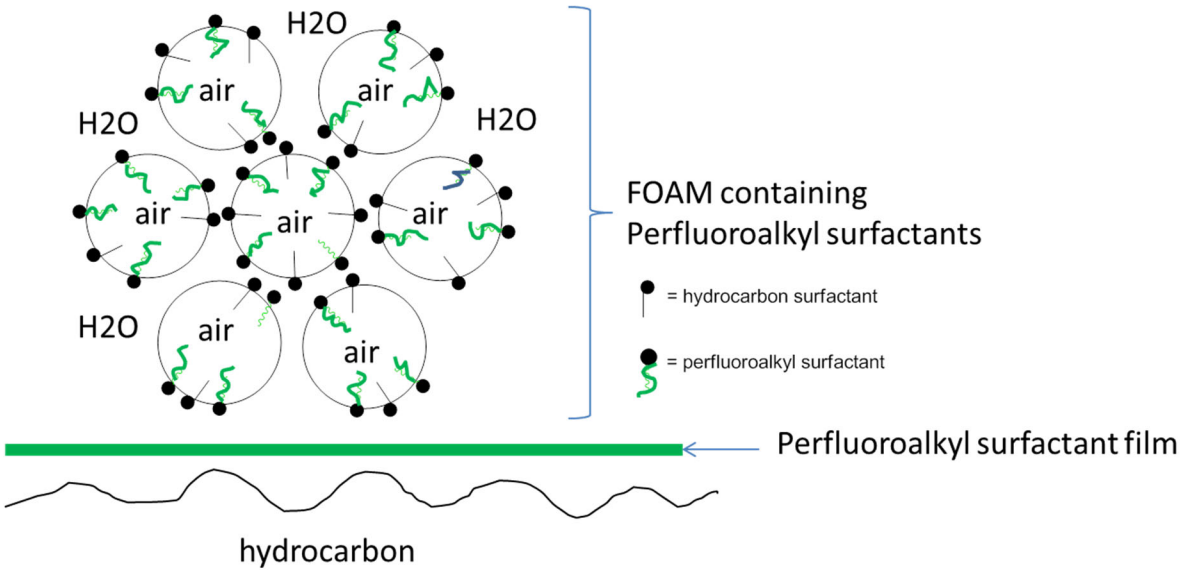


Figure 3 Perfluoroalkyl surfactant foam on surface of fuel

The specifications for AFFF have been collected in a military specification and the most important criterion of these specifications are shown in Table 2. The AFFF must be able to extinguish a 28 ft^2 pan fire of gasoline in 45 seconds and have a spreading coefficient on cyclohexane of at least 3 or greater.

Table 2 Extinction times and spreading coefficient for AFFF from MIL-F-25485F.

	Extinction Times (sec)	

Specification	1.5% Type 3 and 3% Type 6	3% Type 3 and 6% Type 6	Type 3 and Type 6
28 ft^2 gasoline pan fire	45	30	
Spreading Coefficient mN/m			≥3

Objectives: The objective of this limited-scope research project was to explore an innovative approach in using polyhedral oligomeric silsequioxanes (POSS) as well as aminoalkylsiloxanes as drop-in replacements of perfluoroalkyl surfactants found in current aqueous film forming foam (AFFF) concentrates used by Department of Defense (DoD) for fire-fighting. Foams containing the new surfactants will be formulated to extinguish small-scale, unleaded gasoline pool fire in 45 seconds or less (1.5% Type 3 and 3% Type 6) as dictated by MIL-F-24385F. In addition, the POSS and aminoalkylsiloxanes may have low acute toxicity to fish and be biodegradable according to measurements of chemical oxygen demand and biological oxygen demand of microorganisms.

Technical Approach: Silicon is the second most abundant element in the Earth's crust and so new surfactants made from this element might be environmentally-friendly materials. Polyhedral oligosilsesquioxanes (POSS) are thermally stable silicate materials that could be made into surfactants by asymmetric attachment of poly(ethylene)glycol 'tails' to increase water solubility, Figure 4. Aminopropylsiloxanes (e.g. APS) were another platform that could be chemically modified by salt formation or quaternization to create fluorine-free surfactants.

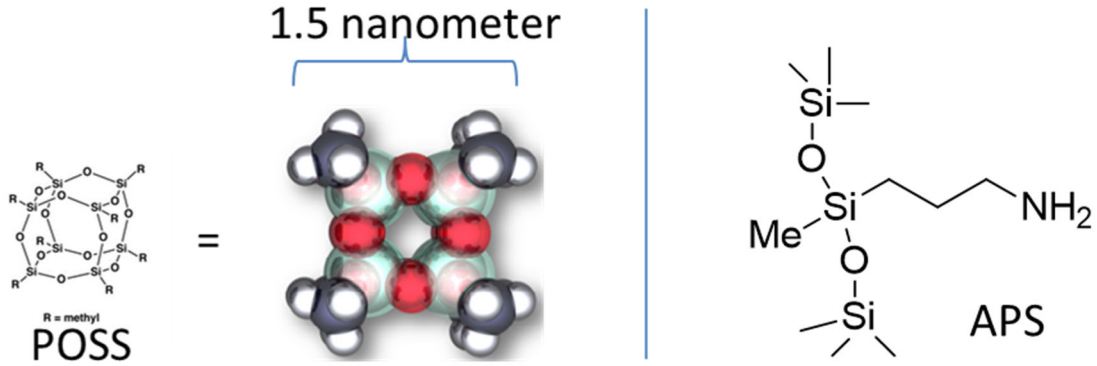


Figure 4 Chemical structures of octamethylPOSS and 3-aminopropyl-methylbis(trimethylsiloxy)silane (APS).

The surfactant properties of these new silicon-containing materials will be measured such as surface and interfacial tensions against cyclohexane, specified by MIL-F-24385F. Silicon-based surfactants with spreading coefficient > +3 mN/m will be tested for extinguishing small-scale hydrocarbon pool fires.

Results and Discussion: The commercially available heptaisobutyl POSS trisilanol, an incompletely condensed POSS cage, was reacted with dimethylchlorosilane to cap the three free

silanol corners, Figure 5. The incomplete POSS trisilylhydride was reacted with methoxy-allyl-PEG_{550} in a platinum-catalyzed hydrosilylation reaction to form the desired incomplete PEGylated POSS in modest yield.

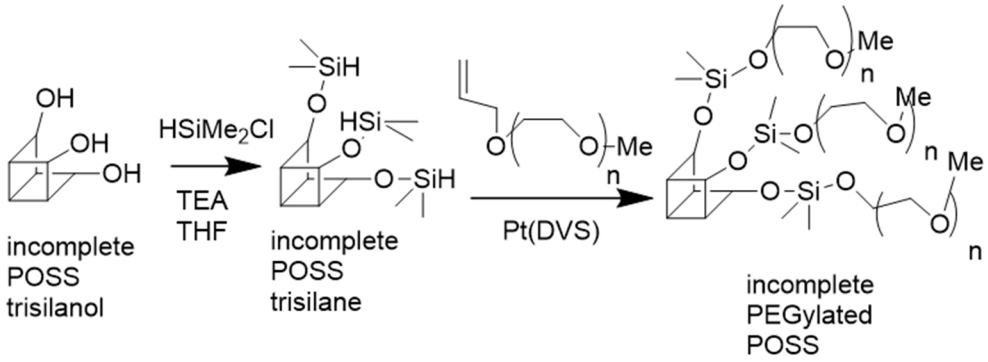


Figure 5 Chemical synthesis of a surfactant made from POSS.

The incomplete PEGylated POSS had NMR spectra consistent with the target structure and the product was water soluble with surface tension in air of 48 mN/m at 9 wt% loading which was well above the value for dilute Phos-Chek (~ 27 mN/m), an AFFF product, Figure 6.

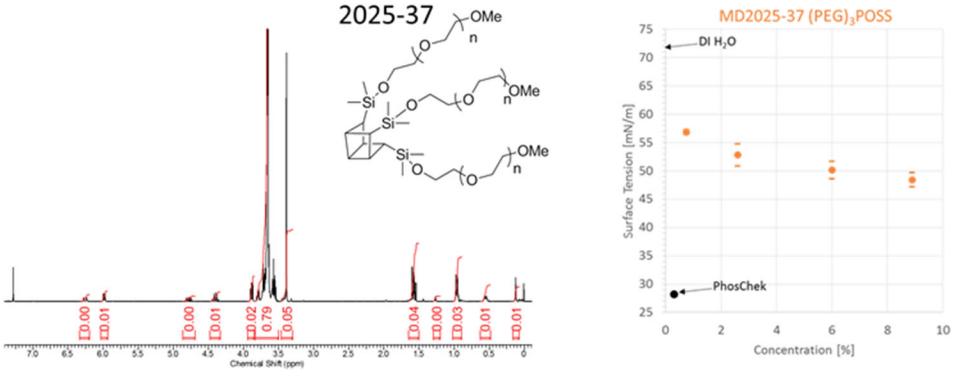


Figure 6 Proton NMR spectrum of tri(PEGylated) incomplete POSS 2025-37 (right); plot of surface tension in air of the POSS surfactant in air.

The interfacial tension of the incomplete PEGylated POSS versus cyclohexane was also measured by the pendant drop method which gave a value of 18.49 mN/m. Thus the incomplete PEGylated POSS had a spreading coefficient –49.8 mN/m on cyclohexane which is typical of non-fluorinated surfactants. We tried to improve the water solubility of the incomplete PEGylated POSS by making the methyl rather than isobutyl version but had difficulty preparing the incomplete heptamethylPOSS. Other avenues to water solubilize the POSS such as making phosphonates failed owing to the platinum-catalyzed coupling step. Also, sugar acid amides of aminoisobutylPOSS and the ascorbic acid salt of the latter were insoluble in water. Generation of surfactants by metathesis of octa(tetramethylammonium)POSS with dodecyltrimethyl-ammonium bromide appeared to work best at 1:1 ratio and gave surface tension of 37.53 mN/m, although dilute Phos-Chek was ~ 27mN/m, Figure 7.

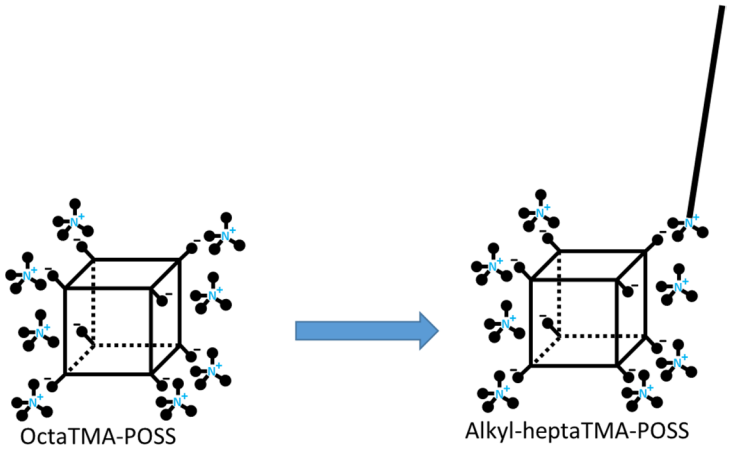
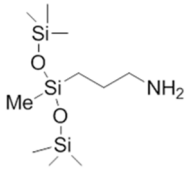


Figure 7 Cartoon showing the displacement or metathesis of one corner trimethylammonium ion by one dodecyltrimethylammonium ion.

Metathesis of octa(tetramethylammonium)POSS with phosphonium salts were also attempted since phosphorus is a known fire retardant. Reaction of OTMAP with tetrakis(hydroxymethyl)phosphonium chloride generated hydrogen gas by an undesired side reaction. With tetrabutylphosphonium hydroxide, exchange of the ammonium cations occurred and the surface tension was measured at 40 mN/m before precipitation of the complex at high concentration.



3-aminopropyl-methyl-bis (trimethylsiloxy)silane

'APS'

Studies with 3-aminopropylmethylbis(trimethylsiloxy)silane (APS) were also made whose sugar acid amide gluconic acid lactone was appeared to be a surfactant. Yet, the isomeric sugar acid amide of APS with gulonic acid lactone had poor solubility in water, Figure 8.

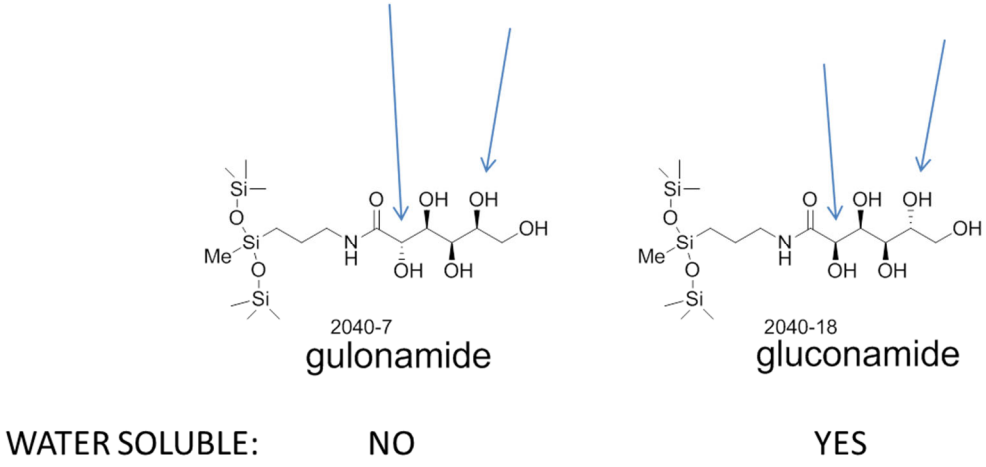


Figure 8 Remarkable stereochemical power of two hydroxy groups, and the APS sugar amide went from water soluble to water insoluble.

A stoichiometric mixture of APS and ascorbic acid made a powerful surfactant with a spreading coefficient of +4.6 mN/m on cyclohexane and +0.74 mN/m on heptane, Figure 9. Yet, this apparently good surfactant could not extinguish a heptane pool fire, Figure 10.

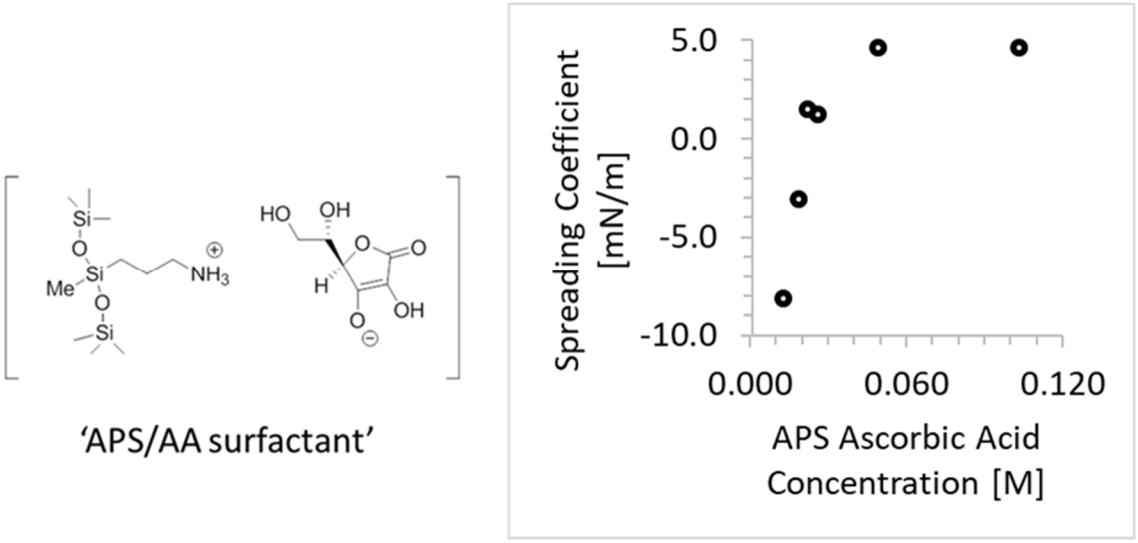


Figure 9 Salt formation between APS and AA in water (*left*); and plot of APS/AA surfactant concentration versus spreading coefficient on cyclohexane (*right*).

Figure 10 The APS/AA surfactant (*left*) could not extinguish heptane pool fire while AFFF (*right*) could do so in just 20 seconds.

The APS readily underwent quaternization with alkyl halide to form ammonium salts that were surfactants with low surface tensions but may also suffer from stability issues like the APS carboxylate surfactants, Figure 11. Apparent surfactants were also made that were structurally similar to the natural product choline by coupling new chlorosilylalkylsiloxanes to dialkylaminoethanol.

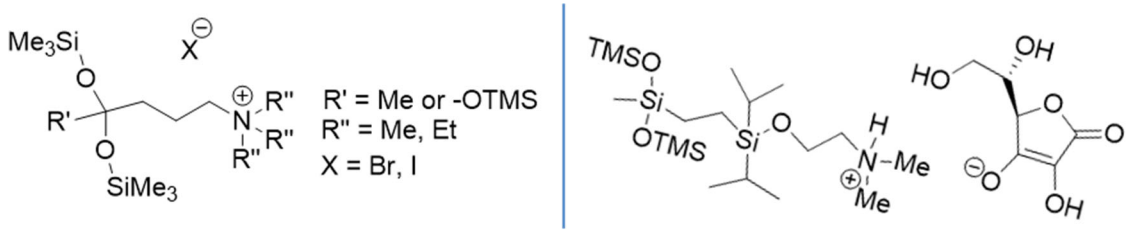
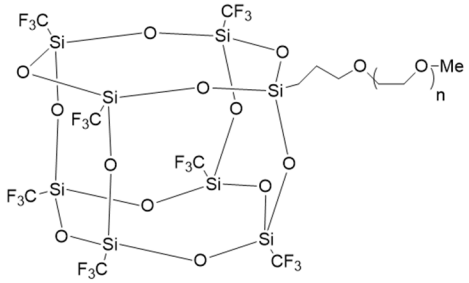
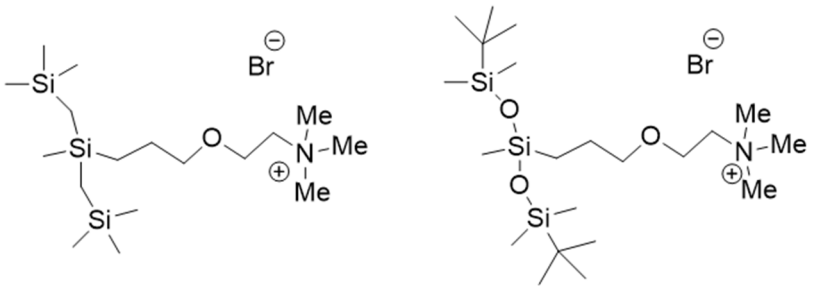


Figure 11 Surfactants made by quaternization of APS (*left*); and choline-like surfactants from a new chlorosilylalkylsiloxane reagent (*right*).

Implications for Future Research and Benefits: POSS can be made into surfactant but would need more synthetic manipulation to achieve lower surface tension. This could be achieved by decreasing the hydrophobicity of the silicate cage by starting from octamethylPOSS but the latter has solubility issue making derivatization difficult. A high-risk idea was to make a perfluorooctamethylPOSS into a surfactant. The compound would have the fluoroalkyl content 'spread out' over the molecule rather than 'concentrated' in long-chain perfluoroalkyls. Such a compound would likely have omniphobic properties similar to AFFF, but may be much more susceptible to breakdown in the environment to potentially less toxic products.



Strong surfactants could be made from stoichiometric neutralization of aminoalkylsiloxanes with simple carboxylic acids. There appears to be much synthetic possibilities with aminoalkylsiloxanes by quaternization since they have low surface and interfacial tension measurements. The aminoalkylsiloxane surfactants appear to have significant stability issues when stored in water solution, something that requires further study. However, one simple example of these, APS/AA, did not extinguish a heptane pool fire. This result was disappointing since tensiometry indicated the surfactant would form a layer. These data showed that favorable tensiometry measurements do not always equate to a good fire-fighting foam. Our NRL colleagues agree that more study should be made of the APS surfactants by making mixtures with alkylpolyglycosides, since the latter tend to have a synergistic effect. The stability issues of the siloxanes could be eliminated by making siloxane surfactants with bulky groups (e.g. *tert*-butyl) to slow down or even prevent hydrolysis, which is the suspected mode of decomposition. Or carbosilanes with structures similar to the siloxanes could be synthesized that would not hydrolyze readily.



Considering all the careful experiments and expensive instruments that are necessary for collecting tensiometry data, maybe a simple empirical test of a large number of a variety of surfactants against pool fires might be a useful method to identify new lead surfactants. There are so many more surfactants available today as opposed to the early days (1960's) of foam fire-fighting research that a cheap and fast screen might uncover surfactant phenomenon that one could not predict beforehand.

Objective

The objective of this limited-scope research project was to explore an innovative approach in using polyhedral oligomeric silsequioxanes (POSS) as well as aminoalkylsiloxanes as drop-in replacements of perfluoroalkyl surfactants found in current aqueous film forming foam (AFFF) concentrates used by Department of Defense (DoD) for fire-fighting. Foams containing the new surfactants will be formulated to extinguish small-scale, unleaded gasoline pool fire in 45 seconds or less as dictated by MIL-F-24385F. In addition, the POSS and aminoalkylsiloxanes may have low acute toxicity to fish and be biodegradable according to measurements of chemical oxygen demand and biological oxygen demand of microorganisms.

Background

The triservices of the DoD use enormous quantities of highly flammable substances, particularly high vapor pressure hydrocarbon liquids (such as gasoline, diesel and jet fuel) which pose serious risks of fire. Even though personnel have excellent training with appropriate procedures and safeguards in place to minimize the risks of fire from these substances, fires can and do happen. Extinguishing such fires as fast as possible must be accomplished in order to minimize damage to infrastructure, vehicles and equipment as well as keep personnel safe from harm on ships or airfields. Fire-fighting foams (F^3) were developed to combat hydrocarbon liquid pool fires as early as 1902 and these are referred to as Class B foams. F^3 are based on surfactants (surface active agents) that can be added to water, typically at the nozzle of a hose by a mixing head inlet, which create a thick foam spray, Figure 12. The F^3 is sprayed onto the pool fire, similar to a wide blanket, and in this way the fire is covered over with a stable mass of small air-filled bubbles.

Figure 12 Navy fire crew extinguishing hydrocarbon pool fire at a test facility with aqueous film forming foam (AFFF).

The burning fuel is thus starved from atmospheric oxygen and is extinguished. Because the aqueous foam is composed mostly of air, it is light and able to rest on top of the hydrocarbon, for example gasoline, whose density is typically less than water (e.g. octane: d = 0.7 g / mL) but also has a very low surface tension of 20.7 mN/m, Table 3. Gasoline is a much harder fuel to form a film on than diesel on account of its lower surface tension.

Table 3 Surface tensions of various DoD hydrocarbon fuels.

FUEL	Surface tension mN/m (24 C)
Diesel	28.3
Jet	26.7
gasoline	20.7

Not all surfactants work well as F^3 and many types have been tried.[1] The best surfactants for F^3 are the perfluorooctanesulfonate (PFOS), Figure 13, and perfluorooctanecarboxylate (PFOA), and related perfluoroalkyl brethren, which were discovered and developed by the US Navy, Figure 14.

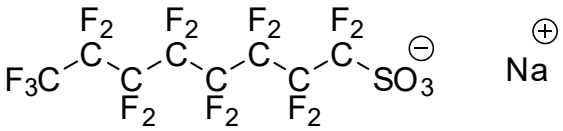


Figure 13 Chemical structure of sodium perfluorooctanesulfonate (PFOS), a typical ingredient that is used in AFFF concentrates that is highly effective at putting out liquid hydrocarbon fires.

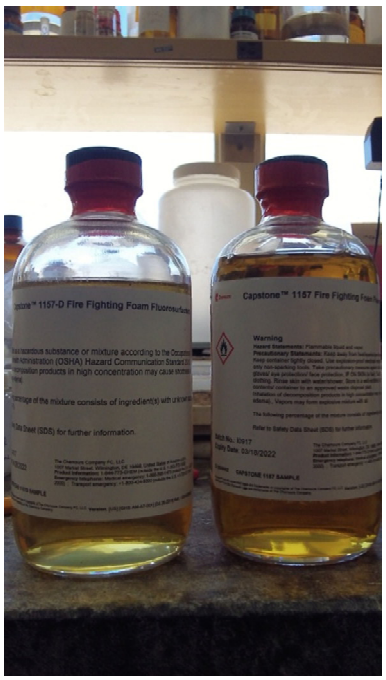


Figure 14 Samples of Capstone 1157 and 1157D courtesy of Chemours, the manufacturer of AFFF, these are the primary fluorosurfactants without additives used in many mil-spec AFFF formulations.

These perfluoroalkyl surfactants maintain good quality foams and also have the unique property of being both hydrophobic *and* oleophobic. This means that the perfluoroalkyl surfactants are

resistance to dissolve in both water and non-polar liquids such as the hydrocarbon fuels, Figure 15.

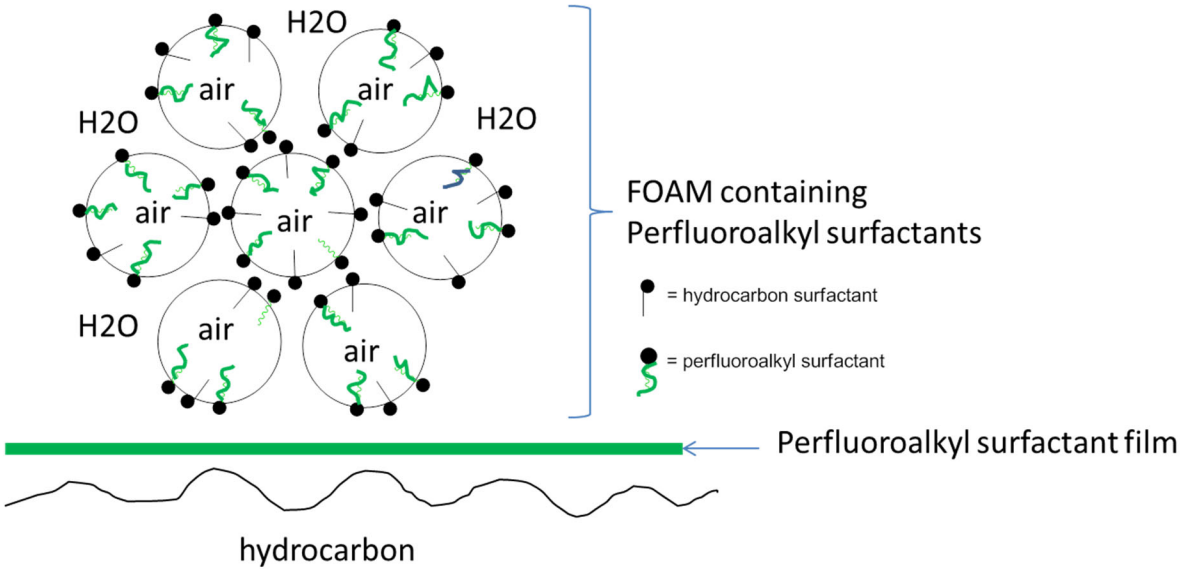


Figure 15 Perfluoroalkyl surfactant foam on surface of fuel[2]

The recent studies by Hinnant *et al.* on the properties of perfluoroalkylsulfonates are important to consider.[3] These authors hypothesize that a barrier to the vapor of the hydrocarbon pool is made because the perfluoroalkyl surfactant at the lamella interface is strongly oleophobic. These authors also demonstrated that foams made from oleophobic perfluoroalkyl surfactants have longer lifetimes than those made from hydrocarbon surfactants when placed on the surface hydrocarbon solvents.[4] What this means then is that the perfluoroalkyl surfactant F^3 when sprayed onto a burning pool fire of gasoline will not be broken down quickly when coming in contact with the flammable liquid or its vapor headspace. As the foam does break down, a film of the hydrocarbon insoluble perfluoroalkyl surfactant is left on top of the flammable liquid, covering it up and starving it of more oxygen preventing further combustion.[5] This is the reason they are called aqueous film forming foams (AFFF). Table 4 below shows that AFFF concentrates are a mixture of ingredients where the perfluoroalkyl surfactant, in this case Chemguard FS157, is just a minor (5.8%) but critical component. The other ingredients, such as non-ionic surfactants (APG = alkylpolyglycosides), help to maintain a robust foam along with other additives and solvents.

Table 4 Typical ingredients of an AFFF concentrate.

Ingredient	**Purpose**	**Percentage**
water	solvent	60.0
Corrosion inhibitor	Corrosion inhibitor	0.1

Chemguard FS-157 (fluorosurfactant)	Film former	5.8
APG	foamer	17.5
Buffer	buffer	0.1
Diethylene glycol monobutyl ether	solvent	8.7
Ethylene glycol	solvent	5.8
Urea	stabilizer	2.0

Organofluorine compounds are extemely rare in nature, in fact only a handful of fluorine containing natural products (e.g. fluoroacetic acid, fluoroacetone and fluorocitrate) have ever been isolated and reported.[6] Thus, anthropogenic perfluoroalkyl substances released into the environment are highly resistant to biodegradation as microorganism either cannot take up these substances and/or their enzymes will not recognize these substances and break them down. This has caused perfluoroalkyl substances to have accumulated in the biosphere since the 1960's to such an extent that there may be no place on the Earth's surface not contaminated (ppm level) with these materials. In fact, these issues prompted 3M Company to begin phase out manufacture of perfluoroalkyl surfactants in 2003. Although perfluoroalkyl surfactants are excellent for F^3, it may be possible to identify new F^3 made from surfactants that pose less of a burden on the environment but do the same job.

Looking at the composition of the Earth's crust, one sees that silicon is second only to oxygen in natural abundance. It was conceived that if one could instantaneously create a flexible blanket of lightweight foam made of glass and air, that would make a perfect suffocating material to throw on a gasoline pool fire which was both impervious to the hydrocarbon liquid as well as thermally stable to the heat from its flame. A step in this direction was recently reported by Vinogradov *et al*.[7] who made an F^3 composed of water soluble silicates. The technology is interesting, while a water solution of soluble sodium silicate and sodium dodecylsulfate was sprayed, some acetic acid is dosed into the solution at the nozzle, Figure 16. The change in pH neutralizes the sodium silicate causing precipitation of insoluble silicate (SiO_2) while in the air. The net result was to literally cover the burning area with a thick layer of amorphous silica gel. These researchers did not attempt to put out hydrocarbon pool fires with their technology. Silica gel is dense and heavy and so would not likely form a surface layer on a hydrocarbon pool. While their technology may be useful in certain situations such as forest fires, the cleanup of the resulting silica gel mess on airbases and ships could be difficult and even dangerous. The silica gel will not wash away with water and will have to be manually dislodged with tools. In addition, the silica gel can form dust which is a respiratory hazard (e.g. silicosis) so personnel would require protective breathing gear. The benefit of their technology is that the silica gel F^3 is non-toxic and highly biodegradable since it is only composed of a common hydrocarbon surfactant and silica gel which is essentially inert.

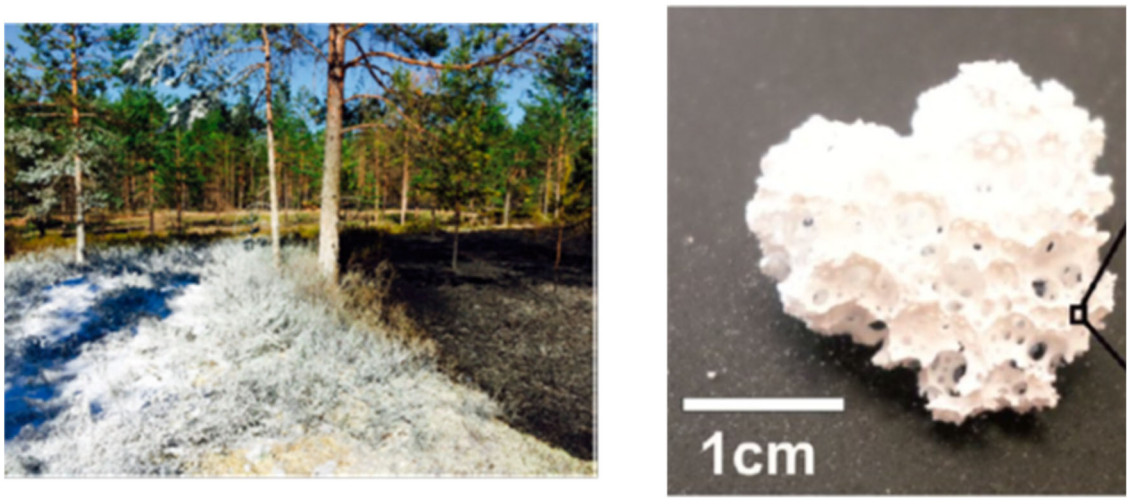


Figure 16 Vinogradov *et al.* demonstrated fire fighting with a foam that created massive quantities of silica gel to cover a fire. In brief, a solution of sodium silicate is neutralized with acetic acid creating an amorphous silica blanket; enlarged photo of the resulting silica product.

We thought a blend between the chemistries of silicon, carbon and oxygen (the organosilicates) could lead to a new class of AFFF for firefighting. Polyhedral oligomeric silsesquioxanes (POSS) are nanometer size, rigid, non-volatile and thermally robust organosilicates which have tremendous possibilities as smart materials, Figure 17.[8] POSS are a class of materials with an empirical formula of $RSiO_{1.5}$ where the R group is an organic substituent (alkyl, aryl, et cetera) or hydrogen. The chemistry of POSS has advanced tremendously since the early 1990's and has matured enough that many have become commercially available from companies such as Sigma-Aldrich, Hybrid Plastics, Phantom Plastics, Nanoshel and Gelest. For example, octamethyl-POSS is only $75 / 25 grams. Since octamethylPOSS (molecular weight = 537) is approximately 1.5 cubic nanometer, just 6 milligrams (6.7×10^{18} molecules) could theoretically form a monolayer covering 28 square feet!

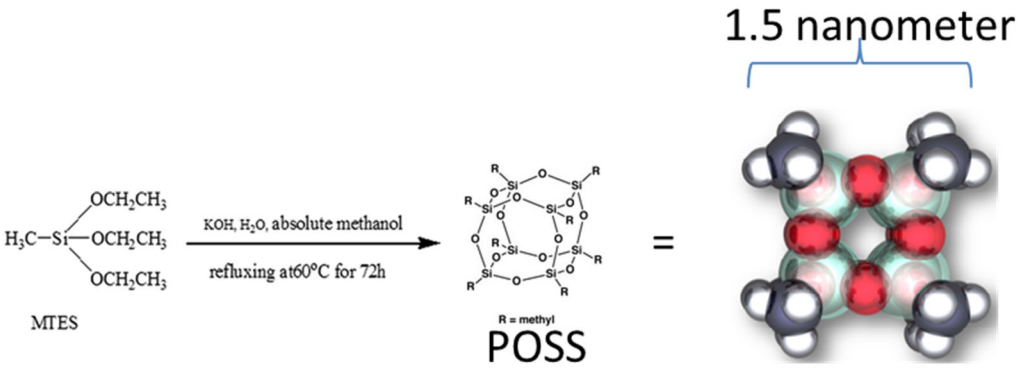


Figure 17 An example of POSS cage and how they are made, octamethylPOSS: silicon = green, oxygen = red, carbon = grey and hydrogen = silver.

POSS compounds can form a variety of random, ladder or cage-like structures, for example the Si_8-membered POSS complete cage (T_8) or Si_7 incomplete cage, Figure 18. Since the dimension of the T_8 POSS is on the order of a 1.5 cubic nanometer, POSS cages can be thought of as the smallest particles of silica (SiO_2). However, unlike simple silica, POSS cages have organic groups decorating the outside which can be tailored for specific solubility and reactivity.

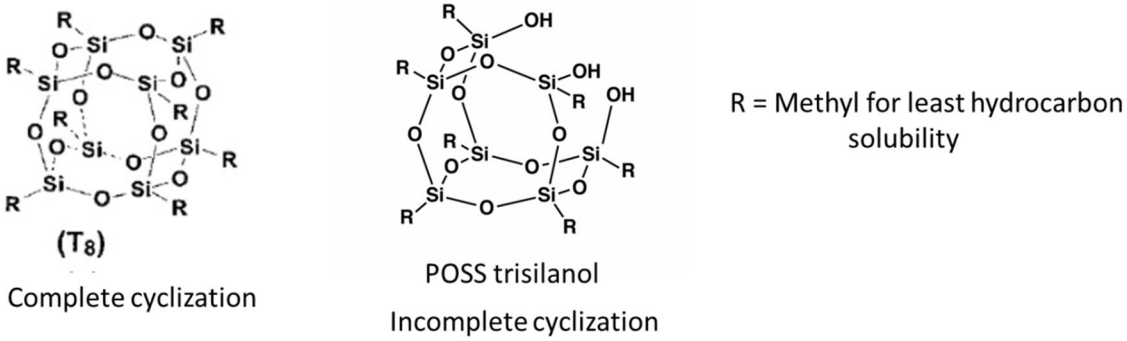


Figure 18 Complete and incomplete POSS derivatives.

During this project we planned to make novel POSS derivatives, by targeted chemical functionalization, into surface active agents (henceforth called surfactants) whereby the organosilicate cage will reside at the air-water boundary of aqueous film foams, Figure 19. A water-solubilizing 'tail' made from polyethyleneglycol (PEG) will be added by chemical synthesis to the complete POSS cage to give the material amphiphilic character, so called 'PEGylation'.[9] The POSS 'head' of the new surfactants will be designed to reside at the air-water boundary layer.

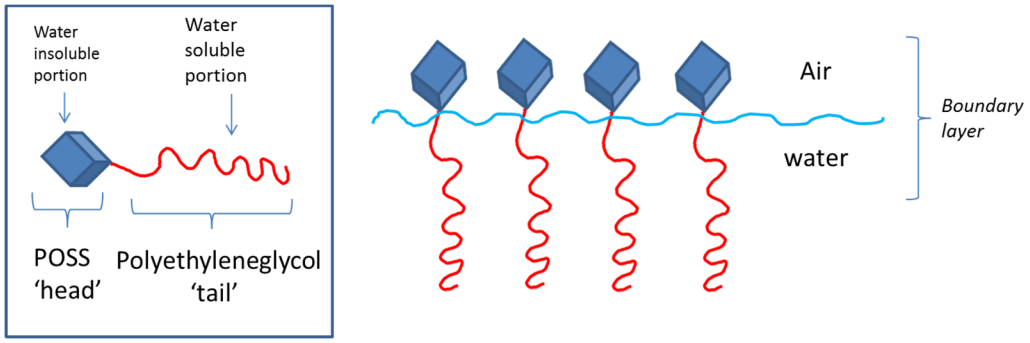


Figure 19 General concept of POSS surfactant structure

When these new POSS surfactants are mixed with the conventional ingredients that make up a typical AFFF formulation, the POSS 'heads' may create a pseudo-ceramic shell to the foam bubble lamella which may be impervious to both the heat and vapors of the hydrocarbon pool. As the resulting foam naturally breaks down, a layer of thermally stable POSS will be deposited on the flammable liquid, capping it from further combustion, Figure 20. It should be mentioned that octa(isobutyl)POSS has a density of 1.1 g/mL[10] but that will decrease when modified with a PEG substituent. In any case, perfluoroalkyl surfactants are also denser than hydrocarbon and yet they make a film on top of the hydrocarbon well enough.[11]

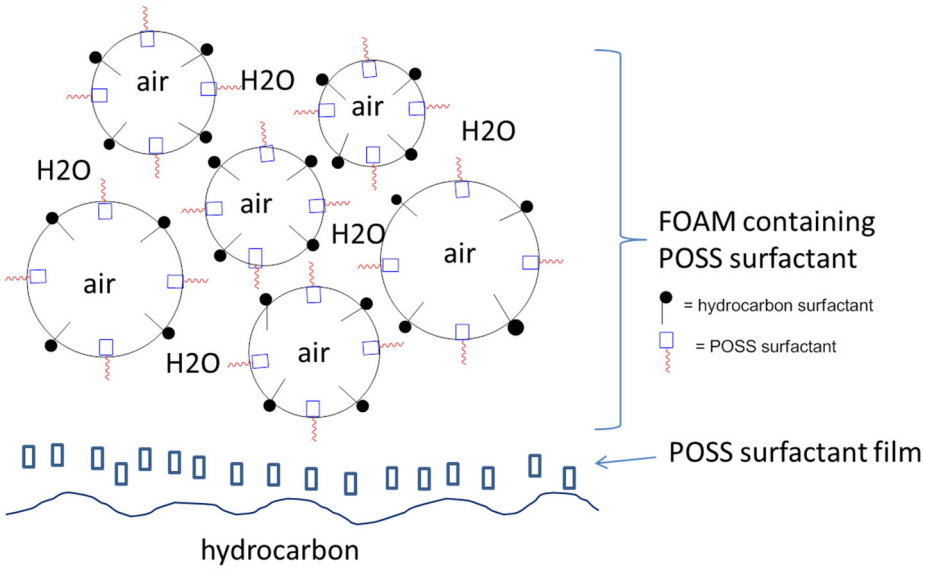


Figure 20 POSS surfactant foam on surface of fuel.

Midway through the course of the project, a PEGylated POSS compound was prepared that we measured to have a rather high surface tension in air (48 mN/n at 8.9 wt% loading). Such a high surface tension would mean the PEGylated POSS would have very little chance of spreading on the surface of cyclohexane. In addition, the synthesis of the PEGylated POSS compound was tricky to carry out owing in part to the capricious nature of the platinum-catalyzed hydrosilation step. Keeping within the purview of the research project, other derivatives of POSS were made and their surfactant properties studied. In addition, derivatives of 3-aminopropylsiloxanes were synthesized and their surfactant properties were also studied, Figure 21. The 3-aminopropylsiloxanes turned out to have much better surfactant properties than any of the POSS derivatives made in this study.

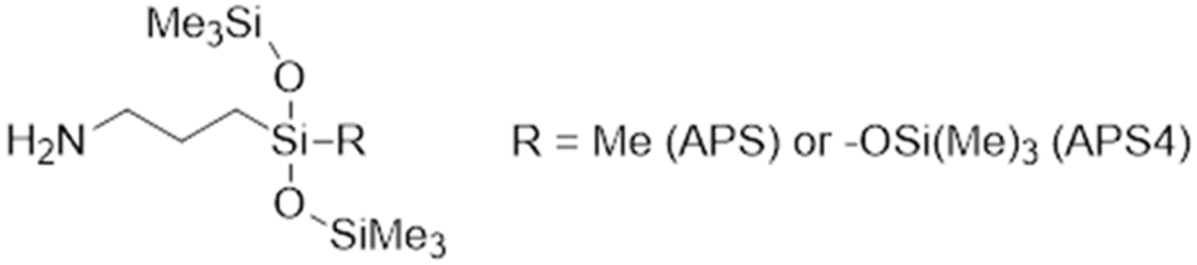


Figure 21 Structures of 3-aminopropylsiloxanes that were derivatized into surfactants during the project and their properties studied.

Materials and Methods

Chemicals and Reagents

OctaTMA POSS (OTMAP) and trisilanolisobutylPOSS were purchased from Hybrid Plastics, Hattiesburg MS. 3-Aminopropylmethylbis(trimethylsiloxy)silane (APS), 3-Aminopropyltris(trimethylsiloxy)silane (APS4), dimethylchlorosilane, diisopropylchlorosilane, vinylmethylbis(trimethylsiloxy)silane, and *tert*-butyldimethylchlorosilane were purchased from

Gelest, Morrisville PA. Glucopon® 215 was a gift from BASF. L-Ascorbic acid (AA), trichlorosilane, iodomethane, decyltrimethylammonium bromide, dodecyltrimethylammonium bromide, octyltrimethylammonium bromide, bromoethane, Karstedt's catalyst, tetrabutylphosphonium hydroxide (40 wt%) in water, tetrakis(hydroxymethyl)phosphonium chloride (80 wt%) in water, lactobionic acid, D-glucuronic acid, L-gulonic acid γ–lactone, monomethoxy-polyethylene glycol (MW 550), and all other reagents were purchased from Sigma-Aldrich, Milwaukee WI and used as received. Phos-Chek (3 and 6%) was obtained from commercial sources.

Chemical Characterization

Nuclear magnetic resonance spectroscopy used to characterize the surfactants and intermediates made during the project. The data was collected on a Bruker Ascend 500 and processed using 1D NMR Processor software from ACD Labs (Toronto).

Surface and Interfacial Tension Measurement and Spreading Coefficient

The spreading coefficient is the measure of the ability of foam solution to spread on surfaces of hydrocarbon liquids and impose a barrier to mass and heat transfer from flame to fuel. The MIL-F-24385 specification requires that the spreading coefficient (S) of the foam mixture must be greater than +3 mN/m on cyclohexane. The spreading coefficient is calculated based on the following equation:

$$S = \sigma_{fuel} - \sigma_{foam\ solution} - \sigma_{interface}$$

where S = spreading coefficient; surface tension (fuel) in air = σ_{fuel} ; surface tension (foam solution) in air = $\sigma_{foam\ solution}$; interfacial tension between fuel and foam solutions = $\sigma_{interface}$.

The surface and interfacial tension measurements of the surfactant solutions and fuels were made the hanging or pendant drop method using an Attension Theta optical tensiometer manufactured by Biolin Scientific, Figure 22. A pendant drop is formed in air or in another immiscible liquid, Figure 23.

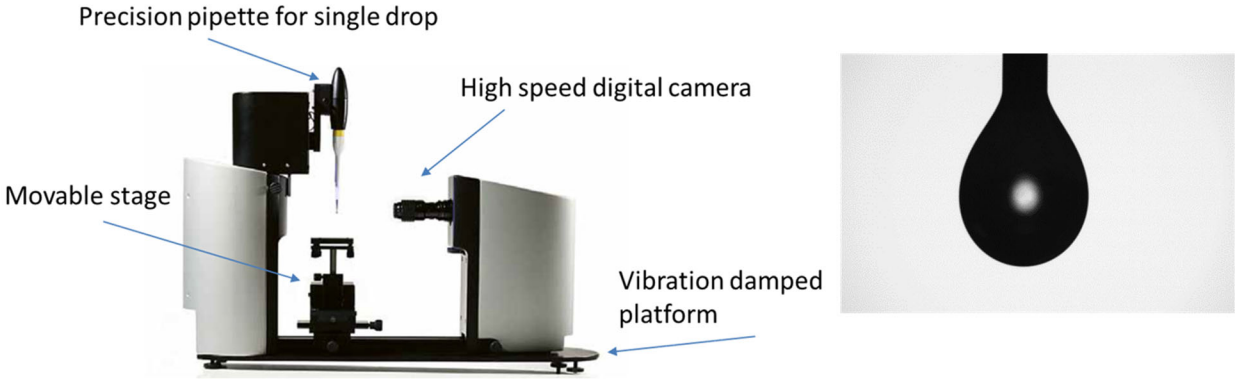


Figure 22 The Attension Theta optical tensiometer from Biolin Scientific used in measuring surface tension of surfactant solutions by the hanging drop method (*left*); and typical image of pendant drop (cyclohexane in air @ T = 23.5 °C) from Attension Theta instrument (*right*).

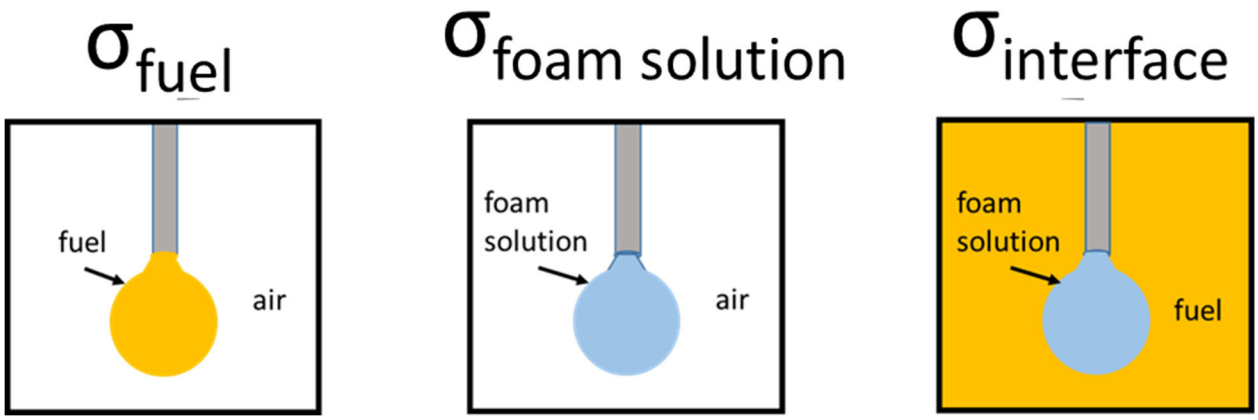


Figure 23 Cartoon representation of the key tension data by the hanging or pendant drop method, required to calculate the spreading coefficient of a surfactant for fire fighting foam.

The profile of the droplet is captured by imaging the droplet and using backlighting. Based on the Young-Laplace equations, the shape of a pendant droplet can be found theoretically.[12] By comparing the actual droplet curvature and the theoretically-predicted shape, the appropriate value for surface (interface) tension can be determined. These measurements of the curvature of pendant drops were all handled by the OneAttension software of the Attension instrument. The surface tension in air measurements were made without any special adapter, air = light phase and water (surfactant solution) = heavy phase. A liquid/liquid chamber accessory was used to measure the surface tension of the surfactant solution (heavy phase) in cyclohexane (light phase), the reference hydrocarbon fuel. Using the above described pendant drop method, the surface tension in air for the reference fuel cyclohexane was determined, Table 5. The data was consistent with literature values.

Table 5 Surface tension of the reference fuel cyclohexane by hanging drop method.

Fuel	Surface Tension in air [mN/m]	Temperature [°C]
Cyclohexane (literature)	25.240	20.0
Cyclohexane (literature)	24.650	25.0
Cyclohexane (NAWCWD)	25.473	23.5

The surface tension of diluted C_6 Phos-Chek 3% was also measured using the Attension instrument, Figure 24. The sample was 15 µL of "C_6 Phos-Chek 3%" concentrate diluted in 5 mL distilled water = ~ 0.3% solution. Data plotted from three runs; two 10-second runs (yellow, green) and one 60 second run (blue)

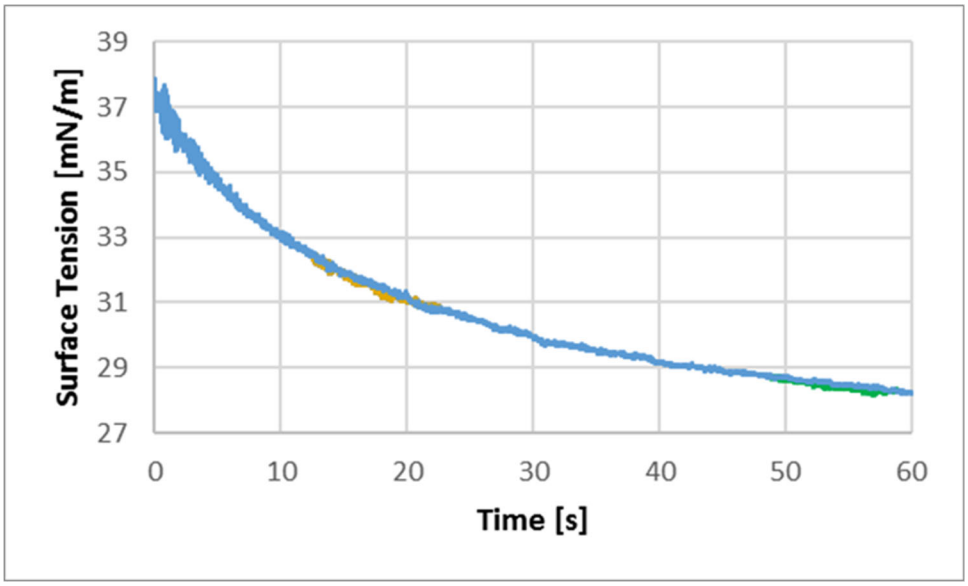


Figure 24 Surface tension of Phos-Chek in water over time by pendant drop, surface tension decreases as the water is evaporating from the drop.

By the pendant drop method, the surface tension in air for the Phos-Check was measured at 16.91 mN/m which was consistent with literature values, Table 6. The interfacial surface tension of Phos-Chek in cyclohexane was 2.41 mN/m.

Table 6 Surface tension in air for Phos-Chek reference AFFF foam.

liquid	Surface Tension [mN/m]	Standard Deviation [mN/m]	Temperature [°C]
DI H_2O (literature)	71.97		25.0
DI H_2O (NAWCWD)	73.638	1.448	24.8
Cyclohexane (literature)	24.650		25.0
Cyclohexane (NAWCWD)	25.649	0.504	23.5
PhosChek3% in air	16.910	0.116	23.5
PhosChek3% in cyclohexane	2.411	0.073	23.5

Thus, the spreading coefficient of Phos-Chek (AFFF) on cyclohexane (+6.51 mN/m) was calculated based on the above data:

$$S = 25.473 \text{ mN/m} - 16.91 \text{ mN/m} - 2.41 \text{ mN/m} = +6.51 \text{ mN/m}$$

Thus, surfactants with a *positive* spreading coefficient on cyclohexane might be useful for fighting foam since it is an indicator the foam will spread out on the surface. Most hydrocarbon surfactants have a *negative* spreading coefficient on cyclohexane, hence are not useful for fire fighting themselves. Although, hydrocarbon surfactants are used in AFFF to increase foamability or the ability of the surfactant solution to generate foam.

Small-scale pool fire apparatus

The MIL-F-24385F specifications calls for evaluating the fire suppression foams using a 28 ft^2 pool fire of gasoline and such a test would require large quantities of surfactant. We would be synthesizing small quantities of surfactants in this project and therefore a small scale pool fire apparatus had to be constructed. The apparatus consisted of an automated, mechanical syringe pump, a 60 mL plastic syringe, connected to a three-way valve and nitrogen gas cylinder. A 3/16" Koflo static tube mixer and mass flow controller (0-500 mL/min) were used to mix the foam solution and nitrogen gas and generate and deliver foam to a 3.25" diameter pool fire, Figure 25. Gasoline was used as the hydrocarbon fuel since this was dictated in the specification.

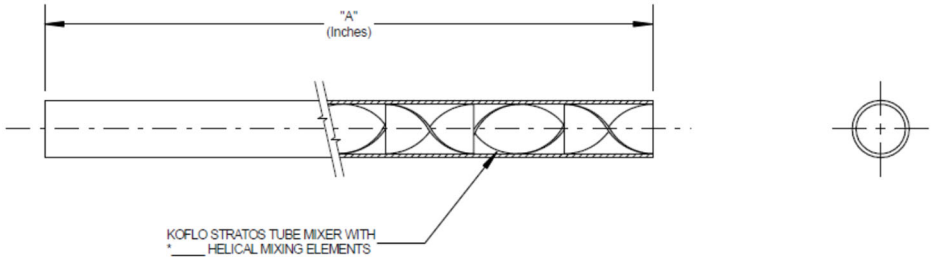


Figure 25 Koflo 3/16" tube mixer used in the small scale foam delivery apparatus.

The system was assembled and tested using tap water with dish soap and it created a good foaming mixture and a predictable and controllable expansion ratio all the way down to 3:1 or higher (mil spec called for minimum 3:1). Foam solution delivery from the syringe pump was the limiting factor at 8.6 mL/min using a 60 mL syringe. With the syringe pump maxed to 8.6 ml/min, a wide range of expansion ratios--from 3:1 to >50:1 could be handled. The flow rate from the syringe pump also provided a rough idea of how big/long a test should take, Figure 26. To summarize, using 8.6 mL/min, and assuming that the apparatus operated at the Mil Spec application rate range of 0.04-0.071 gpm/ft^2, equated to a pool fire size of about 2.5–3.25 in. Using application density of 0.036 gal/ft^2, the small fire should be extinguished by AFFF in about 30–60 seconds with about 4-8 mL of solution.

Liquid Flow Rate		Agent Application Rat			Application Density (Gal/ft2)		
					AD =	0.036	for 28 sq ft fire
517	(ml/hr)	Gallons per minute			AD =	0.033	for 50 sq ft fire
8.616667	ml/min	0.002277					
Air Flow Rate					Fire Area		
500	ml/min	MilSpec Application Rate (GPM/ft2)			0.032064	(ft2)	
		AR =	0.071	for 28 sq ft fire	0.056913	(ft2)	
		AR =	0.04	for 50 sq ft fire			
expansion ratio		Implied Fire Size, based on MilSpec Application Rates, system flow rates			Implied Application Density, based on MilSpec, system flow rates		
20							
		Fire Diameter (ft)			Gallons		
		0.202052			0.001154		
		0.269192			0.002049		
		Fire Diameter (in)			ml		
		2.424621			4.369014		
		3.230301			7.755		
					Time to extinguish seconds		
					30.42254		
					54		

Figure 26 Preliminary calculations for scaling down mil spec 28 ft^2 pan fire for research quantities of new surfactants.

The tests the apparatus were done in 3.25" and 4" pans with 1/2" of gasoline on 1" of water. All firefighting was passive. Except for one test, the nozzle was placed so that the agent was delivered to the leading edge of the pan, Figure 27. Application rates were just below those for the 50 ft^2 fire at 0.039 gpm/ft^2. Application densities for the 3.25" fires was in the mil spec range of 0.033–0.036 gpm/ft^2, Figure 28.

Figure 27 Small-scale pool fire testing apparatus for the new surfactants, gasoline test fuel in 3.25” pan.

Test	Size	Nozzle locatio	Preburn (s	Total time	Time to extinguish							
1	3.25"	leading edge	10	~45	35							
2	3.25"	leading edge	30	83	53							
4	3.25"	leading edge	30	90	60	Avg	St Dev	Application rate (GPM/ft2)			Application densiy (Gal/ft2)	
5	3.25"	leading edge	30	72	42	51.66667	9.073772	**0.03946**			**0.03398**	
3	3.25"	leading edge	40	96	56							
6	3.25"	leading edge	40	107	67	Avg	St Dev					
7	3.25"	leading edge	40	96	56	59.66667	6.350853	**0.03946**			**0.039241**	
8	4"	leading edge	30	139	109							
9	4"	leading edge	45	165	120	114.5		**0.02605**			**0.049712**	
10	3.25"	center	40	103	63							
Agent 3% AFFF												
Agent Flow Rate		8.6 ml/min										
N2 flow rate		34.4 ml/min										
Exp Ratio		5 to 1										
Pan 1 Diameter		3.25"										
Pan 2 Diameter		4"										
Pan 1 Height		~1.625"										
Pan 2 Height		~1.625"										
Pan 1 Area		0.057580295										
Pan 2 Area		0.087222222										
Pans filled with 1" water, 1/2" gasoline, 1/8" below top												

Figure 28 Results of extinguishing times from small scale pan fire using AFFF.

Results and Discussion

Synthesis of PEGylated POSS

After receiving the first batch of reagents and supplies, the chemistry to make a surfactant POSS compound was started. The commercially available heptaisobutyl POSS trisilanol, an incompletely condensed POSS cage, was reacted with dimethylchlorosilane to cap the three free silanol corners. The following reactions, Figure 29, were based on the literature method of Imoto et al.[13] In the first reaction, the trisilanol was reacted with dimethylchlorosilane to give the tris(dimethylsilylhydride)incompletePOSS structure. The reaction was initially carried out with a small quantity of the heptaisobutyl POSS trisilanol (3.16 g). The product was shown to be what was expected by ^{1}H NMR analysis, Figure 30, and so the reaction was carried out a second time using 10X quantities of reagents. In a second silylation reaction, the heptaisobutyl POSS trisilanol was cyclized back into a complete cage by reaction with trichlorosilane, this reaction was carried out successfully on small scale (4 grams), Figure 31. Both of these reactions were quantitative.

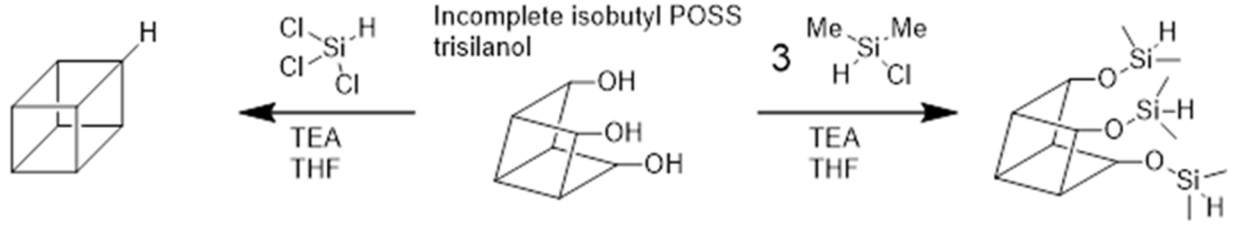


Figure 29 Silylation reactions of heptaisobutyl POSS trisilanol.

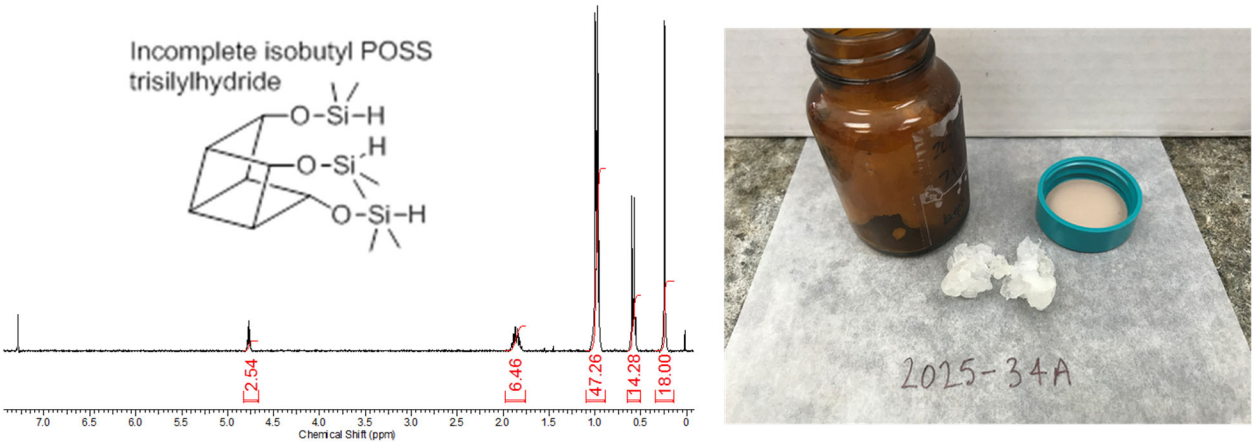


Figure 30 Proton NMR spectra of tris(dimethylsilane) derivative of incomplete POSS (2025-34), a tacky white solid.

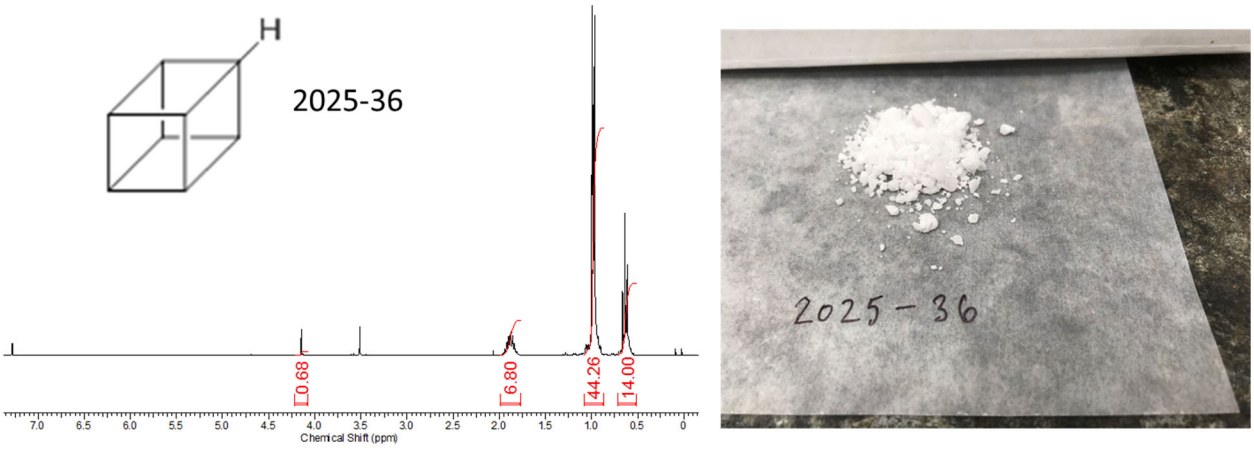


Figure 31 The completed heptaisobutylPOSS-hydride by cyclization of incomplete POSS with trichlorosilane, proton NMR was correct.

With the successful synthesis of the POSS silylhydrides, the next step was functionalization with PEG. The so-called PEGylation of the POSS is made by a silicon-carbon bond forming reaction between the silylhydride and an alkene catalyzed by platinum catalyst, specifically Karstedt's catalyst (platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane (Pt(DVS)), Figure 32. The mono-methoxyPEG purchased with a molecular weight of 550 had to be first allylated. This was carried out using sodium hydride as base and the desired product was obtained in good yield and the purity was good according to proton NMR, which showed the ratio of alkene/methyl protons was 1, Figure 33.

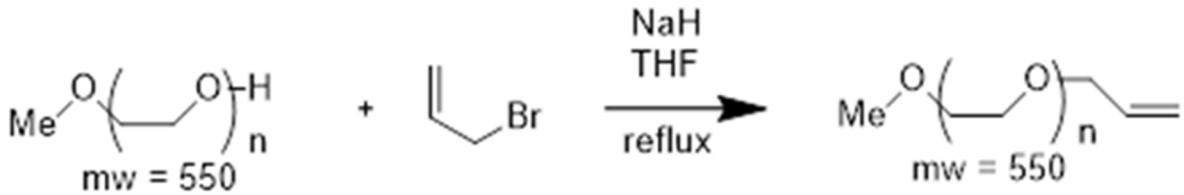


Figure 32 Allylation of mono-methoxy PEG_{550} to create a PEGylating reagent.

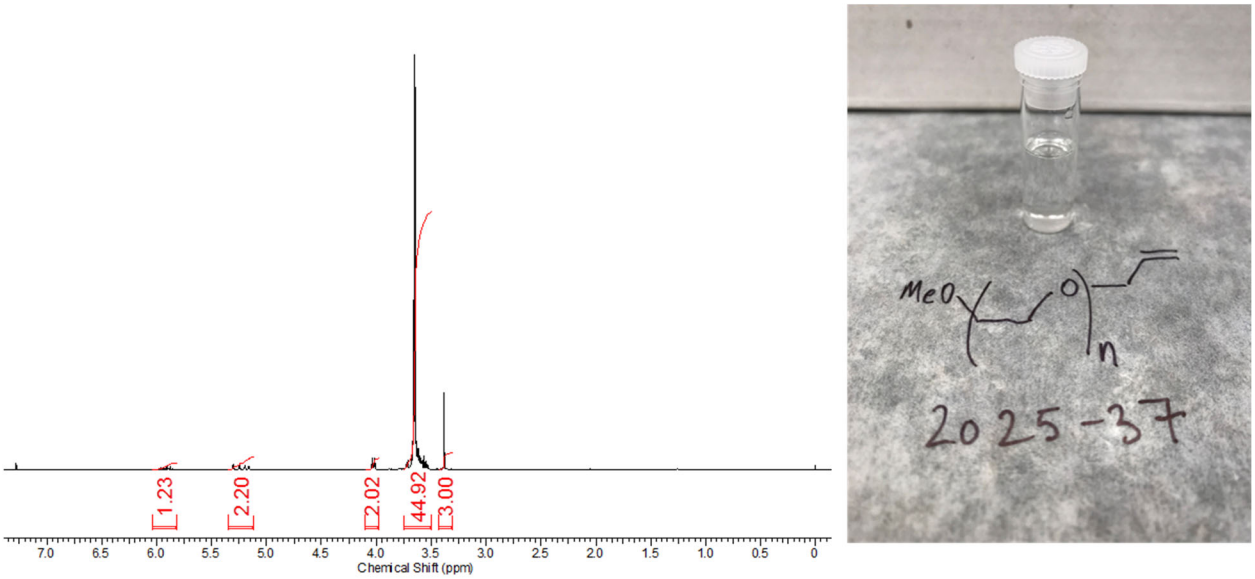


Figure 33 Proton NMR spectra of the allylated mono-methyl PEG_{550}, a colorless oily product.

A second allyl compound was synthesized, namely 3-phenoxypropene as a test piece to make certain that the coupling is done correctly since the platinum catalyst was expensive, Figure 34.

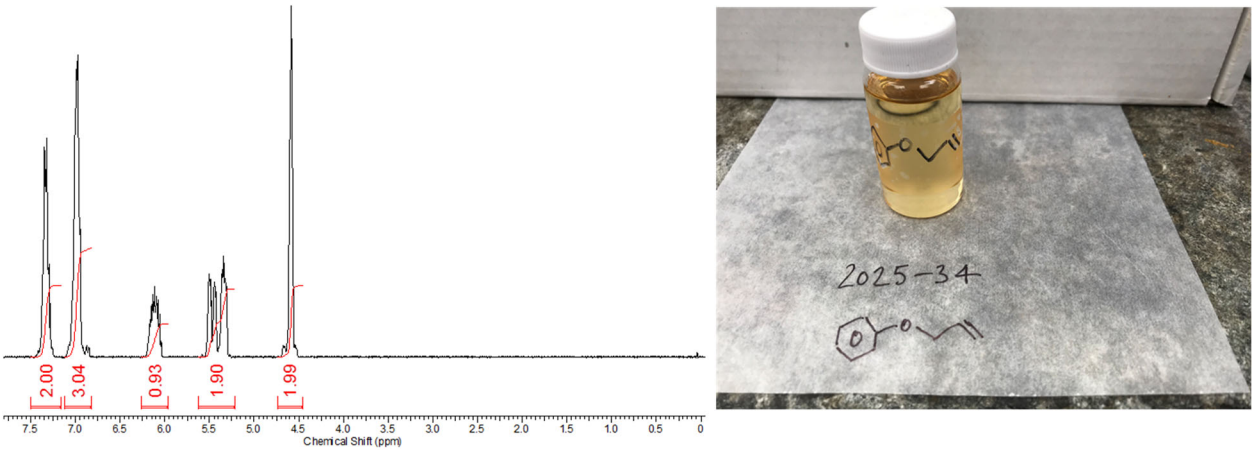


Figure 34 Proton NMR spectrum of allyl phenyl ether which was a colorless oil for testing hydrosilylation reaction.

In addition, the PEGylated POSS might be difficult to characterize fully as it may behave as a polymer. In the event, reaction of 3-phenoxypropene and the POSS silanol tris(silylhydride) and Karstedt's catalyst gave a product which appeared to have resonances in the proton NMR which were what one would expect for the coupling reaction to have occurred, Figure 35 and 36.

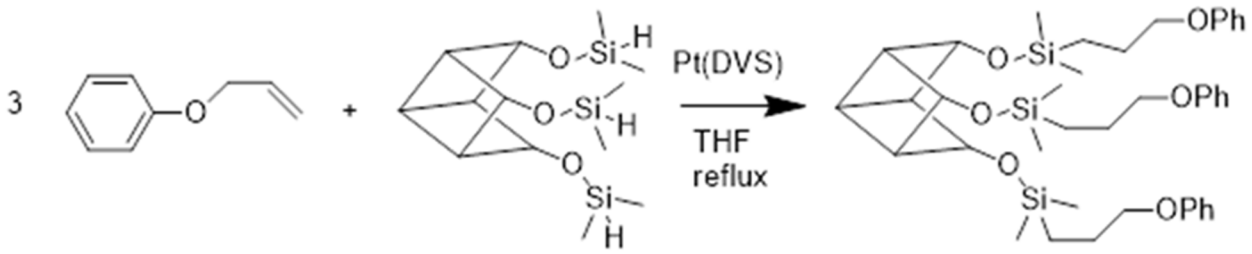


Figure 35 Successful coupling of POSS silane with test alkene.

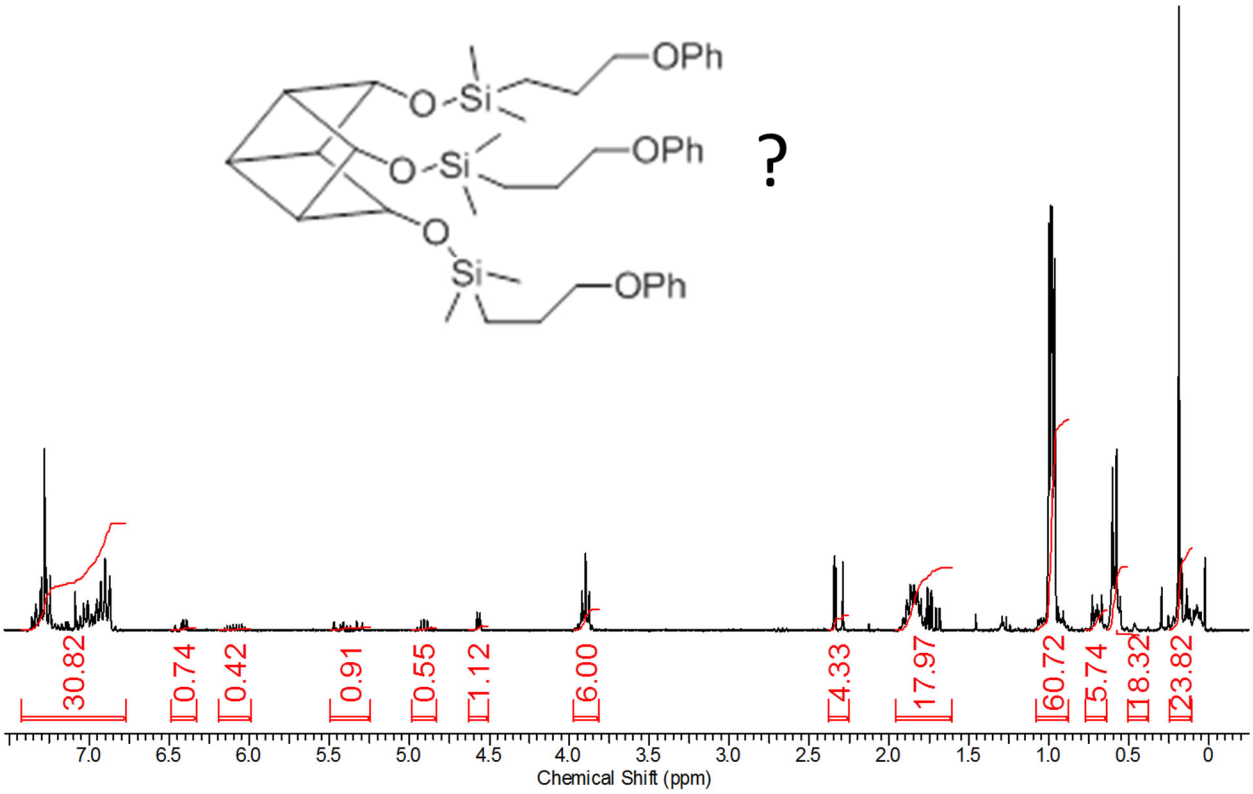


Figure 36 Proton NMR spectrum of test POSS compound coupled to allylphenyl ether.

For example, the silyl hydride peak at 4.8 ppm of the starting material was nearly all disappeared from the spectrum. In addition, the peak for the methylene groups adjacent to the oxygen of the phenoxy group moved upfield to 3.9 ppm. Also, the singlet at 0.2 ppm integrated to the expected 18 hydrogen atoms corresponding to the three dimethylsilyl moieties.

A small-scale coupling reaction of POSS trisilyl hydride with the allylPEG was set up using the same conditions. An oil was isolated after the reaction and the NMR of this product is shown below, Figure 37.

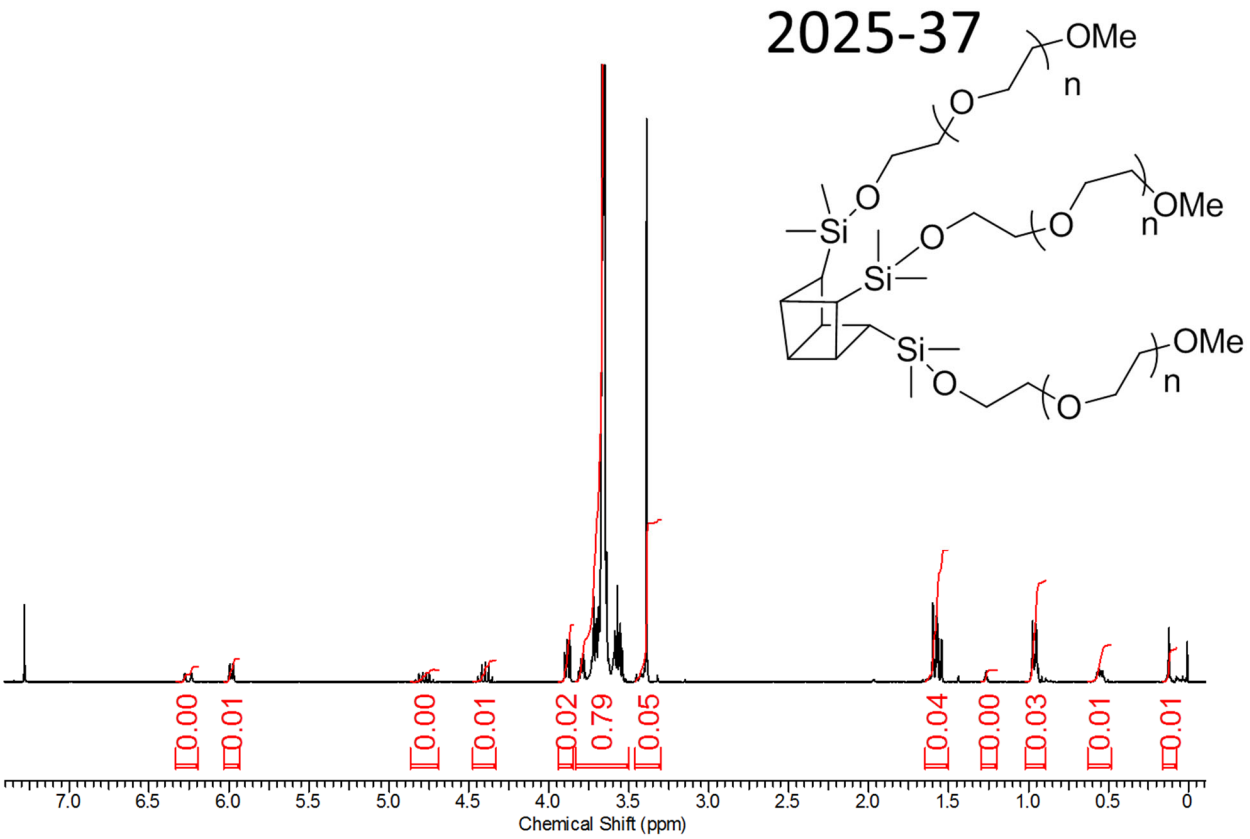


Figure 37 Proton NMR spectrum of crude tri(PEGylated) incomplete POSS 2025-37

The spectrum looked reasonable having both the PEG present as well as the POSS. Of course, that doesn't necessarily mean the coupling reaction took place. However, when a drop of the crude product was mixed with excess water, a homogenous solution was formed. This could only mean that the POSS was PEGylated and hence water soluble as previously reported by Imoto et al. Otherwise, the POSS which has very little solubility in water would have immediately precipitated which would have been immediately recognized. The surface tension in air was measured for 2025-37 by the pendant drop method, Figure 38. Even at 9 wt% loading, the 2025-37 could not decrease the surface tension below 48 mN/m, which is well above the value for Phos-Chek (~ 27 mN/m).

liquid	Surface Tension [mN/m]	Standard Deviation [mN/m]	Temperature [°C]
DI H_2O (literature)	71.97		25.0
DI H_2O (NAWCWD)	73.638	1.448	24.8
Cyclohexane (literature)	24.650		25.0
Cyclohexane (NAWCWD)	25.649	0.504	23.5
MD2025-37 $(PEG)_3$POSS 0.75 wt% in DI H_2O	56.824	0.406	24.1
MD2025-37 $(PEG)_3$POSS 2.6 wt% in DI H_2O	52.768	1.976	25.0
MD2025-37 $(PEG)_3$POSS 6.0 wt% in DI H_2O	50.111	1.564	25.0
MD2025-37 $(PEG)_3$POSS 8.9 wt% in DI H_2O	48.402	1.250	25.0

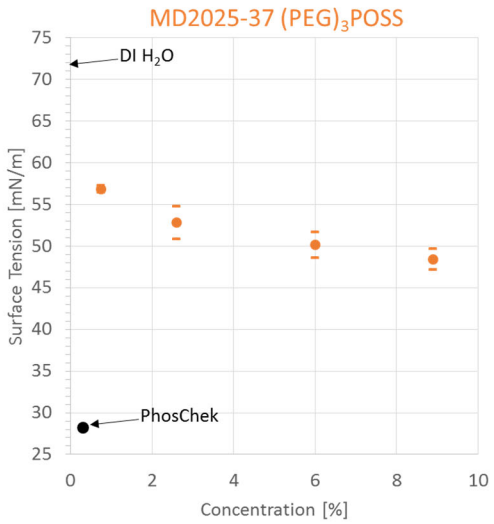


Figure 38 Surface tension in air of the PEGylated incomplete POSS 2025-37 (*left*); and plot of surface tension in air versus concentration for $(PEG)_3$POSS 2025-37 (*right*).

The interfacial tension of the (PEG)sPOSS 2025-37 versus cyclohexane was also measured by the pendant drop method which gave a value of 18.49 mN/m, Table 7.

Table 7 Interfacial surface tension of PEGylated POSS 2025-37 versus cyclohexane.

liquids	Interfacial Tension [mN/m]	Standard Deviation [mN/m]	Temperature [°C]
DI H_2O / cyclohexane (literature)	48 to 50		25.0
DI H_2O / cyclohexane (NAWCWD)	49.448	1.720	23.6
MD2025-37 $(PEG)_3$POSS 0.75 wt% in DI H_2O / cyclohexane (NAWCWD)	18.495	0.809	23.7

By using these values, the spreading coefficient for 2025-37 (PEG)3POSS 0.75 wt% in distilled water versus cyclohexane was –49.8 mN/m. This means this surfactant would have little chance of spreading out on the surface of the cyclohexane because of the negative spreading coefficient, which is typical for non-fluorinated surfactants.

$$S = 25.5 \text{ mN/m} - 56.8 \text{ mN/m} - 18.5 \text{ mN/m} = -49.8 \text{ mN/m}$$

Attempted Synthesis of MethylPOSS trisilanol

A POSS architecture with large hydrocarbon chains will have more non-polar character and hence more solubility in gasoline. Furthermore, the greater is the hydrocarbon content on the outer surface of the POSS, the more material that can be burned. So the article by Lee et al[14] was interesting because they described the synthesis of incompletely condensed POSS with methyl

substituents followed by its hydrolysis to a trisilanol that was soluble in diethyl ether and deuterochloroform, Figure 39.

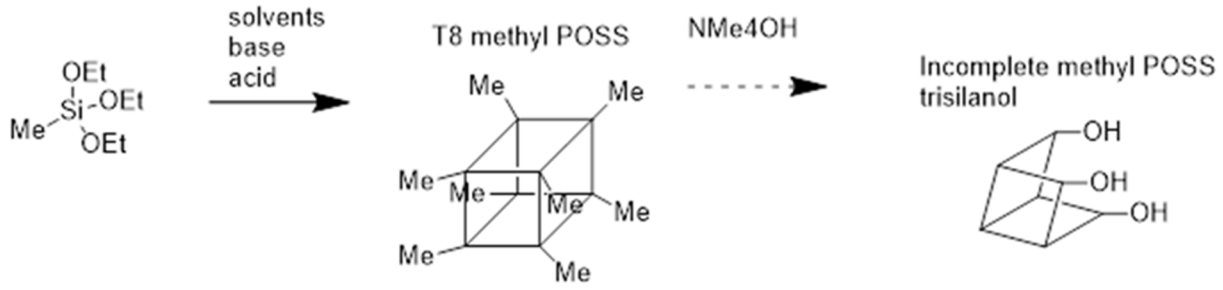


Figure 39 Synthesis octamethylPOSS and failed attempt to hydrolyze to its incomplete trisilanolPOSS.

If the latter trisilanol could be made, then it could be derivatized with PEGs to have a POSS surfactant with the least amount of combustible material on its surface, seven methyl groups (C_7H_{21}) rather than seven isobutyl groups ($C_{28}H_{63}$). OctamethylPOSS has had notoriety as being insoluble in common organic solvents.[15] Fortunately, reagents were on hand for the first reaction of this synthesis, reacting methyltriethoxysilane (100 mL) in a curious solvent mixture of: water, acetone, acetonitrile, triethylamine, formic acid, and concentrated aqueous hydrochloric acid. After refluxing 48 h, the product had precipitated and was collected, obtaining about 40 grams of the product, presumably octamethylPOSS, Figure 40. Indeed, the product was very insoluble, not even in boiling DMSO, and thus NMR could not be carried out.

Figure 40 OctamethylPOSS product from cyclization of methyltriethoxysilane.

A couple attempts were made at the hydrolysis of the octamethylPOSS to its trisilanol but the reaction mixtures did not correspond to the previously reported observations. So this avenue was put on hold to a later date.

Attempted Coupling of POSS to Phosphonates

With the modest success that was achieved in the PEGylation of POSS, some other alkenes were examined in this coupling reaction, alkenes that might also lead to POSS surfactants. From other work, phosphonic acid derivatives are known to impart excellent water solubility to polymers. In addition, nearly any forms of phosphorus are known to impart flame retarding effects to polymers. So it seemed reasonable to try to derivatize POSS with phosphonate and possibly get a surfactant behavior. Some diethyl vinylphosphonate was already available from another project. Reaction of diethyl vinylphosphonate with the POSS trisilylhydride in the same manner as the PEGylation surprisingly did not work, Figure. The product from this reaction was analyzed by proton NMR and showed that both the POSS trisilylhydride and vinyl protons remained, indicating the coupling did not occurr. It had been anticipated that the vinylphosphonate would react even better than an allyl group since the alkene was in conjugation with the electron withdrawing phosphonate ester. Thus, it was decided to try this reaction with a second phosphonate, diethyl allylphosphonate, which would be more similar to the previous successful allyl coupling reaction. Diethyl allylphosphonate was easily synthesized by the Arbuzov reaction between triethyl phosphite and allyl bromide, reagents already on hand, Figure 41.

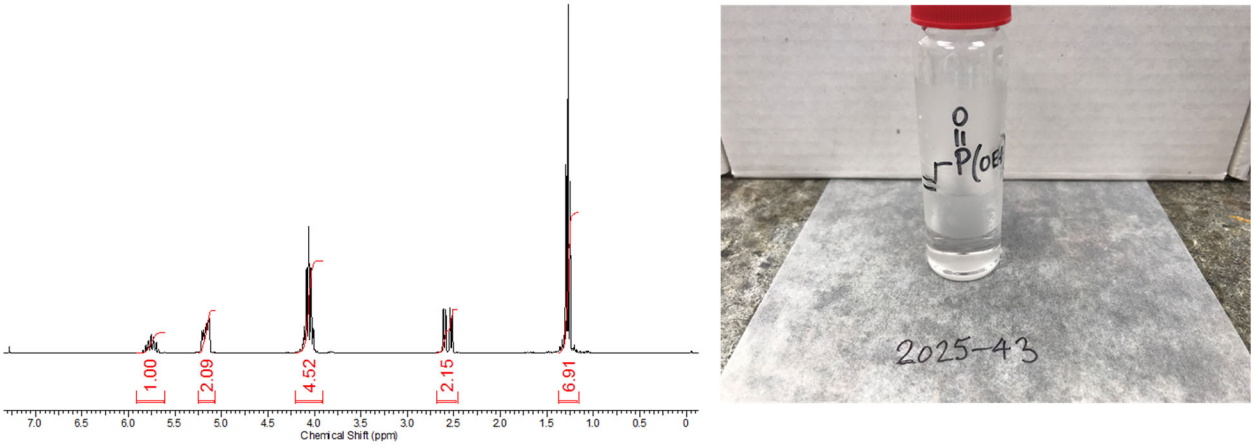


Figure 41 The diethyl allylphosphonate and its proton NMR spectrum.

The coupling reaction of diethyl allylphosphonate and the POSS trisilylhydride was set up in the same manner as the PEGylation. This reaction apparently did not work either, as the resulting product still showed the presence of both silylhydride and alkene protons in the ^{1}H NMR, Figure 42.

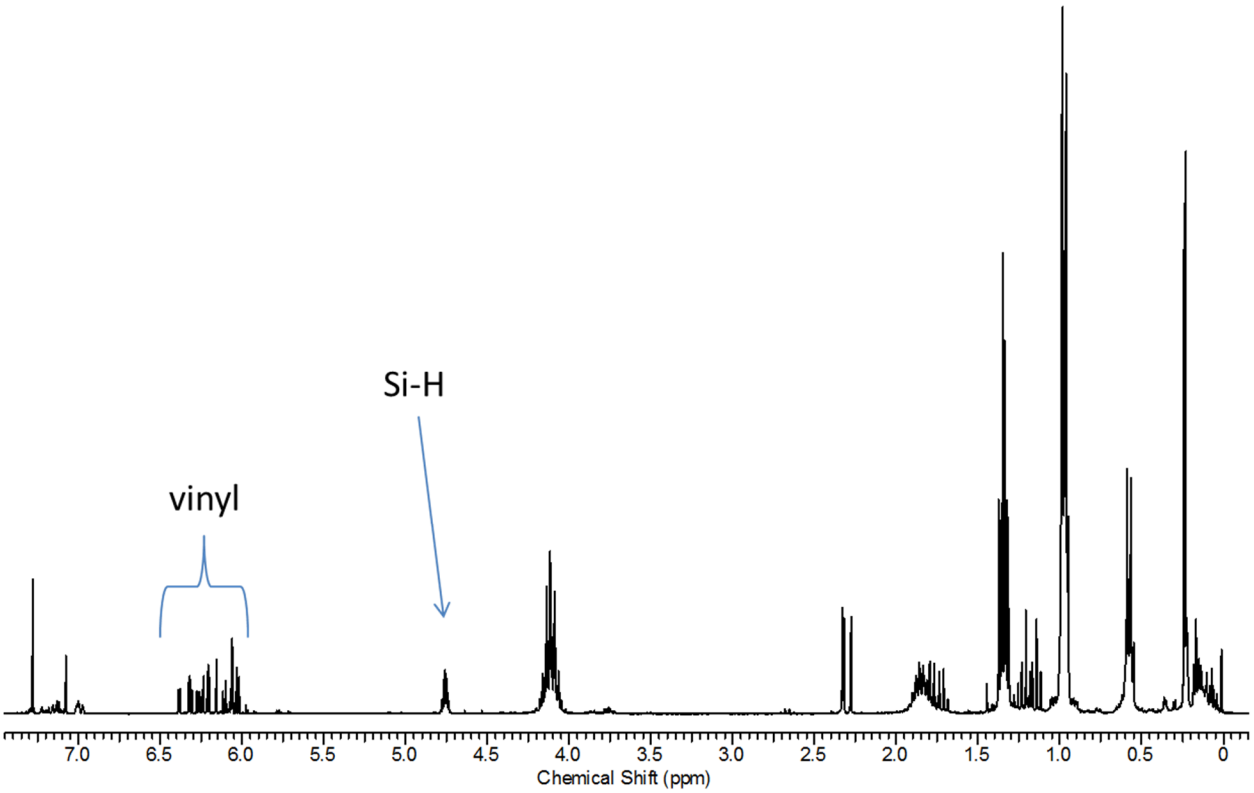


Figure 42 Proton NMR spectra of product from failed coupling of incompletePOSS-trisilylhydride and diethyl vinylphosphonate.

The literature does have some precedence for these two reactions to work,[16] why they didn't in this case remains unclear and so making these POSS derivatives was put on hold, Figure 43.

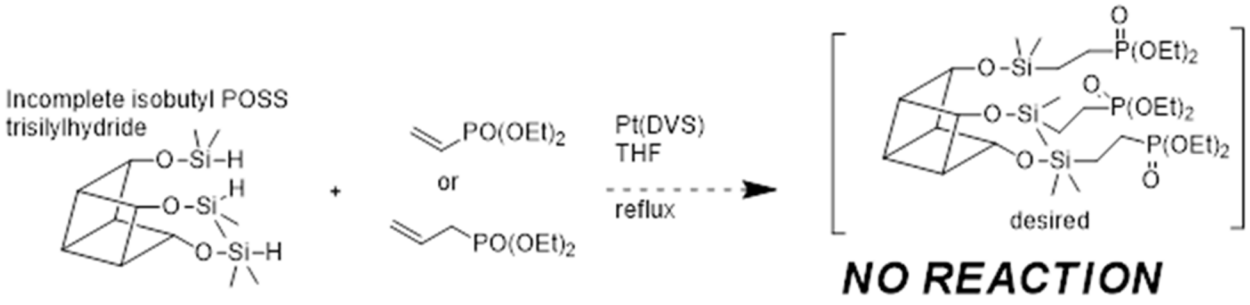


Figure 43 Unsuccessful coupling between POSS silylhydride and alkenylphosphonates

Attempted Synthesis of Surfactants from AminopropylisobutylPOSS

The palladium-catalyzed coupling reaction between the POSS silyl hydrides and an alkene appeared a little tricky although PEGylation by this method was successful on small scale. Other ways to functionalize POSS with water soluble groups to make surfactants may be useful. The work of Hetzer et al. appeared very interesting for the goals of this project. They made siloxane modified sugars, Figure 44, that not only had good surfactant properties but was also shown to have good fire suppression as well when mixed into fire fighting foam concentrates.[17] They made several other derivatives which were taught in a recent patent.[18]

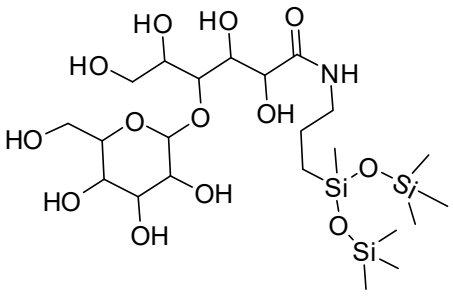


Figure 44 Hetzer et al. sugar-siloxane fire extinguishing surfactant.

So it was hypothesized that attachment of a sugar group to POSS might also be a method to make a POSS surfactant. POSS has been substituted with sugars previously, but these derivatives were those with global substitution thus making a completely water soluble POSS compound.[19] For this project, POSS that is asymmetrically substituted with sugar will likely be the only manner to have surfactant characteristic in the product. As Hetzer employed an amide linkage, it was found that aminopropylheptaisobutylPOSS can be conveniently made from the already purchased heptaisobutylPOSS trisilanol by the reaction sequence below, Figure 45.

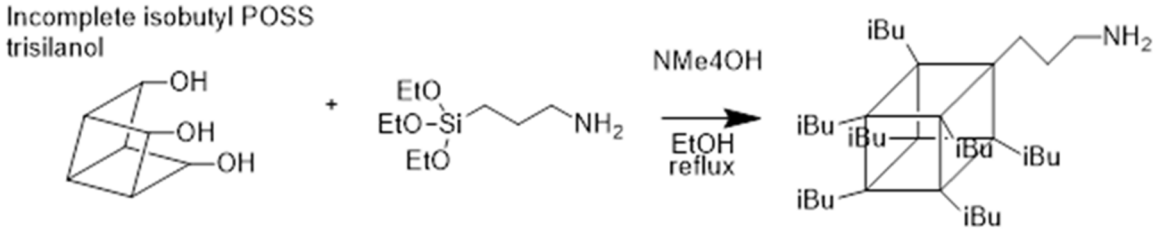


Figure 45 Synthesis of asymmetric, aminopropylhepatisobutylPOSS

This reaction was carried out starting with 20 grams of heptaisobutylPOSS trisilanol and gave 12.5 g of good quality product. This compound was reacted with L-gluconic acid lactone in a 1:1 ratio in refluxing tetrahydrofuran and methanol. The product was obtained as a white solid and the proton NMR in deuterochloroform showed the characteristic peak for amide at 7.11 ppm indicating the covalent attachment was successfully made, Figure 46 and 47. However, the compound had no solubility in water.

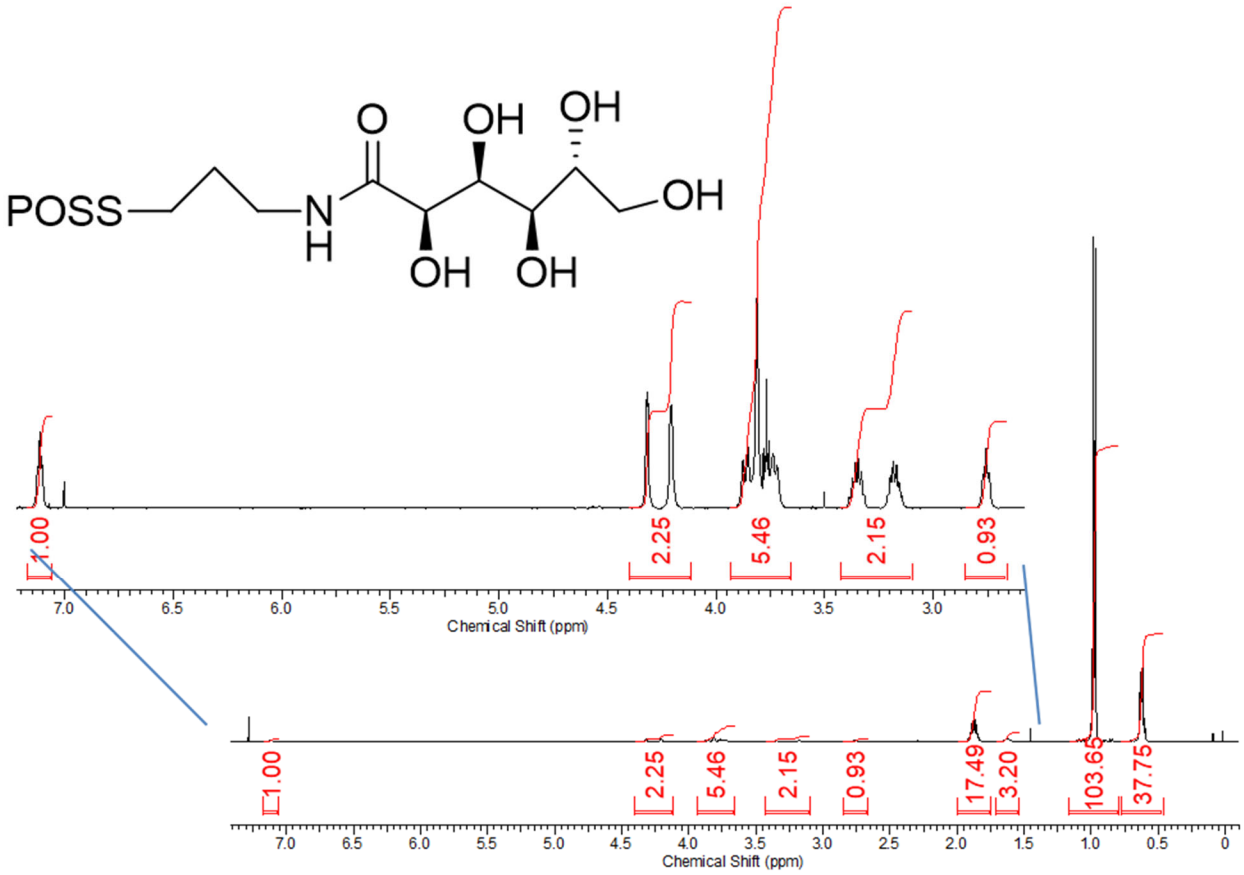


Figure 46 Proton NMR spectrum of POSS-gluconamide in $CDCl_3$ showing the characteristic amide NH signal at 7.1 ppm.

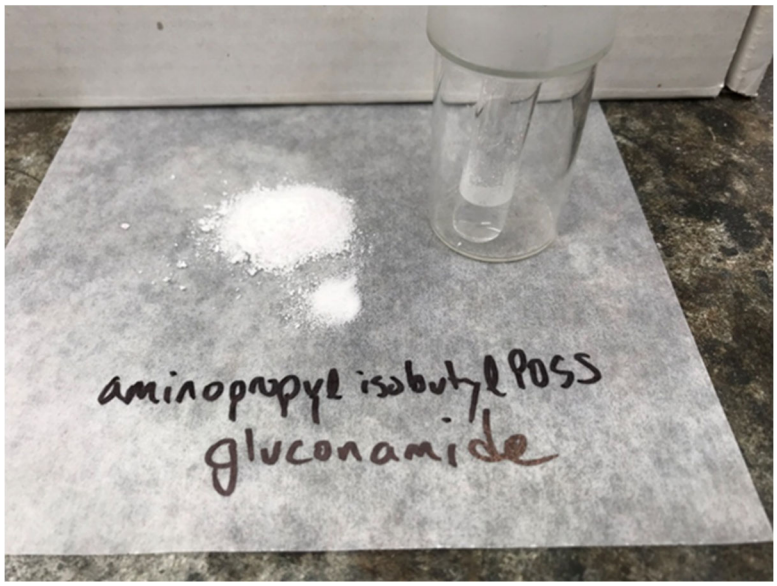


Figure 47 Covalently attached POSS-gluconamide but the product had no solubility in water an simply floated on the surface.

Also attempted was salt formation between the aminopropylheptaisobutylPOSS with L-ascorbic acid in water, however the POSS derivative did not dissolve at all, Figure 48. These experiments showed that to make the hydrophobic POSS head into a surfactant, the polar tail needs to be sufficiently long, perhaps several sugars in length, to get better water solubility of the complex.

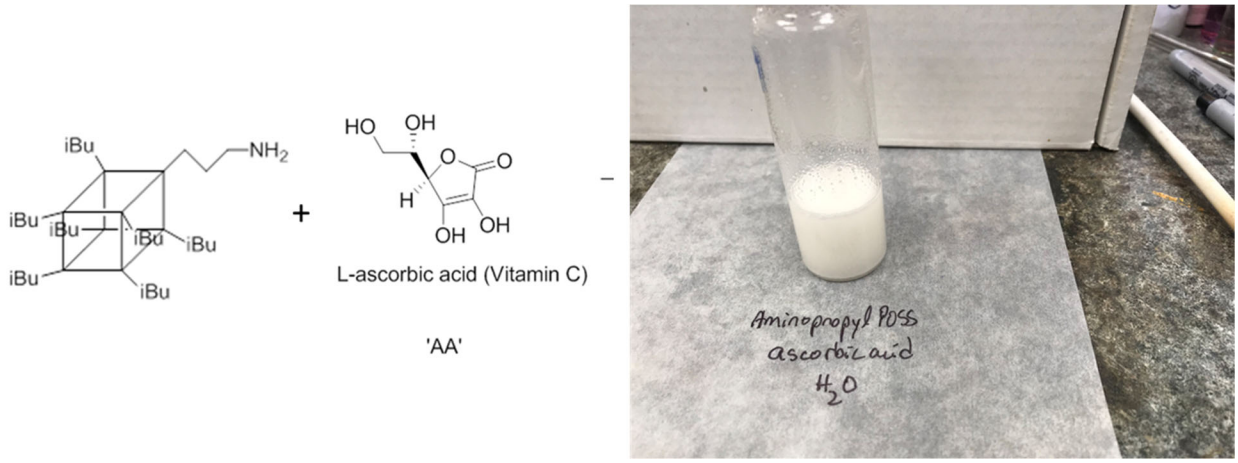


Figure 48 Attempted salt formation between aminopropylisobutylPOSS and ascorbic acid, the POSS derivative had no solubility in water even with AA present, no surfactant formed.

OctaTMA POSS Experiments

The idea here was to simplify the chemistry load of the project a bit and use an off-the-shelf POSS compound that could simply be added to a fire-fighting foam concentrate. In this way, a foam concentrate containing POSS could be studied in actual fire suppression experiments while chemistry was on-going to make the more complex POSS derivatives of the project. Thus, the availability and structure of octa(tetramethylammonium)POSS (OTMAP) appeared to fit, Figure 49. This compound is a white powder that is completely soluble in water and is a POSS cage structure without the usual hydrophobic encapsulation but has deprotonated hydroxide on its outer shell.

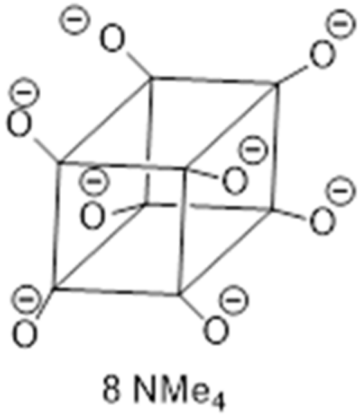


Figure 49 Chemical structure of octa(tetramethylammonium)POSS (OTMAP), a water soluble POSS derivative.

The water solubility of this material was confirmed. However, the compound was not soluble in diethylene glycol monobutyl ether, a solvent that has been used in AFFF foam concentrates. It was also shown that OTMAP readily dissolved in the 3% Phos-Check at 50% wt loading without issue. There appeared to be no detrimental effects to the solution as the OTMAP loaded foam concentrate still made copious foam when shaken by hand. Also, the same was true with a simple water solution of Alconox laboratory cleaner and OTMAP. Any change to the foam drainage time was not measured at that time. Some thermal stability analysis of OTMAP has been reported.[20] By thermal gravimetric analysis, there was about 50% mass loss of the material which corresponds to the burning off of the combustible hydrocarbon of the tetramethylammonium groups. Afterwards, there was a 50% char yield up to 600 °C since the remaining material is simply refractory silicate.

An interesting study made by Liu et al. was discovered in a literature search.[21] Here they dissolved OTMAP in water and reacted it with one molar equivalent of an unsymmetrical, tetraalkylammonium bromide salt. This reaction gave a precipitate which they believed was a metathesis product where one of the original tetramethylammonium ions was replaced with the tetraalkylammonium ion which must have lower solubility in water owing to the long chain alkyl group. We wanted to take this work a bit further and explore the reaction of OTMAP with shorter chain quaternary ammonium compounds, in order to find those that would perhaps remain in water solution as well as make suitable air-water foams. Therefore, we tried this metathesis reaction with octyl-, decyl- and dodecyl-trimethylammonium bromide, Figure 50 and 51. This reaction is somewhat capricious in that there are observational changes depending on the method of addition of the reagents as well as to the concentration at which the reaction in performed. In any event, we were able to get relatively stable solutions from the dodecyltrimethylammonium bromide reaction.

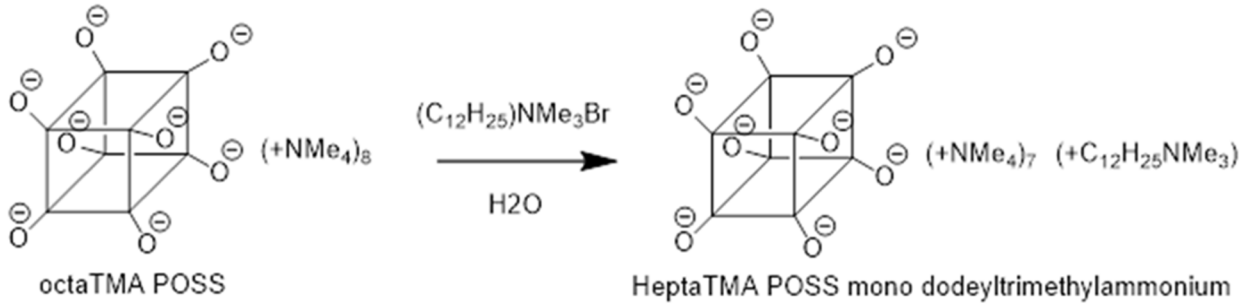


Figure 50 Metathesis reaction of OTMAP with one equivalent trimethyl(dodecyl)ammonium bromide in water.

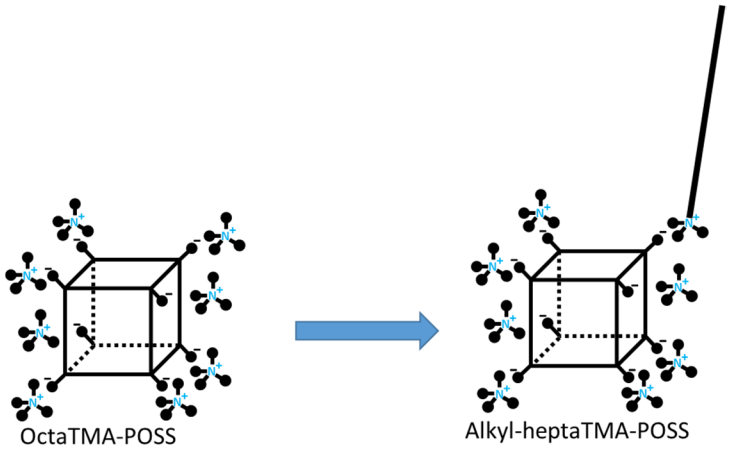


Figure 51 Cartoon showing the displacement or metathesis of one corner trimethylammonium ion by one dodecyltrimethylammonium ion.

Surface tension data in air were collected for the three metathesis products with OTMAP. In the case of octyltrimethyl ammonium bromide, there was a decrease in surface tension to 56.93 mN/m as the ratio of octyltrimethylammonium bromide was increased from 1:2 to 1:8, Figure 52. The decrease in surface tension (44.51 mN/m) was better still by mixing OTMAP and decyltrimethylammonium bromide at 1:6 ratio, respectively, which formed a stable foam, Figure 53. The lowest surface tensions came by using the dodecyltrimethylammonium bromide with OTMAP at a 1:1 ratio gave 37.53 mN/m, although Phos-Chek is ~ 27mN/m, Figures 54 and 55.

liquid	Surface Tension [mN/m]	Standard Deviation [mN/m]	Temperature [°C]
DI H_2O (literature)	71.97		25.0
DI H_2O (NAWCWD)	73.64	1.45	24.8
Cyclohexane (literature)	24.65		25.0
Cyclohexane (NAWCWD)	25.65	0.50	23.5
0.01M OctaTMA-POSS:OctylTMA-Br 1:2 molar ratio	65.31	0.42	23.7
0.01M OctaTMA-POSS:OctylTMA-Br 1:4 molar ratio	62.67	0.55	23.7
0.01M OctaTMA-POSS:OctylTMA-Br 1:8 molar ratio	56.93	0.30	23.7

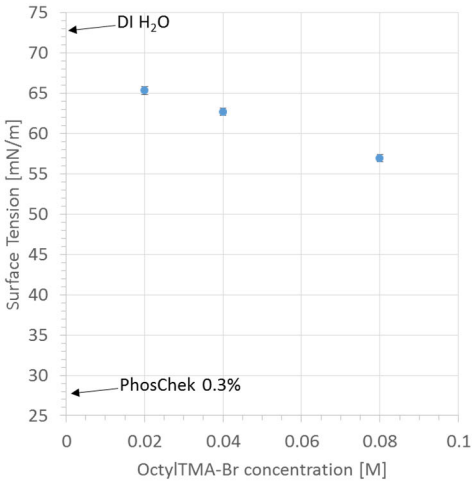


Figure 52 OctaTMA-POSS/OctylTMA-Br Mixture Surface tension Pendant Drop Method.

liquid	Surface Tension [mN/m]	Standard Deviation [mN/m]	Temperature [°C]
0.01M OctaTMA-POSS:DecylTMA-Br 1:1 molar ratio	58.29	0.38	25.4
0.01M OctaTMA-POSS:DecylTMA-Br 1:4 molar ratio	46.81	0.39	25.4
0.01M OctaTMA-POSS:DecylTMA-Br 1:6 molar ratio	44.51	0.27	25.4

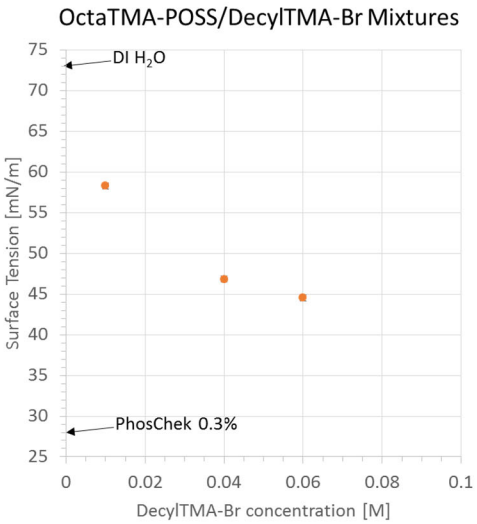


Figure 53 OctaTMA-POSS/DecylTMA-Br Mixture Surface tension Pendant Drop Method

OctaTMA-POSS concentration, M	DodecylTMA-Br concentration, M	Surface Tension [mN/m]	Standard Deviation [mN/m]	Temperature [°C]
0.004	0.008	47.03	1.01	24.8
0.001	0.014	34.10	1.62	24.8
0.031	0.031	37.53	1.19	24.4

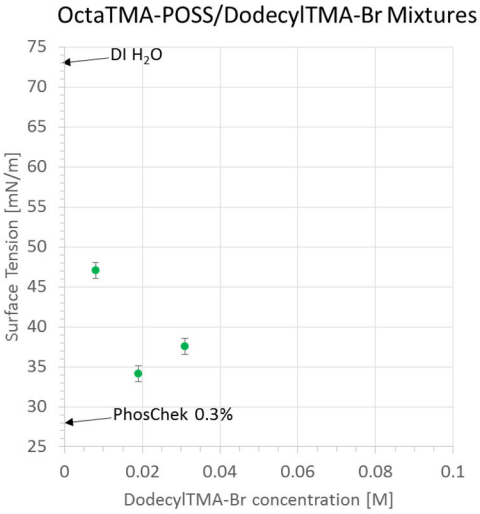


Figure 54 OctaTMA-POSS/DodecylTMA-Br Mixture Surface tension Pendant Drop Method

Figure 55 Foam created by OTMAP and dodecyltrimethylammonium bromide metathesis product in water.

Reactions of Octa(tetramethylammonium)POSS (OTMAP) and Phosphonium Salts

The commercially available octa(tetramethylammonium)POSS (OTMAP) is a water soluble derivative of POSS, thus is might be useful as an additive in fire-fighting foams. The idea was to exchange the tetramethylammonium cations in OTMAP with phosphonium cations because the phosphorus ions might act as an additional fire suppressant in the foam. There were two commercially available phosphonium salts that were used in an attempt at metathesis reaction with OTMAP, tetrakis(hydroxymethyl)phosphonium chloride (THMPCl) and tetrabutylphosphonium hydroxide (TBPOH), Figure 56.

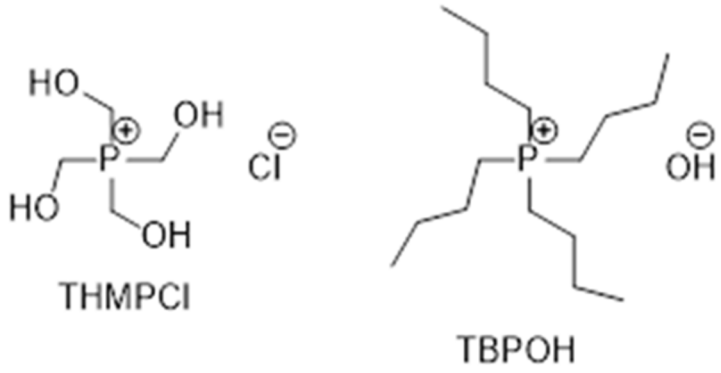


Figure 56 Chemical structures of tetrakis(hydroxymethyl)phosphonium chloride (THMPCl) and tetrabutylphosphonium hydroxide (TBPOH).

In each reaction a full eight equivalents of phosphonium salt was added to the OTMAP. With THMPCl an immediate gas generation occurred which at first was surprising to observe. A literature search found the work of Grayson who showed that THMPCl will react with excess sodium hydroxide in water to form hydrogen gas, formaldehyde and sodium chloride, Figure 57.[22]

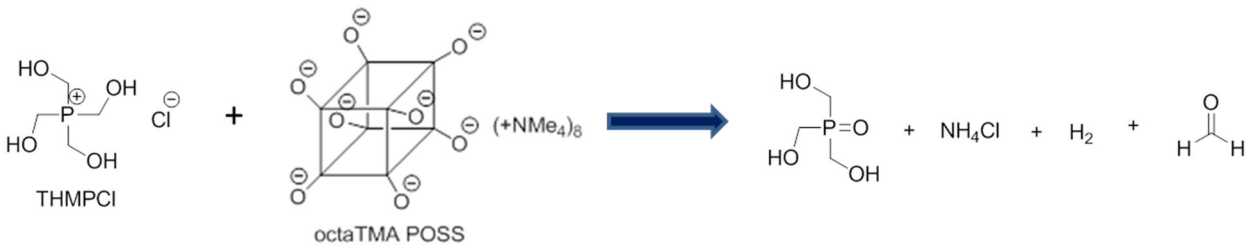


Figure 57 Gas formed from reaction of OTMAP and THMPCl probably from hydrogen generation by this reaction sequence.

OTMAP is a form of soluble silicate with SiO- groups neutralized with tetramethylammonium cations. It was found that the OTMAP is very basic in water solution, with pH paper showing pH ~11 so it is very basic although it is a 'neutral' salt with tetramethylammonium cations. Apparently, the silicate ion is basic enough to bring about the decomposition of THMPCl much like sodium hydroxide can. Based on the reaction equation, it is not clear what the product of this reaction with OTMAP was and if the POSS cage was intact but no solid precipitated from the reaction solution.

Mixtures of Triton X-100 (4-(1,1,3,3-Tetramethylbutyl)phenyl-polyethylene glycol), a common non-ionic surfactant, and OTMAP and THMPCl were made so that surface tension in air could be made by pendant drop, Figure 58. Pure water has a surface tension in air of 73.2 mN/m and dissolving 3.48 wt% Triton X-100 in the water decreased the surface tension to 31.1 mN/m, the normal effect of a surfactant. A mixture of both Triton X-100 (3.45 wt%) and a large quantity of OTMAP (29.6 wt%) did not seem to effect the surfactant properties deleteriously since the surface tension in air was 29.6 mN/m, Table 8. This amount of OTMAP was at the limit of its solubility in water since a fire-fighting foam would likely need to have the highest level possible to achieve maximum effect of this POSS derivative. The THMPCl did not have very much surfactant qualities since it did not lower the surface tension of water (65.9 mN/m) significantly. A mixture of all three reagents had a relatively good surface tension of 30 mN/n indicating that the OTMAP and THMPCl are spectators and do not affect the surface tension of this particular hydrocarbon surfactant.

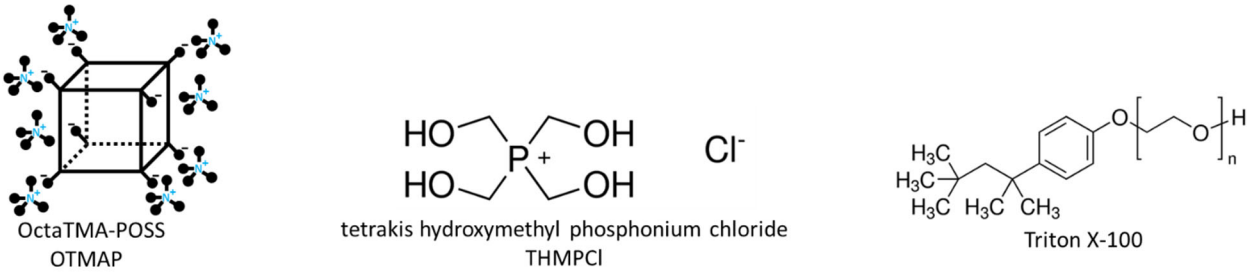


Figure 58 Chemical structures of OTMAP, THMPCl and Triton X-100

Table 8 Surface tension measurements in air for mixtures of Triton X-100, OTMAP and THMPCl.

Triton X-100 concentration, wt%	OTMAP concentration, wt%	THMPCl concentration, wt%	Surface tension (air) [mN/m]	Standard deviation StDev.P
0	0	0	73.2	0.27
3.48	0	0	31.1	0.14
3.45	29.6	0	29.6	0.15
0	0	0.99	65.9	3.66
0	25.8	0.45	68.5	1.84
0.77	8.98	0.43	30.0	0.33

Reaction of an aqueous solution of TBPOH with OTMAP gave shortly after mixing a fine crystalline precipitate. The solid was filtered and air dried and was soluble in DMSO so a proton NMR of the material was taken. The proton NMR spectrum showed signals for butyl groups indicating that phosphonium cations may have replaced the original tetramethylammonium cations of OTMAP, Figure 59. The tetrabutylphosphonium cations would make the POSS salt much less water soluble than tetramethylammonium cations, resulting in precipitation.

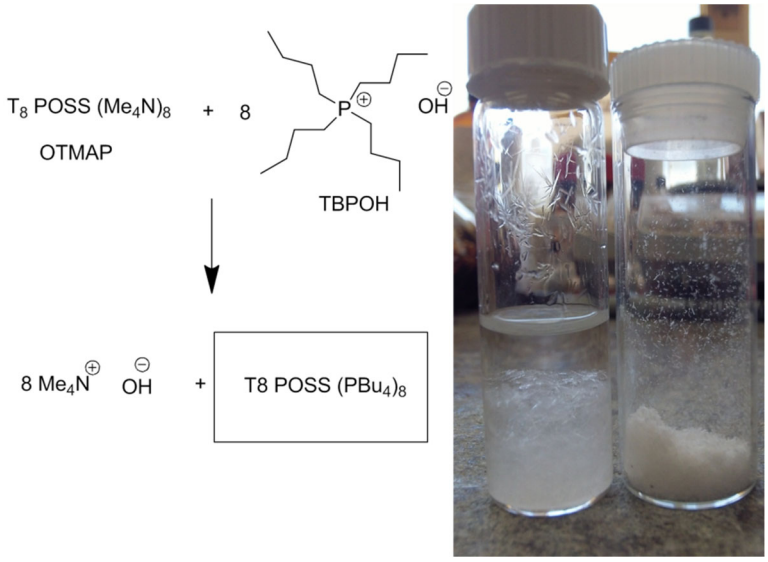


Figure 59 OTMAP reaction with TBPOH in water gave a crystalline precipitate that is likely the desired octa(tetrabutylphosphonium)POSS complex.

Unfortunately, the crystalline material did not have good quality for X-ray analysis and the product did not recrystallize from methanol or ethanol but left an oil. A literature search did find the work of Gerke et al. who were able to get a crystal structure of POSS cages surrounded by tetrabutylphosphonium cations so this is likely what was synthesized.[23] The compound was soluble in water and unfortunately the project came to a close before it could be formulated into a

fire-fighting foam concentrate. We did collect surface tension in air for mixtures of OTMAP and TBPOH, Figure 60, unfortunately the mixture precipitated at around 20 wt% loading of the phosphonium salt, Figure 61.

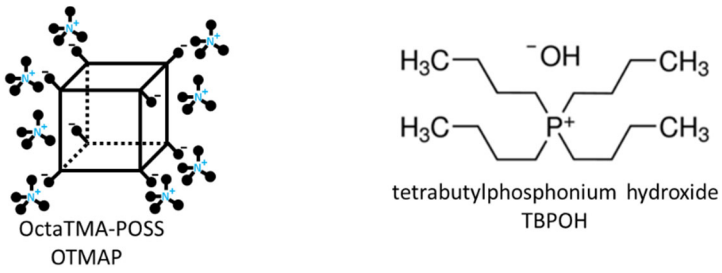


Figure 60 Chemical structures of OTMAP and TBPOH.

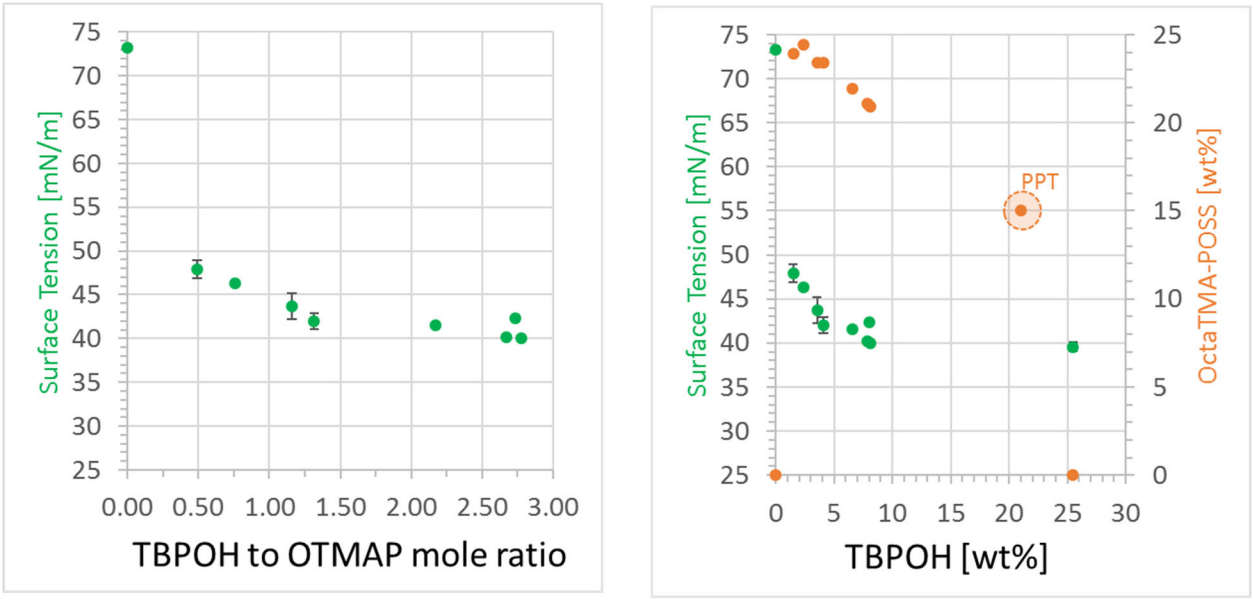
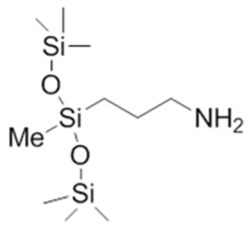


Figure 61 Surface tension in air for mixtures of TBPOH and OTMAP appeared to plateau at 1:1 with ~ 40 mN/m (*left*); with 20 wt% TBPOH and 15 wt% OTMAP precipitation occurred of the phosphonium salt (*right*).

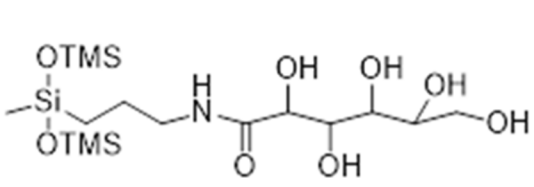
Synthesis of 3-Aminopropylmethylbis(trimethylsiloxy)silane Sugar Amides

It was decided to try to make some of the related siloxane containing foam agents such as those made by Dirk Blunk's groups which are siloxanes bonded to sugars. This group made an advance study of such sugar-siloxane surfactants as fire fighting foams and have a US patent on their technology. Although contact/inquiry with Dr. Blunk by e-mail was not successful. In 2010, Guoyong et al.[24] had reported on both the gluconic acid and lactobionic acid amides of APS and found them to exhibit surfactant characteristics.[25] The glucoamide of APS had CMC of 0.000413 M and interfacial surface tension in air of 20.54 mN/m, Figure 62. The lactobionamide of APS had CMC of 0.00103 M and interfacial surface tension in air of 21 mN/m.

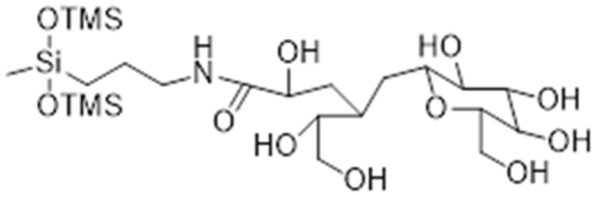


3-aminopropyl-methyl-bis (trimethylsiloxy)silane

'APS'



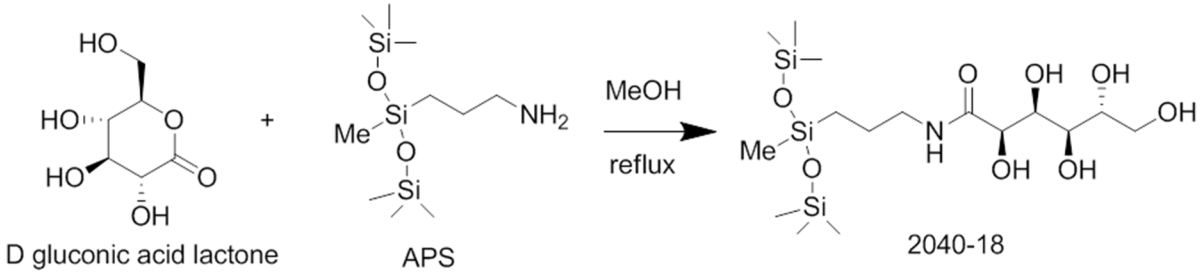
gluconamide of APS



lactobionamide of APS

Figure 62 Sugar amides of APS found in the literature with good surface tensions in air.

These were pretty good numbers although they did not measure interfacial surface tension against a hydrocarbon solvent (e.g. cyclohexane). It is likely they would have positive spreading coefficient against cyclohexanes based on the measurements we made on the APS/AA system (*vide infra*). A 2014 patent by Blunk et al. described the use of the gluconamide of APS as a fire fighting foam agent.[26] They mentioned that an aqueous solution of the compound spreads on the surface of cyclohexane when a drop was added on top of this solvent, which confirms our suspicions that this surfactant likely has a positive spreading coefficient on cyclohexane. Since there was APS available, it was decided to try to make the gluconamide of APS, Figure 63.



D gluconic acid lactone APS 2040-18

Figure 63 Synthesis of the gluconamide of APS.

This we did without issue by refluxing equimolar amounts of APS and gluconolactone in methanol. The methanol was stripped away leaving the product as a solid that could be slurried with ethyl acetate, forming a nice white crystalline powder that could be filtered easily. The yield of product was nearly quantitative and the proton and carbon-13 NMR spectra were consistent with the expected product and were consistent with the literature values, Figure 64.

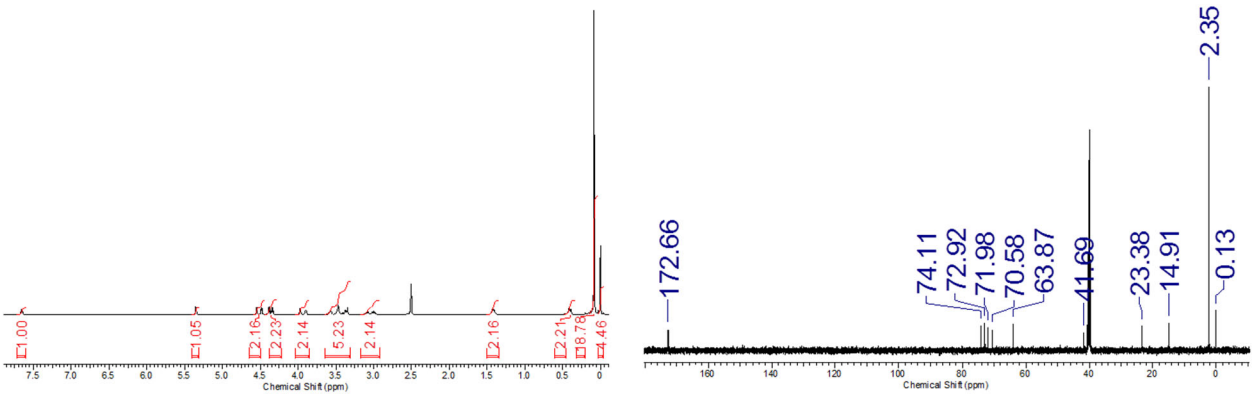


Figure 64 Proton (*left*) and carbon-13 (*right*) NMR spectra of APS gluconamide in DMSO.

The product appeared to have some water solubility as simple bench test showed that it would create a foaming mixture in water, though not very strong, Figure 65. Since the interfacial tension had already been measured, all that was left was to try the surfactant in small-scale foam fire. But, we did not have the time to get to test the material against pool fires.

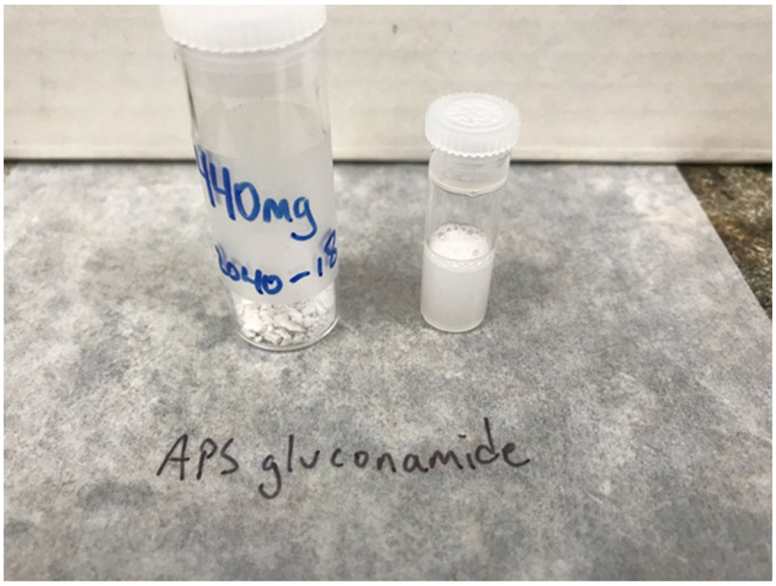
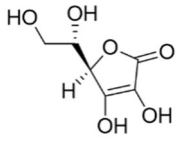


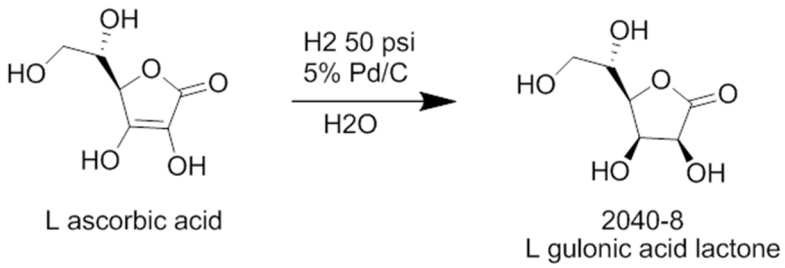
Figure 65 The APS gluconamide (*left*) was water soluble and made foam (*right*).



L-ascorbic acid (Vitamin C)

'AA'

We thought that the common L-ascorbic acid (AA), also known as Vitamin C, might be useful for derivatization of APS. Based on the fact that AA has redox potential and that several manifolds were available for reaction, we thought it would be interesting to convert AA into its dihydro-form. The dihydro-AA would lack redox ability and would presumably behave exclusively as a lactone in its reactivity. Dihydro-AA is also known as *gulonic* acid lactone (not to be confused with the more common isomer *gluconic* acid lactone) after the traditional nomenclature from carbohydrate chemistry. Dihydro-AA has been prepared previously in several reports, which all described heating a mixture of AA in water with 10% palladium or other catalyst in a high pressure hydrogen atmosphere, Figure 66.[27]



L ascorbic acid

2040-8
L gulonic acid lactone

Figure 66 Catalytic hydrogenation of AA (vitamin C) to dihydro-AA (gulonic acid lactone).

However, we found that AA reduced readily at room temperature and just 50 psi hydrogen pressure with 5% palladium on carbon, a safe and inexpensive version of this catalyst. The reduction was typically complete in just 24 hours even when scaled up to 50 g. After rotary evaporation of the water, the dihydro-AA could be recrystallized from a mixture of methanol in ethyl acetate, Figure 67.

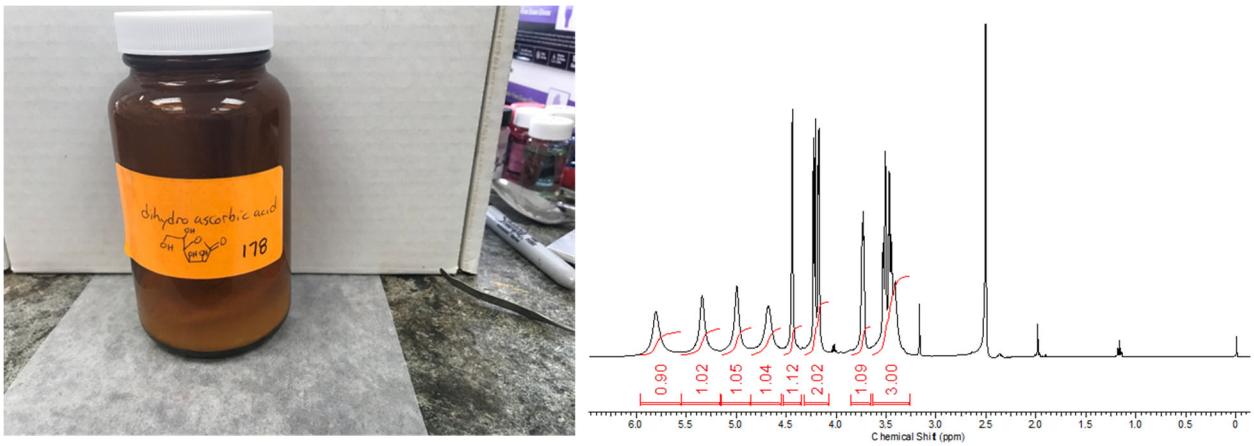
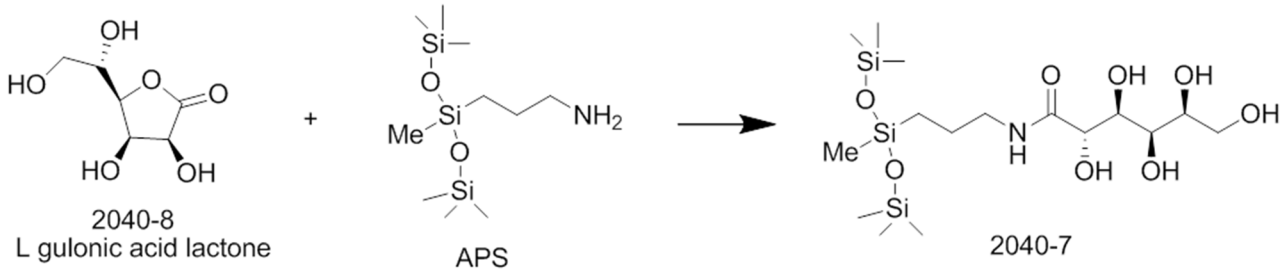


Figure 67 The reduction of AA to dihydro-AA (gulonic lactone) was easy to carry out at 50 g scale, and its proton NMR in DMSO.

Reaction of APS with dihydro-AA happened unevently just like the case of the isomeric gluconolactone. The methanol reaction mixture was evaporated leaving a semi-solid product which was then purified further by silica gel chromatography eluting with a mixture of methanol in ethyl acetate, Figure 68.



2040-8
L gulonic acid lactone

APS

2040-7

Figure 68 Synthesis of gulonamide of APS using dihydro-AA.

It was noted that the product seemed to have more non-polar character since it would dissolve in deuterochloroform readily. The proton NMR had the characteristic triplet for the amide proton at 7.4 ppm indicating amide bond formation had occurred, Figure 69.

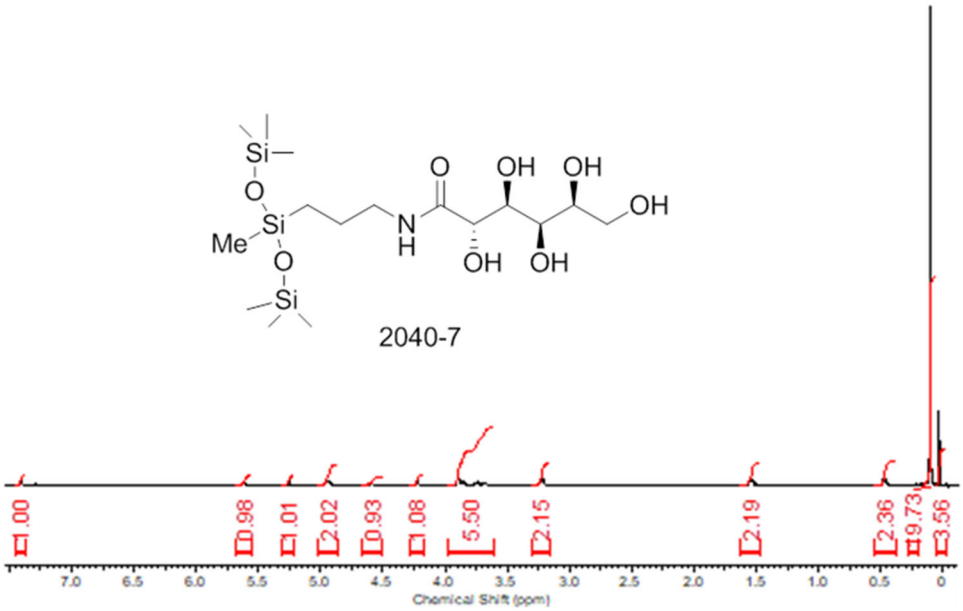


Figure 69 Proton NMR spectra of APS gulonamide in $CDCl_3$.

The pure gulonamide of APS was a somewhat tacky solid, not a free-flowing powder, Figure 70. The compound was not very polar since it would dissolve in toluene but not in acetonitrile. Surprisingly, the gulonamide of APS had very little solubility in water and did not create a foaming mixture at all. The sample and data were carefully re-checked again and the lack of solubility of the gulonamide of APS was confirmed.

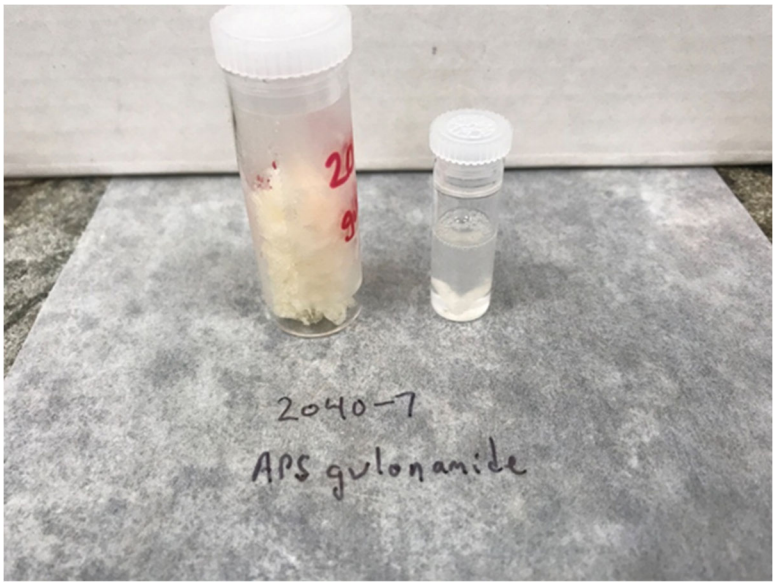


Figure 70 The APS gulonamide (*left*), unexpectedly poor solubility in water and no foam (*right*).

This was not expected since both the APS gulonamide and APS gluconamide are simply isomers at the 2- and 5-carbon atoms of the sugar portion. They both have the same number of hydoxyl groups, yet the glucoamide was water soluble while the gulonamide was not, Figure 71.

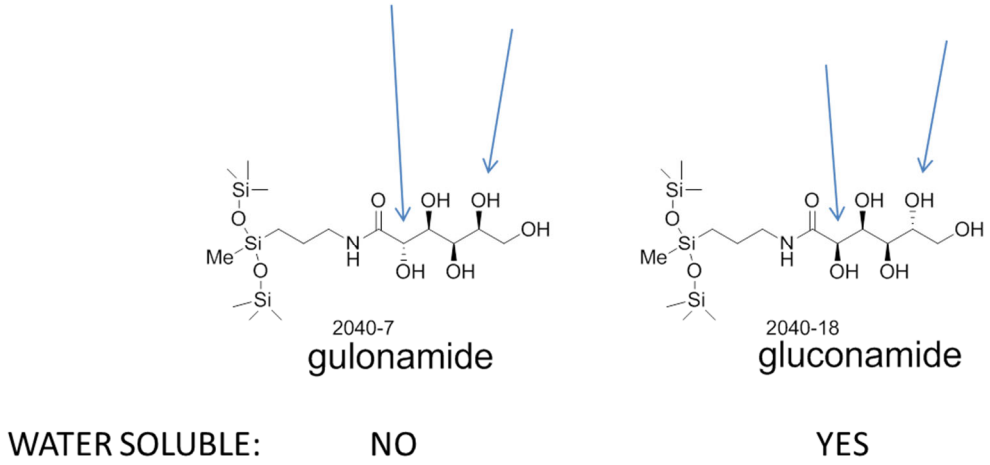


Figure 71 Remarkable stereochemical power of two hydroxy groups, and the APS sugar amide went from water soluble to water insoluble.

A literature search did find a couple reports describing the differences in solubility of carbohydrates based on their hydroxyl group configuration, a fact that was not understood at the outset.[28] There are eight different aldohexoses based on stereochemistry, so it would be interesting if the other six aldonic acids could be obtained and reacted with APS to make a complete study of the role of stereochemistry/solubility.[29] A couple of attempts to make lactobionic acid lactone from lactobionic acid were made, but the product from this reaction was very hygroscopic and was not easy to crystallize.[30] So on account of these difficulties the synthesis of the lactobionamide of APS was not pursued further.

Studies on the Surfactant Between 3-Aminopropylmethylbis(trimethylsiloxy)silane (APS) and L–Ascorbic Acid (AA)

The structure of ascorbic acid is shown below, Figure 72. It is more commonly known as vitamin C, and is found in many plant species but especially concentrated in fruits (i.e. citrus).

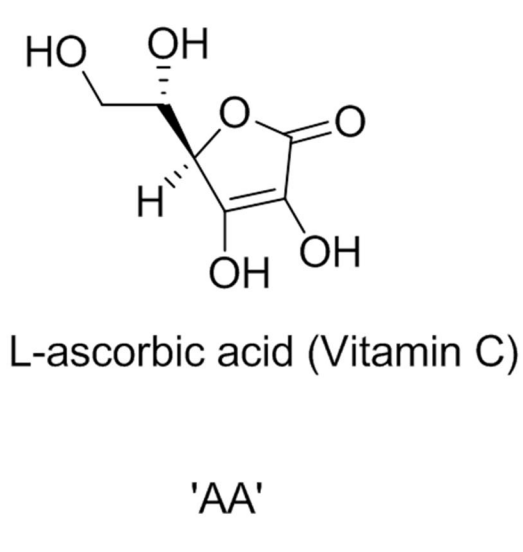
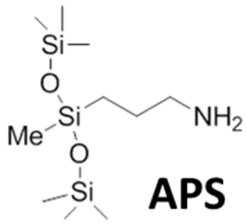


Figure 72 L-Ascorbic acid, also known as Vitamin C.



It was hypothesized that ascorbic acid would undergo a reaction with an amine such as APS to form a covalent bond between the two reagents. The reaction was anticipated to occur at the lactone site. The reaction between APS and AA was tried on several occasions by heating equimolar quantities in methanol or tetrahydrofuran. In all cases, the product isolated was an oil that was initially clear and colorless. Immediately after isolation, the product would dissolve in water and created a foaming solution indicating some surfactant properties were present. Proton NMR of the product did not show the expected peak for amide (~ 7 ppm) if reaction at the lactone had taken place, Figure 73.

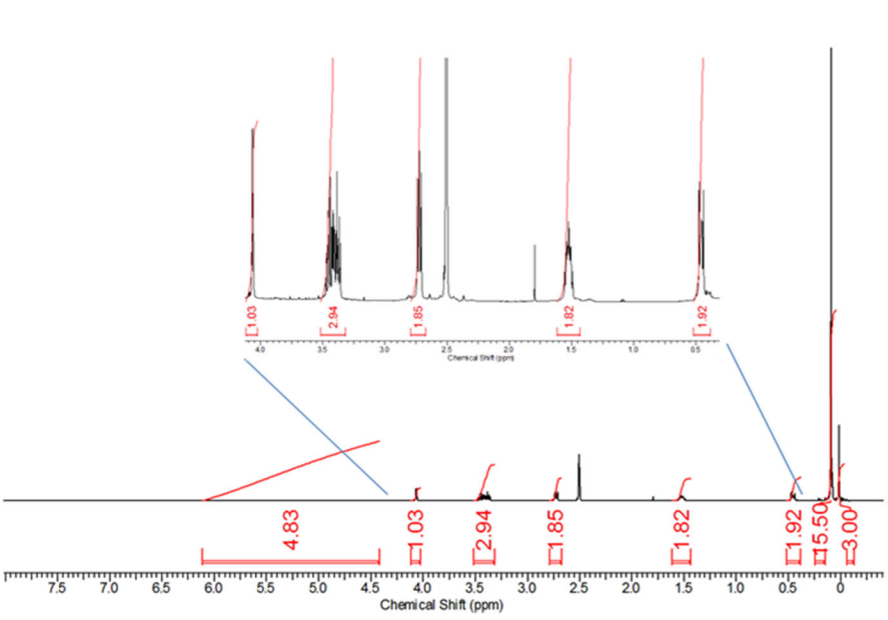


Figure 73 ^{1}H NMR spectra of product from reaction of APS and AA (1:1 ratio) in refluxing methanol (*left*); and photo of water solution which made some foaming action (*right*).

However, after storing the product under atmospheric conditions, the compound slowly developed an orange or brown color, Figure 74. From experience, this browning is typical of amines and more so between amines and sugars, the so-called Maillard reaction. If an amide bond had been made between the APS and AA, such amine oxidation chemistry should have been neutralized.

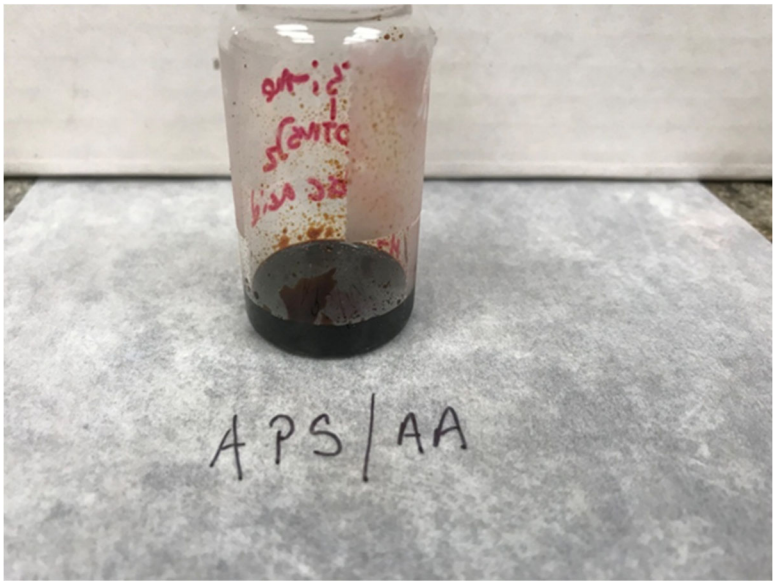


Figure 74 After storage for 24 hours, the product from the APS and AA reaction in methanol had decomposed badly.

There had been one report of the identical reaction of APS and AA by Blunk et al. but this was in a patent and there was no supporting spectroscopic data for the amide product apart from a figure of this reaction sequence.[31] In a patent to Bayer, a slightly different aminoalkylsiloxane was reacted with AA in boiling methanol and they drew the product as an amide, Figure 75. This report gave ^{13}C NMR data for their product but the data they included did not truly establish whether or not a covalent bond had been established between their two reactants.[32]

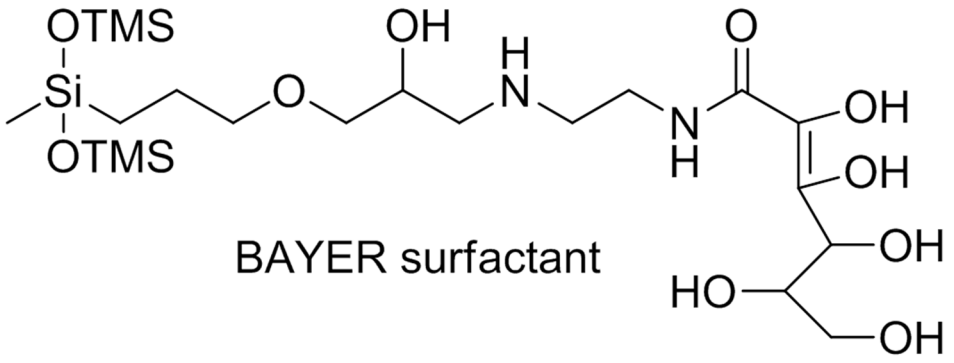


Figure 75 Surfactant reportedly made by reaction of aminoalkylsiloxane and AA from Bayer patent.

A literature search for reactions of AA with amines was undertaken and the work of Pischetsrider et al. was found.[33] They showed that AA reacted with N-propylamine at the C-3 position to form 3-deoxy-3-(propylamino)ascorbic acid, no amide product was formed or mentioned, Figure 76. However, in a Japanese patent, they describe a covalent product (no structure in abstract) made by reaction of long-chained amines with AA when reacted at 198 °C.[34] Our reaction conditions were not nearly as rigorous as the latter.

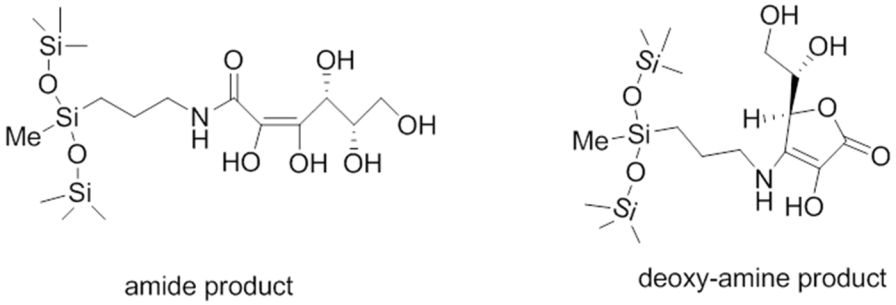


Figure 76 Putative structures of a condensation product between AA and APS.

The ^{1}H NMR of our product did show a downfield shift of the –NC<u>H</u>$_2$– perhaps indicating that reaction at the amine had occurred. Yet another possibility that would also explain the downfield shift of the –NC<u>H</u>$_2$– group in both ^{1}H and ^{13}C NMR was that the AA had simply protonated the APS, a simple acid base neutralization reaction, which is well known for causing such a shift in the NMR spectra of amines.

The failure of APS and AA to form a meaningful product in our hands was surprising and unfortunate but led to a new idea. Ascorbic acid is readily soluble in water though APS is not. It was hypothesized that AA might be sufficiently acidic to protonate the APS and form the APS/AA salt which might have better solubility in water, Figure 77.

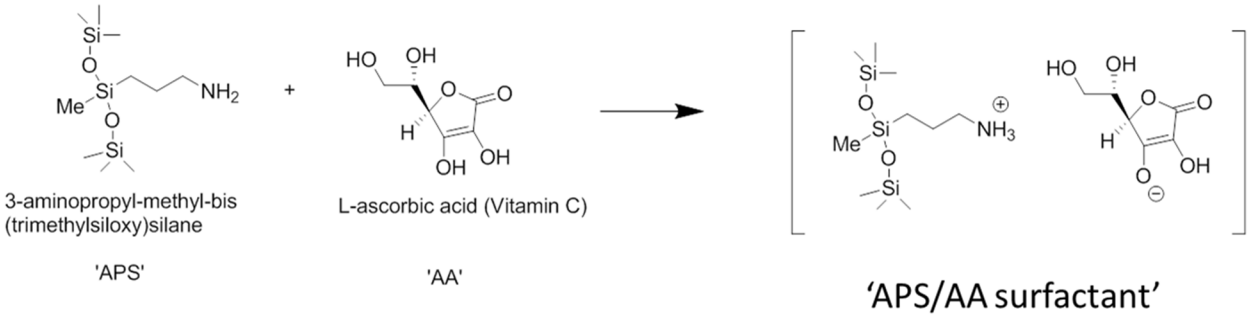


Figure 77 Salt formation between APS and AA in water.

This was tested on a 1:1 molar ratio of the two reagents. The AA was dissolved in water and then the equivalent amount of APS was added to the solution in a single portion, Figure 78. Initially, the less dense APS formed a layer on top of the aqueous solution of AA. In shaking up this mixture, the APS did in fact become homogeneous in the mixture. The resulting mixture of APS/AA in water created an intense foaming surfactant that was empirically similar to the foamability of Triton X-100.

Figure 78 (*left*) APS added onto water solution of AA (1:1 ratio); (*center*) mixture then vigorously shaken; (*right*) freshly made APS/AA had strong foamability.

Because the APS/AA salt appeared to behave as a surfactant, it was decided to attempt to collect surface tension and spreading coefficient by the hanging drop method, Table 9. The concentration of APS/AA (MD2040-15) that was first made arbitrarily in the laboratory was a 0.0175 M solution or 8 grams/L. The surface tension measurements were made relative to cyclohexane which is specified by the Mil-Spec for AFFF.[35]

Table 9 Surface tension measurements by the hanging drop method of an aqueous 0.0175 M APS/AA solution against cyclohexane.

liquids	Interfacial Tension [mN/m]	Standard Deviation [mN/m]	Temperature [°C]
DI H_2O / cyclohexane (literature)	48 to 50		25.0
DI H_2O / cyclohexane (NAWCWD)	49.448	1.720	23.6
MD2040-15 Ascorbic Acid/APS in DI H_2O / air (NAWCWD)	20.345	0.129	23.0
MD2040-15 Ascorbic Acid/APS in DI H_2O / cyclohexane (NAWCWD)	0.431	0.050	23.0

The surface tension of cyclohexane which we measured as 25.5 mN/m. The interfacial tension of the APS/AA solution in air was also collected which was 20.3 mN/m. The last piece of data was the interfacial tension of the APS/AA solution in cyclohexane which was found to be 0.43 mN/m. With these three measurements collected, the data can be input into the spreading coefficient calculation. Thus, the spreading coefficient (S) for 0.0175 M APS/AA surfactant on cyclohexane calculated to be +4.7 mN/m.

$$S = 25.5 \text{ mN/m} - 20.3 \text{ mN/m} - 0.4 \text{ mN/m} = +4.7 \text{ mN/m}$$

This was an interesting result since most common hydrocarbon surfactants have a negative spreading coefficient on cyclohexane. Thus, hydrocarbon surfactants have limited use for fighting fire because they can't spread on a gasoline fire. Only fluorinated surfactants (e.g. PFAS and PFOA) such as those found in AFFF have positive spreading coefficients on cyclohexane, which is what makes them so useful in fighting hydrocarbon pool fires.

We tried to fight a gasoline pool fire using the 0.0175 M APS/AA solution with our small-scale foam apparatus. The mixture failed to make a layer on the surface of gasoline and thus did not have any effect in putting out the fire. In hindsight, there were several issues with this result that may have contributed to the failure. Our small-scale foam apparatus made a weak foam, not a thick and dense foam, at least empirically, when compared to photos of other groups surfactants such as Blunk's group or the Naval Research Laboratory.[36,37] Also the rate at which the foam was delivered may have been too slow or at least required changing in order to have the APS/AA perform better. We were fighting a gasoline fire, which is probably the most challenging fuel to fight, since the surface tension of gasoline is so low (20.8 mN/m). In fact, Blunk's group had so much success with their siloxane surfactant because they were fighting pool fires of diesel (28.3 mN/m) which has a much higher surface tension and so surfactants can float on it more readily. As will be discussed below, the 0.0175 M APS/AA solution was below the critical micelle concentration (CMC) and thus not optimal for this surfactant. At the time we were simply basing our concentration on the typical AFFF formulations. Now it is understood that each surfactant will have its own unique properties and that the concentration of fluorinated surfactants in AFFF can't be used as a template for all other new surfactants. It is likely that any new surfactant would have to be at a higher concentration to get them to work effectively at putting out hydrocarbon pool fires. Lastly, the APS/AA salt may have been made a day or two before the scheduled burn room time, and probably had undergone some degradation as will be discussed below.

We further studied the APS/AA surfactant to obtain its CMC value which is an important concentration above which the material will behave as a surfactant. The concentration of APS/AA ranged from 0.002 – 0.2 M and the interfacial surface tension in air of each individual concentration was measured by the hanging drop method, Figure 79. The data show a very nice 'hockey stick' form where the surface tension steadily decreases as the concentration of the surfactant increases finally reaching a plateau. This was a 'text book' curve and the CMC concentration for APS/AA was found to be 0.023 M, the intersection of the two best fit lines of the downward and flat portions of the data.

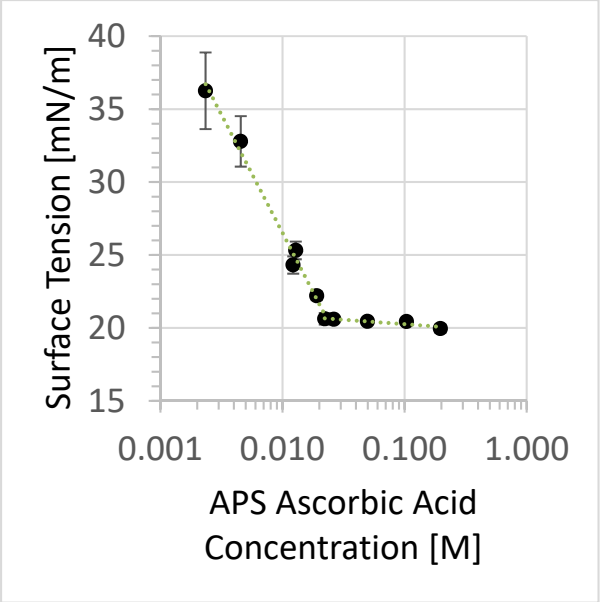


Figure 79 Plot of surface tension versus concentration for APS/AA surfactant.

We continued further with the hanging drop method and measured the spreading coefficient on cyclohexane using the calculation described above for a series of APS/AA concentrations (0.013 – 0.104 M), Figure 80. In this way, the concentration of APS/AA which gave the highest spreading coefficient on cyclohexane was determined to be 0.05 M APS/AA yielding a spreading coefficient of +4.6 mN/m. One can clearly see by this plot how important it will be to test a surfactant for hydrocarbon pool fire at the 'right' concentration at which the surfactant has its highest spreading coefficient. Testing the new surfactant at concentration below the maximum spreading would probably lead to a false negative.

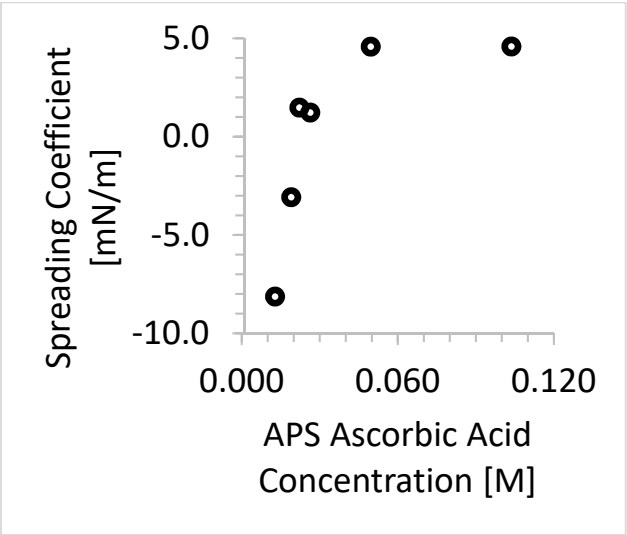


Figure 80 Plot of APS/AA surfactant concentration versus spreading coefficient on cyclohexane.

The initial value for surface spreading on cyclohexane for APS/AA which was +4.7 mN/m at 0.0175 M probably had a bit of error in it owing to the difficulties in measuring the drops in

cyclohexane. Also, that earlier sample may have sat around longer than a day and may have degraded. The later value of +4.6 mN/m at 0.05 M was measured with freshly prepared solutions of APS/AA and we believe is more accurate for the material. It should be noted that the initial solution of APS/AA (0.0175 M) that was made during early experimental work just happened to be below yet close to the CMC for the surfactant (0.023 M). This was a little bit of luck because the mixture made excellent foam at this concentration, at least empirically. One can see that the bench chemist could have a 'false negative' were the concentration made more dilute and well below CMC, in which case the new material might not appear to be a useful surfactant. This emphasizes the fact of how important surface tension data is to surfactant chemistry and ultimately to AFFF replacements.

After much of the work with and knowledge about APS/AA was learned, a literature search found the recent work of Li et al. on simple carboxylic acid salts of APS, Figure 81.[38] They synthesized protic ionic liquids (e.g. salts) of APS with acetic, propionic and butyric acids by reaction equimolar quantities in boiling methanol followed by evaporation.

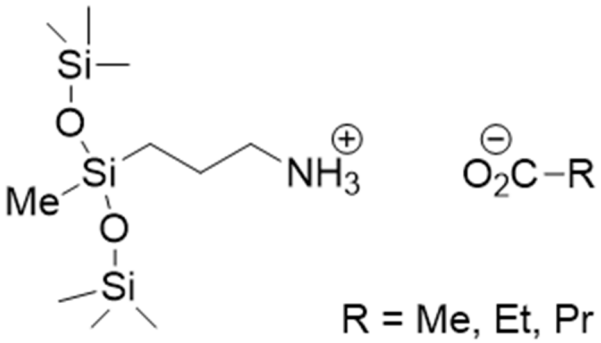


Figure 81 Ionic liquids of APS and simple carboxylic acids which were good surfactants reported by Li et al.

Li et al. recognized these salts had surfactant properties and measured the surface tension in air (20.19 – 21.11 mN/m) and CMC (0.0152 – 0.0225 M) for each salt. These data for their salts were very similar to the data of our APS/AA. Li et al. did not measure surface tension against other solvents (e.g. cyclohexane) or study them further as surfactants including surface spreading. We believe these salts would probably also have positive spreading coefficients on cyclohexane based on the data we collected for APS/AA.

We made the APS/acetic acid surfactant by our method of simply dissolving the acetic acid in water and adding the APS and shaking. This method worked as expected and a foaming mixture was generated which means that reacting APS and carboxylic acid in boiling methanol is not necessary to generate the surfactant. We also tried to make the ionic liquid of APS and AA in a vial, but no reaction took place, the AA did not dissolve in the APS. The important point to take from the Li et al. work was that a carboxylic acid protonation of APS made a strong surfactant and so that in the earlier reported reactions of APS with ascorbic acid to make surfactants, perhaps nothing more than base neutralization reactions and not a covalent bonding forming reaction had occurred.

Other acids were tried with APS to generate surfactant solutions. The APS/lactic acid and APS/lactobionic acid salts made good strong foam solutions, Figure 82. It is hypothesized that

hydroxyl groups in the acid component may contribute to better foams. However, neither trifluoroacetic acid or hydrochloric acid created foams, and it may be that these acids are too strong and may have cleaved or hydrolyzed the siloxane head group. Pivalic acid also did not form a foam solution with APS probably due to the low water solubility of this acid in water since the solid acid never completely dissolved.

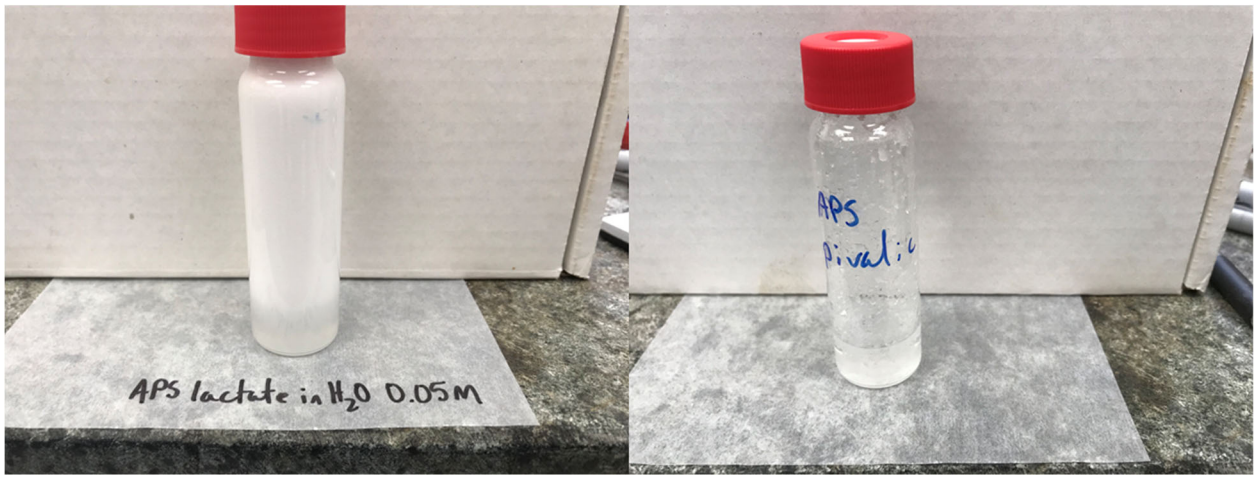


Figure 82 Surfactant solution made from APS and lactic acid at 0.05 M made strong foam (*left*), but pivalic acid and APS did not react (*right*).

Along the way of this APS/AA research, we noticed that the solutions that were made tended to lose strength over time eventually leading to a biphasic mixture. At low concentrations the second phase was less dense that water and at high concentration, the second phase had greater density. The aged APS/AA mixture slowly became orange or yellowish in color indicating something was happening, Figure 83. After 24 hours the mixture was ok but after seven days, the mixture had completely lost any foamability. It is well known that AA is an antioxidant and may undergo some sort of chemical change (these APS/AA solutions were not protected under nitrogen). The same deterioration of APS salts occurred with lactic acid, acetic acid and lactobionic acid although in these cases there wasn't a strong color change. Other possibilities are that the siloxane head group could undergo oligomerization or that carbon dioxide is slowly being absorbed from the air which would change the pH and could affect the surfactant. The APS/AA surfactant would probably be very sensitive to pH changes since it is a protic salt rather than a stable and covalent quaternary ammonium type.

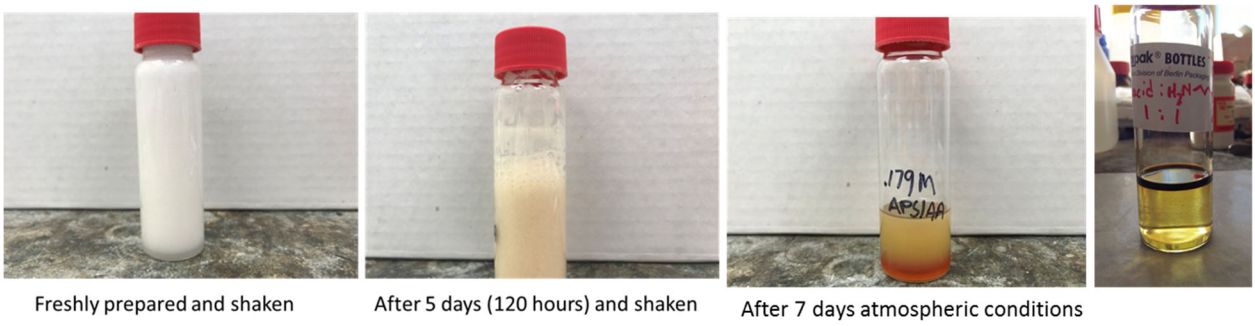


Figure 83 The 0.179 M APS/AA surfactant deterioration over time (~3X the CMC) and second phase is denser than water;(*far right*) degradation of lower concentration solution and less dense layer formed.

We did one experiment to try to understand what is happening during aging of an aqueous solution of APS carboxylate salt. The APS acetic acid salt was made in water in the usual way and allowed to sit at room temperature for several weeks. After this time, there was a layer floating on the surface of the water and the mixture no longer made foam when shaken. The mixture was then extracted with ether, washed with brine and then dried with anhydrous magnesium sulfate. The solvent was evaporated leaving a small amount of liquid residue and proton NMR was taken of the residue in deuterochloroform solvent, Figure 84. This was compared with the proton NMR spectrum of the starting APS, although the latter was dissolved in dimethylsulfoxide since it has low solubility in deuterochloroform.

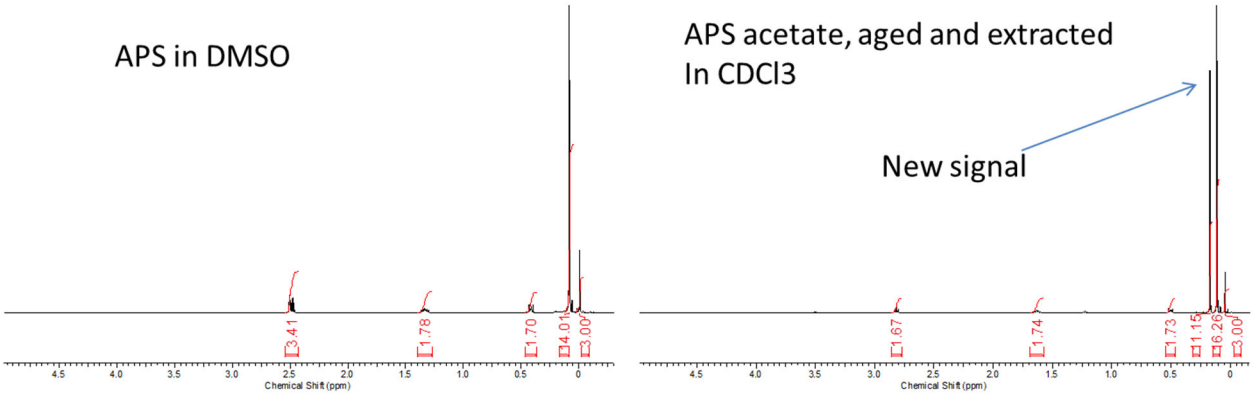


Figure 84 Proton NMR spectra of pure APS and the organic phase from APS/AA after aging, a new peak has formed in the latter (~0.25 ppm) in the region of alkylsiloxane.

The first point to note was that there was no peak for acetate in the aged sample, although it had one equivalent of acetic acid present originally. The spectra appear similar in that all three $C\underline{H_2}$ groups appear in both, although all of these peaks are all downfield for the aged sample relative to APS. The NH_2 group was not observed in the spectrum of the aged extract, but this is common for exchangeable protons. The major difference seen was the new peak in the aged spectra down around 0.2 ppm about where silyl groups show up. This might indicated that the aged extract has undergone some kind of change in the siloxane head group. This could be hydrolysis (trimethylsilanol or trimethylsilyl ether) or oligomerization, a change that has caused the APS acetate salt to no longer have surfactant properties, Figure 85. More time was needed to try to

elucidate the stability issue of the APS carboxylate salts. Although we did find a report by Snow et al. who found that some of sulfobetaines of APS and similar aminosiloxanes do hydrolyze and rearrange with formation of trimethylsilyl ether ($(TMS)_2O$).[39]

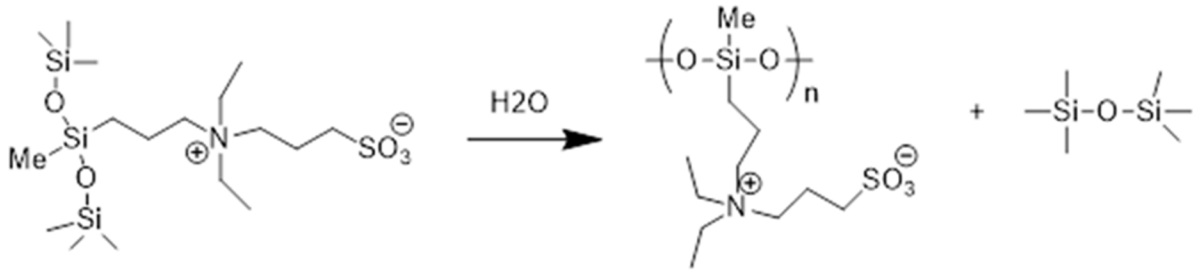


Figure 85 Possible breakdown pathway of quaternary aminosiloxane surfactant at siloxane head group.

Testing APS/AA Against Heptane Pool Fire at NRL

Owing to the difficulties with our small-scale foam fire fighting apparatus, contact was made with Drs. Ramagopal Ananth and Art Snow at NRL who have extensive experience in surfactant chemicals and foam behavior. They were interested in the APS/AA because it had a high positive spreading coefficient on cyclohexane. They agreed to test out the APS/AA surfactant in their foam fire fighting apparatus against heptane pool fire. The apparatus for 19 cm diameter pool-fire extinction is illustrated in the Figure 86.

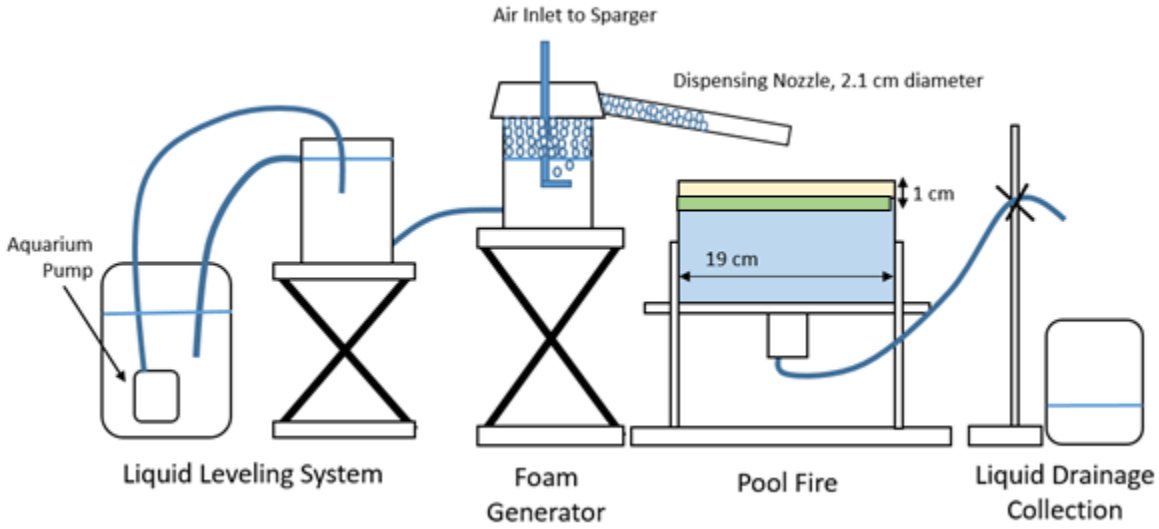


Figure 86 Bench-scale foam generation and pool fire suppression

The NRL apparatus was operated in the following manner. The foam solution was placed in a reservoir where an aquarium pumps it to a second reservoir whose height was adjusted relative to a third solution container immersed a glass frit to generate the foam by controlled air flow rate passage. These three containers require a volume of about 2.5 L. The generated foam flowed through a side arm in the container cap to a connected glass tube that deposited the flowing foam on to the burning pool. The pool was filled to a level 2 cm below its lip with water followed by a

1 cm layer of heptane. Extinction experiments were conducted using a range of foam flow rates usually between 100–2500 mL/min. Also, immediately before and after the extinction time experiment, foam flow rate and expansion ratio measurements were made by measuring the time needed for the generated foam to fill a 500 mL beaker and the foam's mass. The extinction time measurement was conducted by giving the pool a 60 sec preburn, then the dispensing nozzle was rotated to the center of the pool fire and then times needed for coverage of the pool by the foam and for extinction of the fire were observed and recorded.

The apparatus was pseudo-calibrated by using a Reference AFFF composed a fluorosurfactant (Capstone 1157), an alkyl polyglycoside surfactant (Glucopon 215UP) and a solvent (diethylene glycol monobutylether) which passed MilSpec extinction evaluation. Data for this Ref AFFF benchtop pool-fire testing is shown in Figure 87 and shows the ideal fire suppression.

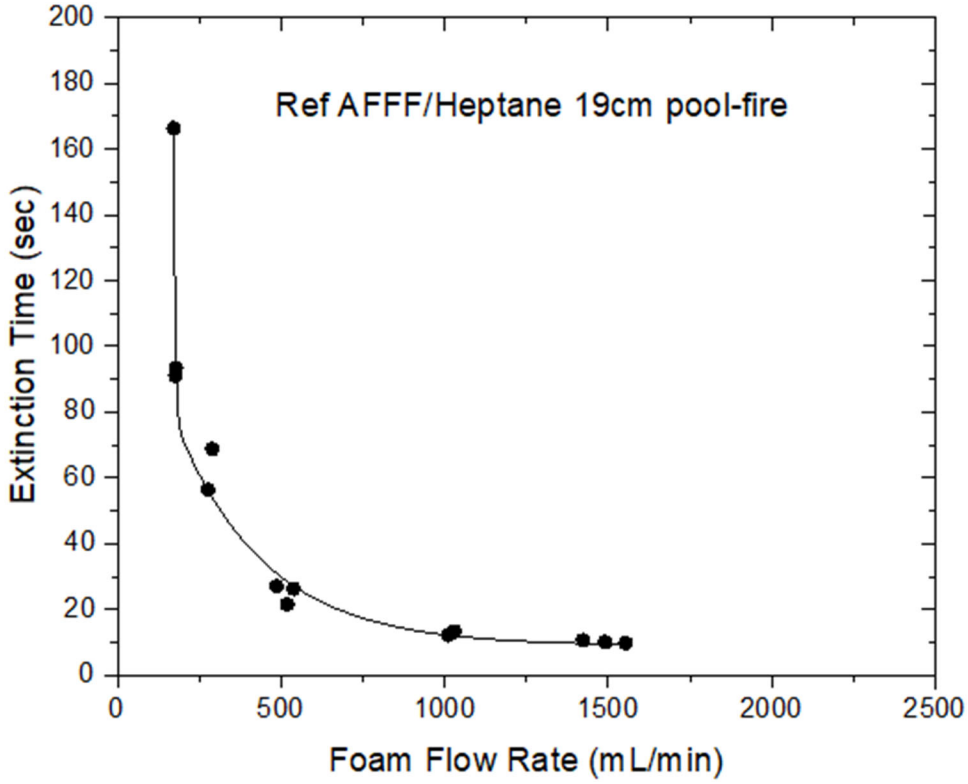


Figure 87 Heptane pool fire suppression by Ref AFFF

For the NRL experiments, a relatively large quantity of surfactant was necessary because about 4 L of concentrate was required for collecting meaningful data. Fortunately, APS was available in 50 g (0.178 mole) quantities from Gelest and ascorbic acid was widely available. The NRL team made up 3.58 L of a 0.05 M solution of APS/AA for their tests. This concentration was above the CMC as well as just about at the maximum spreading coefficient for this surfactant. The stability issues of the surfactant were discussed and they collected all of their foam fire-fighting measurements in one working day, which is perfect since the APS/AA solution appears to be stable

for about 24 hours before noticeable loss of foamability occurs, Figure 88.

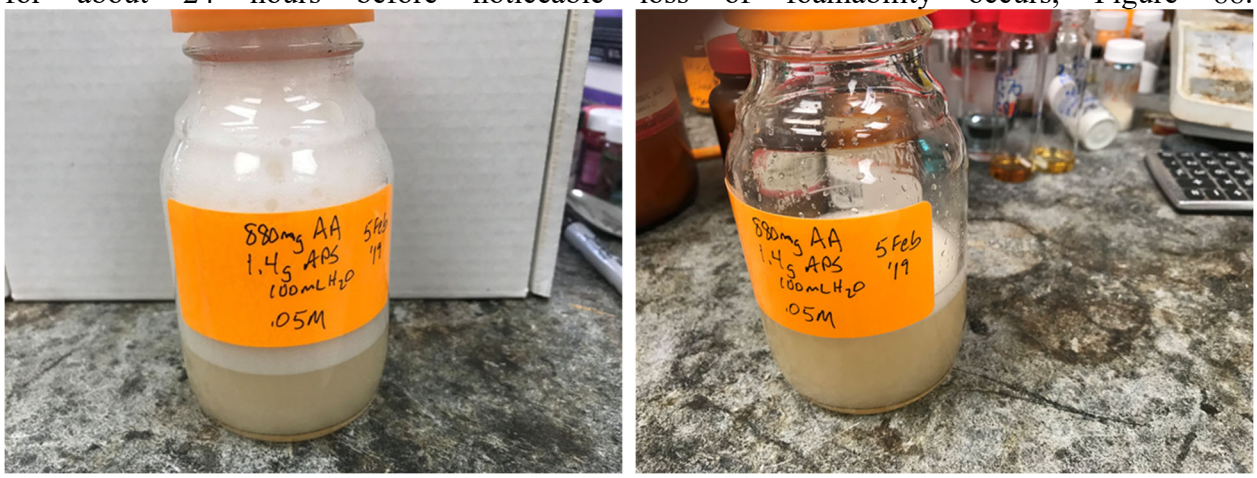


Figure 88 A test batch of 100 mL of 0.5 M APS/AA made strong foam (*left*), but had lost most of its surfactancy after 10 days of room temperature storage (*right*).

In the NRL apparatus the APS/AA surfactant solution appeared to generate a quality foam, and the experiments were started with a foam flow rate of 400 mL/min. Unfortunately, a very small coverage was observed (15–20% in 90 sec) and no extinction occurred. Next, the flow rate was increased to 1500 mL/min. The amount of coverage increased (75% in 90 sec) but again no extinction of the fire. Finally, the flow rate was increased to the highest rate possible, 2500 mL/min and still there was incomplete coverage without extinction of the fire. These observations along with expansion ratio data are summarized in Table 10. Some photographs of these experiments with APS/AA and along with the RefAFFF are shown in Figures 89 and 90.

Table 10 Heptane pool fire suppression by Siloxane foam formed from a mixture of 3-aminopropylmethylbis(trimethylsiloxy)silane (APS) – L-ascorbic acid (AA)

Foam Flow Rate	% Coverage	Expansion Ratio
402 mL/min	15-20%/90sec	6.7
1502 mL/min	75%/90sec	8.0
2508 mL/min	60%/60sec	6.4

Figure 89 0.05 M APS/AA Foam Flowing onto Heptane Pool-Fire at 1500 mL/min

Figure 90 Ref AFFF foam flowing onto heptane pool fire at 1500 mL/min which extinguished the fire in just 12 seconds at this rate.

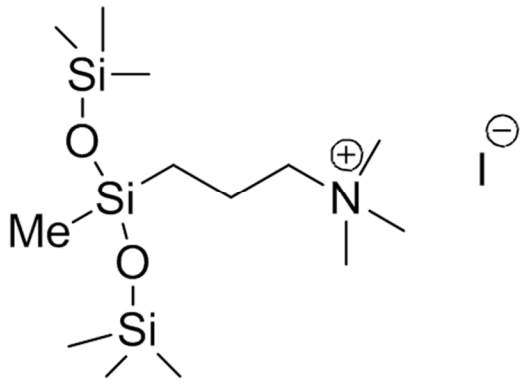
The NRL team also measured surface and heptane-interface tension measurements on the 0.05 M APS/AA. The APS/AA solution surface and heptane-interface tension measurements were 18.9 mN/m and 0.5 mN/m, respectively, by Du Noüy ring tensiometer. Calculating spreading coefficient using a literature value for heptane shows that the APS/AA has a positive number and should theoretically spread on this hydrocarbon:

$$S = 20.14 \text{ mN/m} - 18.9 \text{ mN/m} - 0.5 \text{ mN/m} = +0.74 \text{ mN/m}$$

The NRL team had experience with other siloxanes which did not have such low values for surface tension. With regard to the extinction result, it may be that the APS/AA foam may have an issue with rapid degradation particularly in the presence of hot heptane vapors. We hope to have the chance to measure the loss in surface tension of the APS/AA surfactant over time and understand what exact chemical changes are happening to the components. Such an understanding may lead to an explanation for the poor results in the heptane pool fire test.

Quaternary Ammonium Salts of APS

Discovering such low spreading coefficients with the APS/AA surfactant led to further literature searches of siloxane based surfactants. The work of Bela Prokai on cationic salts for fire fighting was very interesting and included compounds that were quaternary ammonium salts of APS, Figure 91.[40]



7 minute foam duration on gasoline

4 hour film duration on gasoline

Figure 91 Prokai patent describing quaternary ammonium salts of APS and details mentioned about their foams.

The 1972 patent did not include surface tension or surface spreading measurements for their ammoniumalkylsiloxanes, however it did mention intriguing data such as a 7 minute duration of the foam on gasoline and a 4 hour duration of a film on gasoline. Unfortunately, 3-(dimethylamino)propylmethylbis(trimethylsiloxy)silane was not a commercial product because using it to make quaternary salts would have been very easy. Prokai described synthesizing their salts by the platinum-catalyzed hydrosilation reaction of bis(trimethylsiloxy)methylsilane and N,N-dimethyl-allylamine, a reaction we had mixed results with and wanted to avoid. But since we had APS available, it was decided to try to quaternize the amine by reaction with iodomethane, Figure 92.

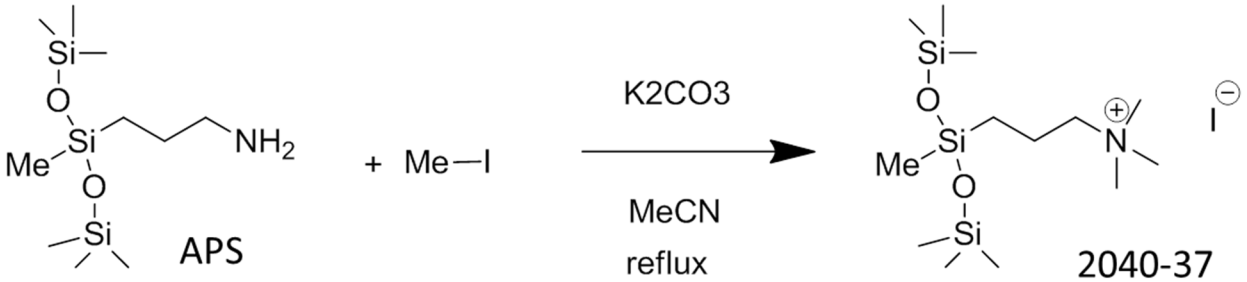


Figure 92 Synthesis of 2040-37 by quaternization of APS, product was mentioned in the Prokai patent.

There were concerns that the hydroiodic acid by-product might hydrolyze the siloxane head group. A mixture of APS in acetonitrile was refluxed in the presence of 3 equivalents of potassium bicarbonate and 6 equivalents of iodomethane. The base was necessary to neutralize the 2 equivalents of by-product hydroiodic acid. After refluxing two hours, the mixture was filtered and rotary evaporated. The residue still contained inorganic salts and so was taken up in acetone and filtered a second time. Then rotary evaporation gave the product as a white solid requiring no further purification. Proton NMR in deuterochloroform showed that the compound was indeed the desired trimethyl ammonium salt, with a singlet integrating to 9 protons at ~ 4 ppm, Figure 93. The carbon-13 NMR spectra also showed that a new carbon signal had formed, presumably the methyl groups of ammonium at 69.51 ppm.

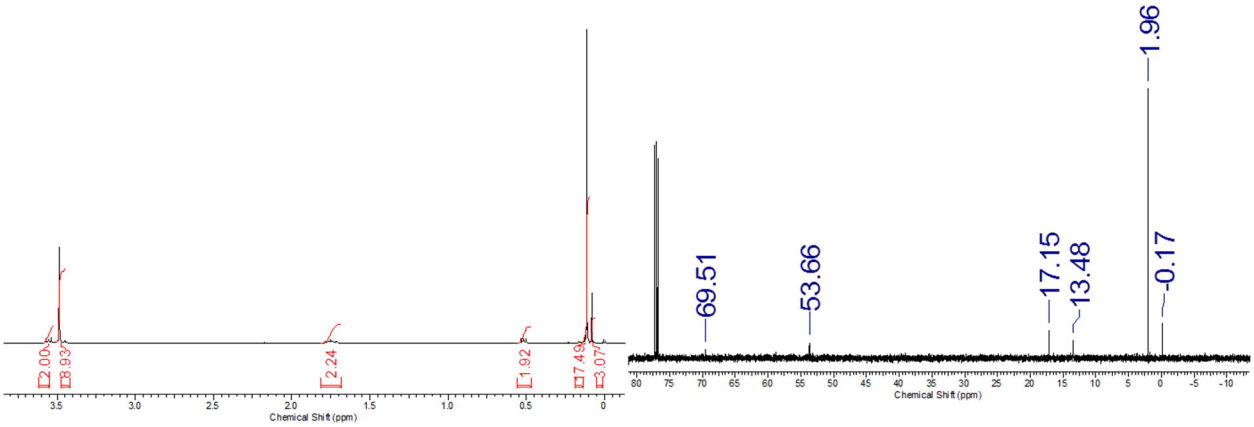


Figure 93 NMR spectra of APS quaternary salt 2040-37.

The salt which will be referred to as 2040-37 had good solubility in organic solvents: toluene, hexanes, water, THF, acetonitrile, ethyl acetate, ether, methanol, methylene chloride, and dimethoxymethane. It would recrystallize from several of these solvents the best of which were cyclohexane, hexanes and toluene. The salt would also dissolve in water to a certain extent and made a foaming solution although it did not appear to be either as strong or long lasting as APS/AA, Figure 94. We also obtained an X-ray crystal structure of the product grown from water, Figure 95.

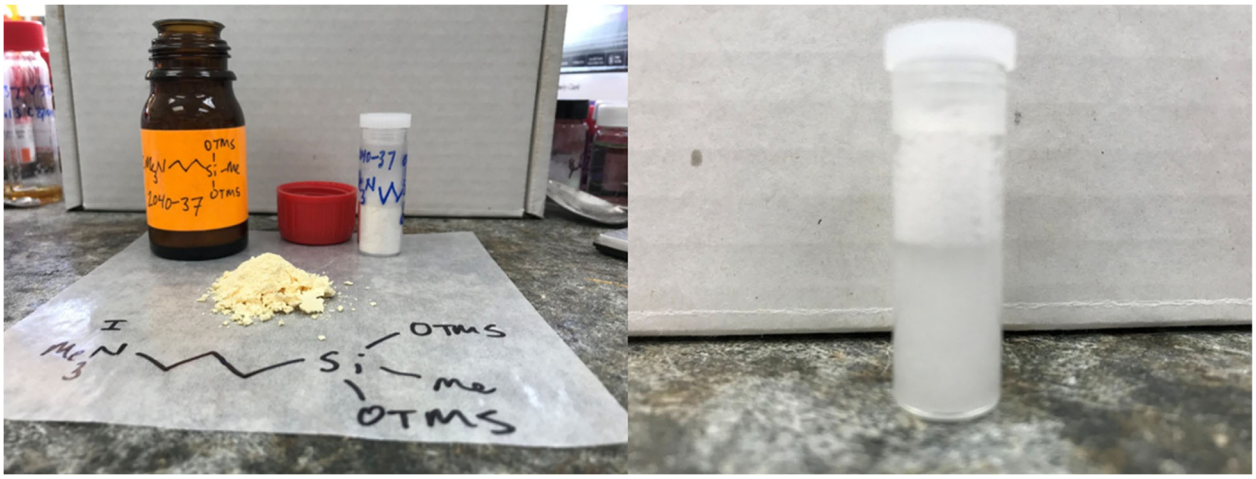


Figure 94 Quaternary ammonium salt 2040-37 of APS from reaction with iodomethane, makes foaming solution in water.

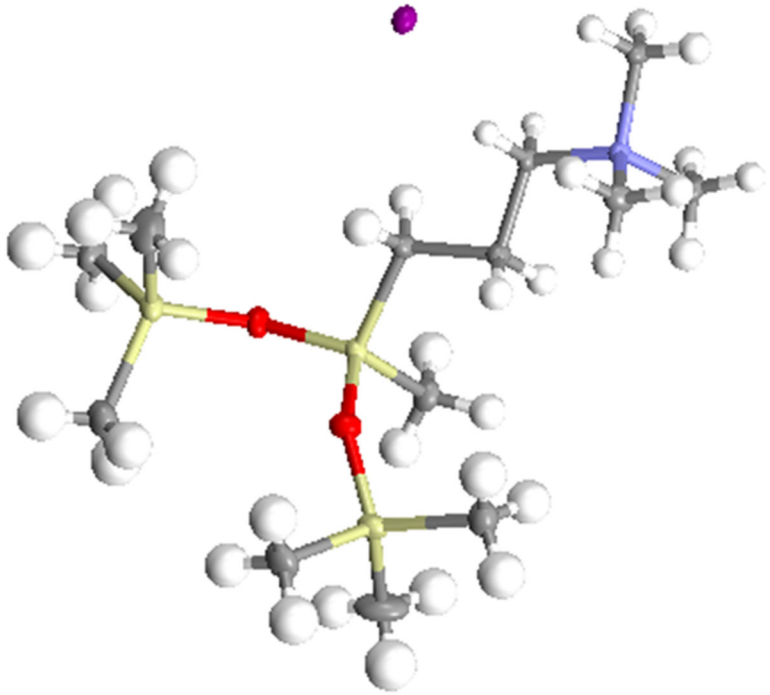


Figure 95 X-ray crystal structure of the iodide salt 2040-37, yellow = silicon; grey = carbon; blue = nitrogen; red = oxygen; white = hydrogen; iodine = magenta.

Owing to the data reported by Prokai in the patent, we decided to collect surface tension measurements on 2040-37 by the hanging drop method. We found the interfacial surface tension in air for a 0.002 M solution of 2040-37 to be about 32 mN/m. This corroborated a literature report found afterwards by Schmaucks et al. who measured 2040-37 to have 30.7 mN/m in air at 0.002 M concentration.[41] This inadvertently showed that the hanging drop method we were using to measure the surface tension was fairly accurate and was close to data obtained by the conventional de Noüy ring method. In the Schmaucks et al. report they synthesized 2040-37 in the same manner as Prokai by platinum catalyzed hydrosilation of N,N-dimethylallylamine with methylbis(trimethylsiloxy)silane. The quaternization reaction of APS is a much easier method to make this compound. We did not have time to measure the spreading coefficient of 2040-37 by the hanging drop method. However, it probably will not be quite as good at spreading on cyclohexane as APS/AA (20.5 mN/m) since the interfacial surface tension of 2040-37 was only 32 mN/m.

We also tried to quaternize APS using bromoethane since the counter ion may have some importance in surfactant properties. Following the above method, a mixture of APS and 6 equivalents of bromoethane and 3 equivalents of potassium carbonate was refluxed in acetonitrile, Figure 96.

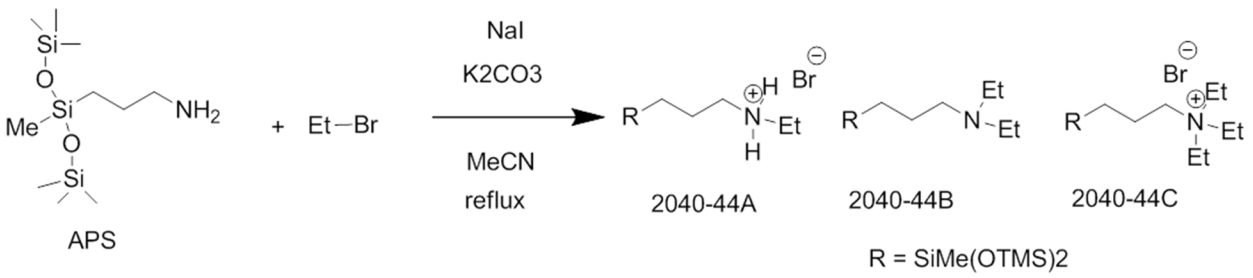


Figure 96 Quaternization reaction of APS with bromoethane and products isolated.

There was also about 100 mg of sodium iodide in the reaction mixture to get Finkelstein displacement to iodoethane and speed up the reaction. It was noted that after about 20 minutes, there was vigorous foaming in the reaction mixture that led to poor refluxing. Since there was so much foam present, it was thought that the reaction had gone to completion very quickly or had gone to something else altogether. Thus, the reaction was cooled down and rotary evaporated. The crude white solid was slurried with hexanes and filtered. To our surprise, the proton NMR of the white solid product was the hydrobromide salt of the N-ethyl-APS compound 2040-44A, Figure 97.

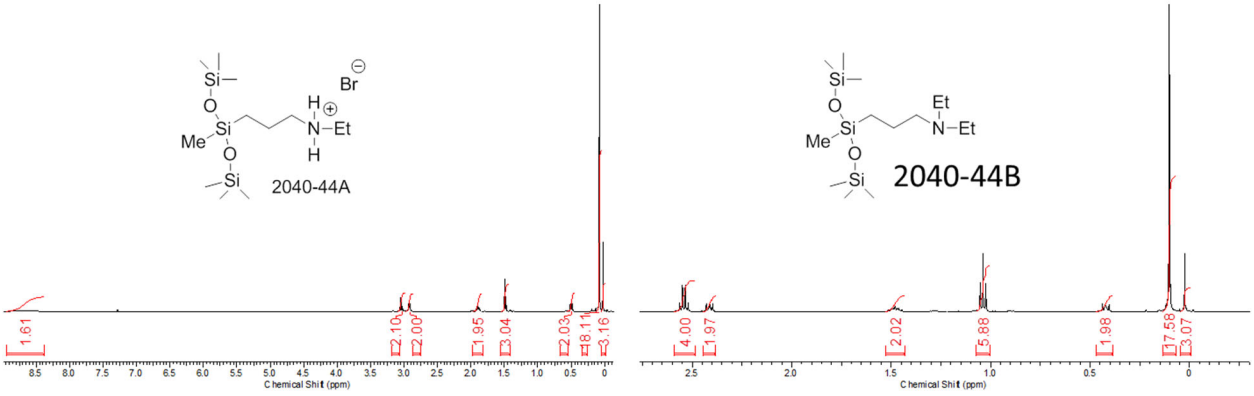


Figure 97 Proton NMR spectra of N-Ethyl-APS hydrobromide salt (*left*) and N,N-diethyl-APS by brief reaction of APS with bromoethane in acetonitrile.

Obviously, the reaction had not gone long enough. Indeed, evaporation of the hexanes filtrate gave a colorless oil that when analyzed by ^{1}H NMR was an exact match the neutral N,N-diethyl-APS compound 2040-44B. Apparently, the bromoethane is a weaker alkylating agent that would require more time to achieve quaternization. Interestingly, the hydrobromide salt 2040-44A gave respectable foam when dissolved in water and shaken well. Also, the neutral diethylamine 2040-44B would also make a surfactant solution was mixed in water with one equivalent of ascorbic acid, Figure 98.

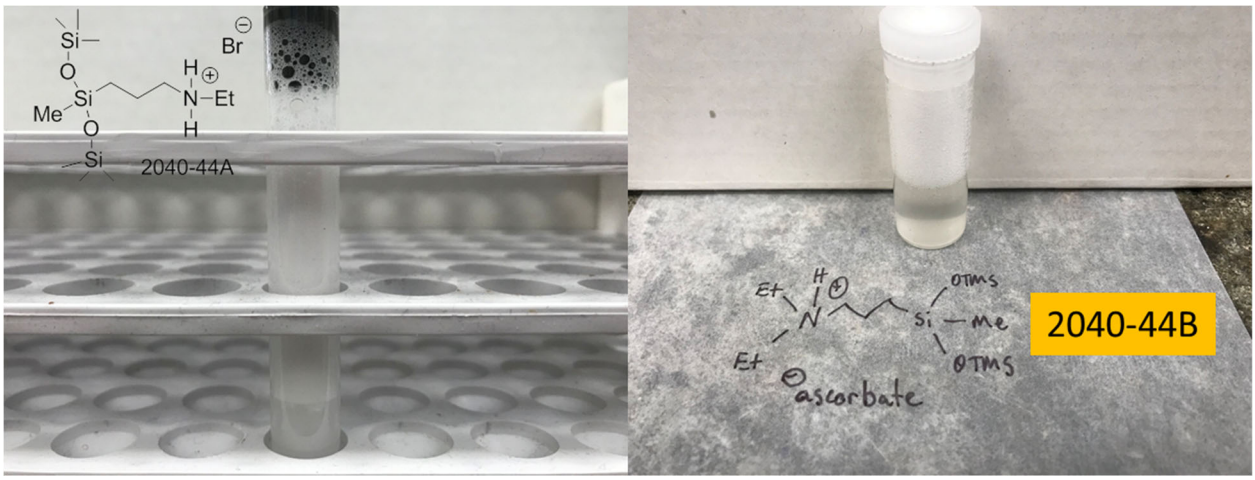


Figure 98 Hydrobromide salt 2040-44A was a surfactant in water and so was 2040-44B after protonation with ascorbic acid.

The reaction was repeated a second time with only 3 equivalents of bromoethane and 1.5 equivalents of potassium carbonate and stirred at room temperature for 48 hours. These conditions gave the desired triethyl ammonium salt of APS, Figure 99. Apparently the first reaction did not proceed long enough but also the refluxing probably only exacerbated the foaming nature of the intermediate alkylated species. There was not enough time left on the project to obtain surface tension data on these compounds. The bromoethane monoalkylation reaction on APS might allow for synthesizing quaternary salts of APS with two different alkyl groups on the nitrogen atom, which can impact the characteristics of surfactants.

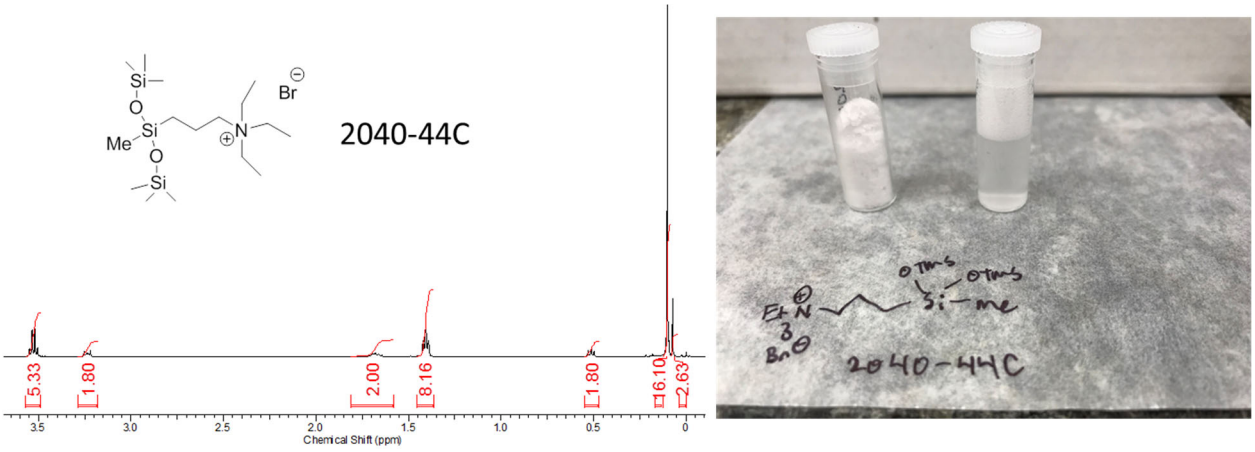


Figure 99 Successful synthesis of the triethylammonium salt of APS, its ^{1}H NMR spectra and the product made good foam in water solution.

However, the Schmaucks et al. paper also measured quaternary salts of 3-aminopropyltris(trimethylsiloxy)silane (APS4) which are tetrasiloxanes and these had better surface tension values than the trisiloxane 2040-37. For the dimethylethyl bromide salt, they measured an interfacial surface tension of 17.9 mN/m at 0.0024 M, Figure 100. They also mentioned that the tetrasiloxane compounds had better foamability than di- and tri-siloxanes they tested.

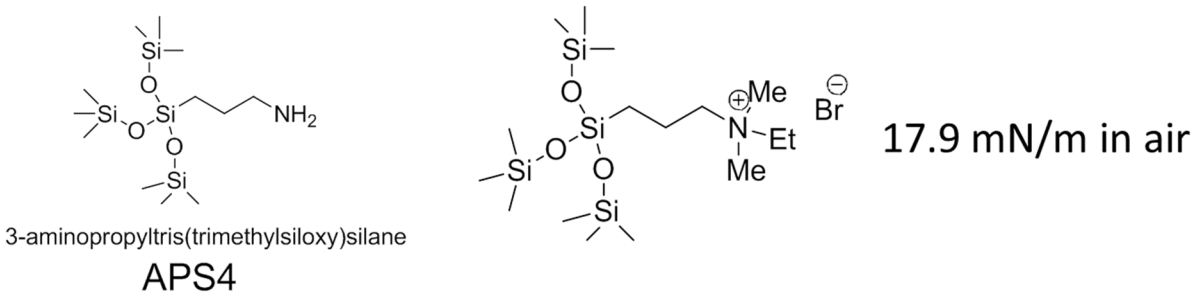


Figure 100 The tetrasiloxane APS4 and the Schmaucks et al. quaternary ammonium salt of APS4 with very low surface tension in air.

It was thought that we might be able to make these quaternary ammonium salts of APS4 by our method using alkyl halides and base, rather than the platinum-catalyzed hydrosilylation reaction. The APS4 reagent was purchased from Gelest and the quaternization with iodomethane was attempted, Figure 101.

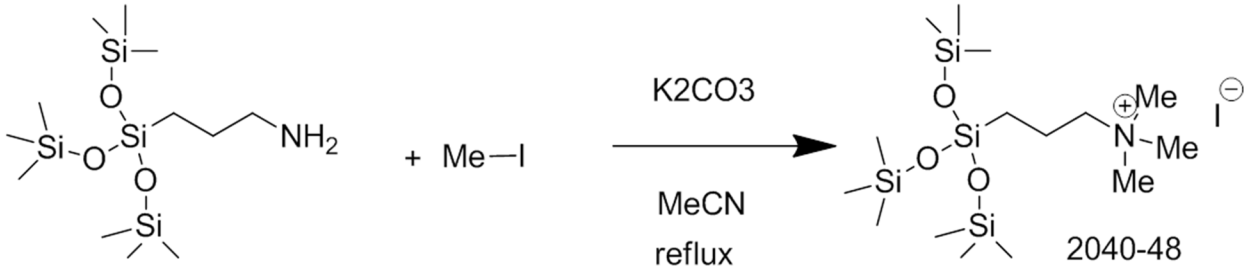


Figure 101 Synthesis of the APS4 trimethyl ammonium iodide salt 2040-48.

After the usual work up, the solid was slurried with hexanes and filtered to give the desired product. The proton and carbon-13 NMR spectra were consistent with the product, Figure 102. The compound had good solubility in organic solvents much like 2040-37.

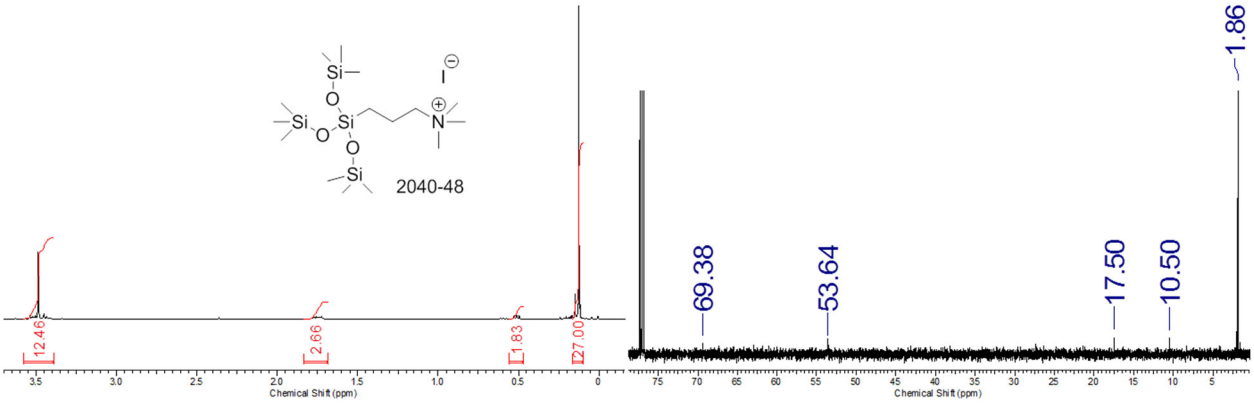


Figure 102 NMR spectra of quaternary APS4 2040-48 in $CDCl_3$.

It was more difficult to recrystallize however as it did not precipitate from various organic solvents as nice quality crystals. The compound did make a slightly better appearing foam in water, Figure 103. We later found a 2016 patent report mentioning this compound which they synthesized by

quaternization of APS4 in a similar manner as described here, but using DMF as solvent and sodium carbonate as base.[42] Unfortunately, we did not have time to measure surface tension of 2040-48.

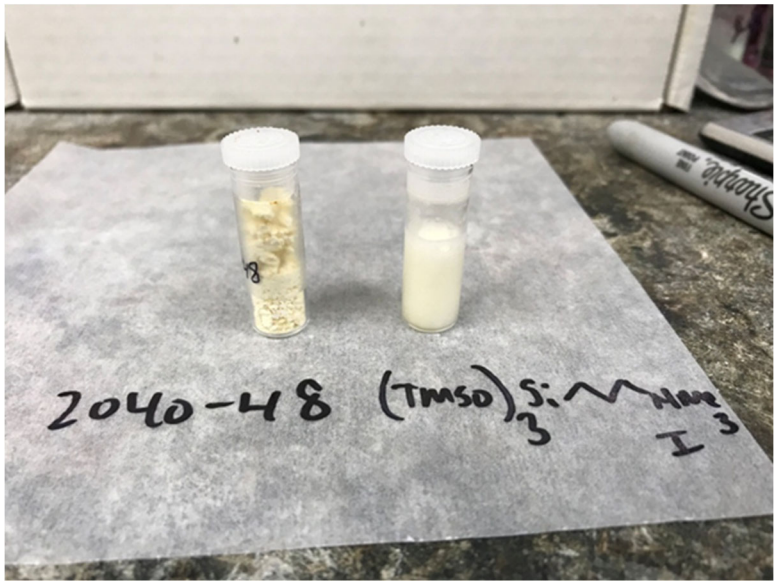
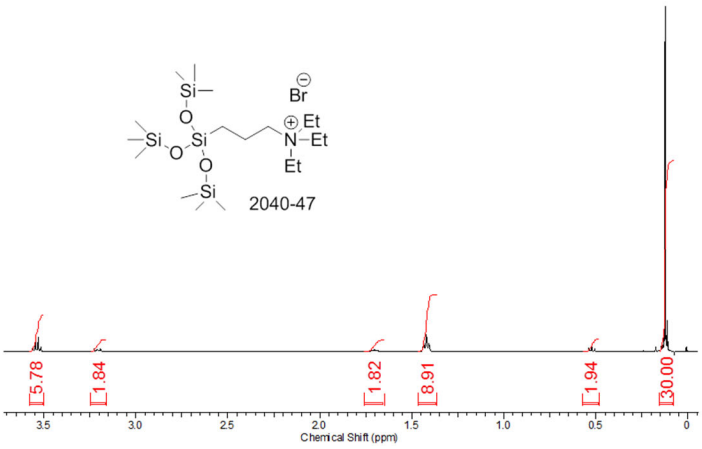


Figure 103 The APS4 quaternary salt 2040-48 was soluble in water and made strong foam.

The quaternization of APS4 with bromoethane was also attempted with 6 equivalents of bromoethane and 3 equivalents of potassium carbonate. After 24 hours, the reaction was worked up and gave a mixture of desired quaternary salt and the tertiary amine as evidenced by proton NMR, Figure 104. The reaction probably needed to continue longer to achieve complete alkylation. However, the crude product was slurried with hexanes and filtered. The insoluble white solid was the pure quaternary salt (2040-47) which appeared to be a new compound that is unreported in the chemical literature. The filtrate, after evaporation, contained the neutral tertiary amine. So it appears that this reaction could be used to synthesize APS4 quaternary salts with two different alkyl groups. Although 2040-47 gave a strong foam in water, there was not enough time to collect surface tension data on the material.



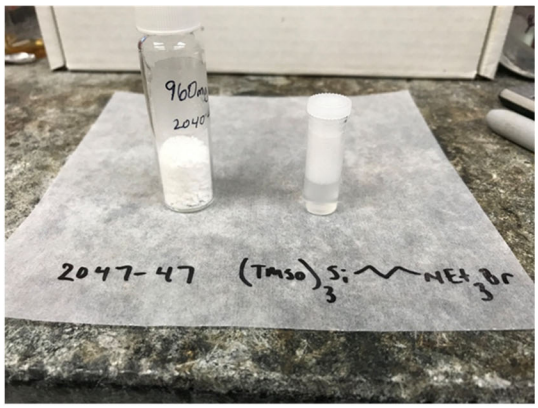


Figure 104 Proton NMR spectra of APS4 triethylammonium bromide salt 2040-47, it made good foam in water.

Formulation of APS/Lactobionic acid Salt into Foam Concentrate

It was anticipated that the formulation of any of the APS/carboxylic acid salts or APS ammonium salts would require a potent hydrocarbon surfactant to achieve the necessary foamability. This is always the case in AFFF formulations because the PFAS and PFOA fluorinated surfactants do not create very long lasting or strong foam themselves. Contact was made with BASF from which a sample of their Glucopon 215 alkylglycoside surfactant was obtained, Figure 105.

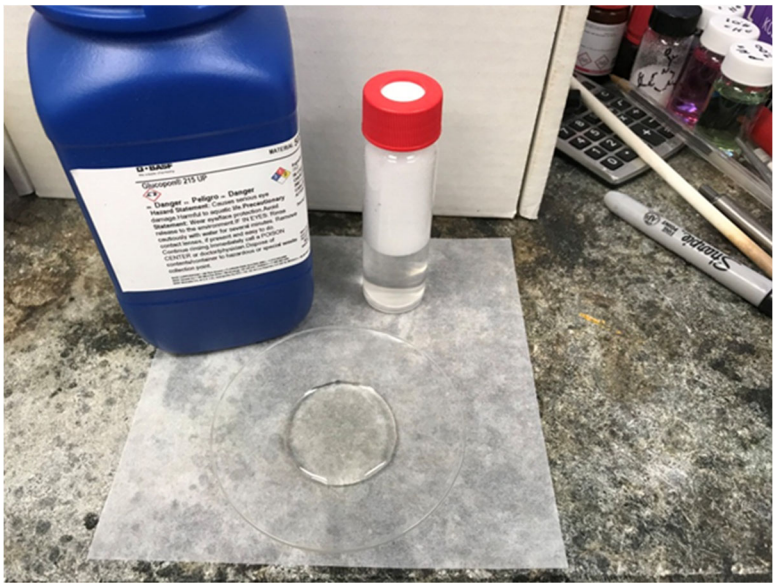


Figure 105 Glucopon 215, a non-ionic, alkylpolyglycoside manufactured by BASF. These strong foaming agents are often used in AFFF to enhance their foamability.

A test formulation of APS/lactobionic acid surfactant was made which also included Glucopon 215, 2-butoxyethanol in water. The lactobionic acid and Glucopon 215 were dissolved in water first which made a good strong foaming mixture. Then the 2-butoxyethanol and APS were added and immediately upon mixing all of the strong foam characteristic disappeared. Allowing the mixture to stand for about 1 hour and the apparent separation of the decomposed APS was seen floating on the surface. Hetzer et al. had mentioned that the BASF surfactant was basic and they had to neutralize this in their preparations of fire fighting foams from thier glycosiloxanes.[43] Thus, it was hypothesized that the basic nature of the Glucopon 215 had caused an issue and that the APS/lactobionic acid surfactant could not form or was otherwise effected. Roxanne Quintana (NAWCWD) gave us assistance by carefully calibrating a pH-meter so that the pH of a Glucopon 215 solution in water could be made accurately. Indeed, 1.4 g Glucopon 215 in 50 mL water gave a reading of 10.92 which is very basic. By adding just 8 drops of a 1M aqueous HCl solution to this Glucopon 215/water solution gave a pH reading of 6.96. So with a method to neutralize the basicity, a second formulation of APS/lactobionic acid was attempted. The Glucopon 215 was dissolved in a portion of water and neutralized using the appropriate amount of 1M HCl. The lactobionic acid was dissolved in a portion of water, and then the APS was added to it. Then the 2-butoxyethanol was dissolved in a portion of water. Finally all the components were brought together into a single mixture and diluted with the required amount of water and a good foaming

mixture was created. The pH of the mixture was 7.35 and the solution was 0.3 wt% in APS/lactobionic acid. This concentration of APS/lactobionic acid was made based on the concentrations of surfactants in AFFF, but we later realized that these concentrations may be too low and CMC for any new surfactant must be determined. Unfortunately, this solution was only a 0.0047 M APS/lactobionic acid and was made before the CMC of APS/AA (0.023 M) was measured. Because these APS salt surfactants are probably all in a similar CMC range, the solution was one order of magnitude lower than its CMC and so not optimal for testing this surfactant against a hydrocarbon pool fire. We did not have a chance to test the formulation against a pool fire in any case.

Synthesis of Si–O–C–Sugar and Si–O–C-Amino Surfactants

There have been several reports of the synthesis of carbohydrates attached to siloxanes (glycosilicones)[44] and their use as non-ionic surfactants. These syntheses are typically multi-step campaigns including protecting group on/off steps because only one of the hydroxyl groups requires functionalization. We thought that a surfactant might be made in one step, simply by reacting a sugar with a silyl protecting group. Glucose was dissolved in pyridine and dimethylformamide and reacted with *tert*-butyldimethylsilyl chloride, Figure 106.

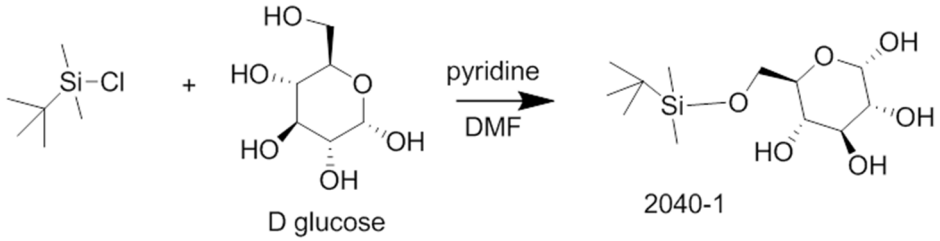


Figure 106 *Tert*-butyldimethylsilylization reaction of D-glucose.

The TBDMS-glucose (2040-1) was isolated in good yield as a white solid and was a single spot by thin-layer chromatographic analysis on silica gel eluting with ethyl acetate. The proton NMR spectrum was consistent with the desired compound but unfortunately the silylated glucose had no solubility in water, Figure 107.

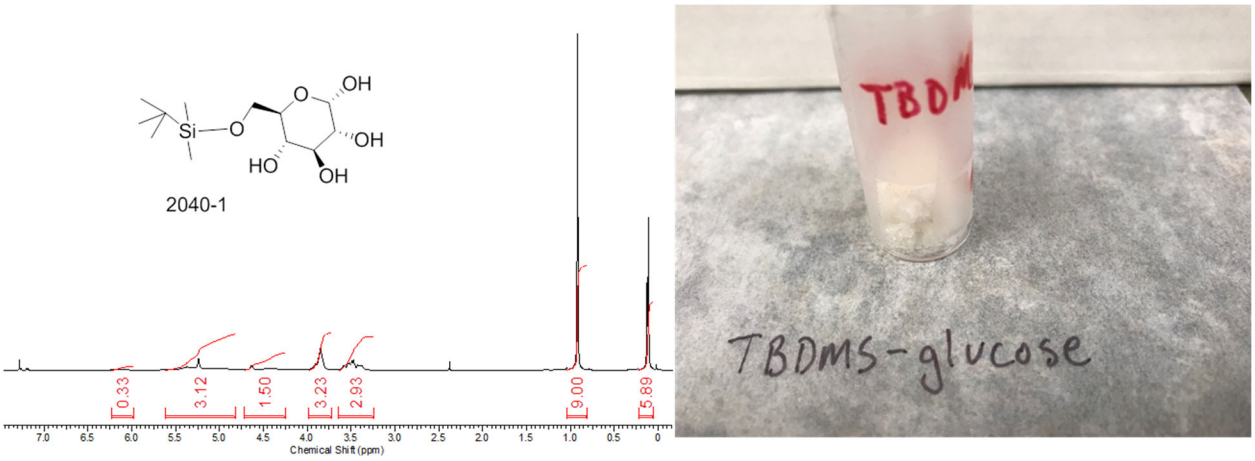


Figure 107 Proton NMR spectrum of TBDMS-glucose in $CDCl_3$, compound was insoluble in water.

Another idea was to synthesize a chlorosilylalkylsiloxane precursor that could be used to attach to hydroxy groups in a single step without any protecting groups. It wouldn't matter which hydroxy group of a sugar was functionalized, only that a single silylation had occurred which could be controlled by stoichiometry. This strategy was adapted from the work of Thompson et al. who made a slightly different compound with a disiloxane attached to the sugar.[45] The diisopropyl group was selected because this might slow down hydrolysis of the silyl ether made from the desired product. Our target molecule (2040-13) was made in a single step using the hydrosilylation reaction catalyzed by platinum, Figure 108.

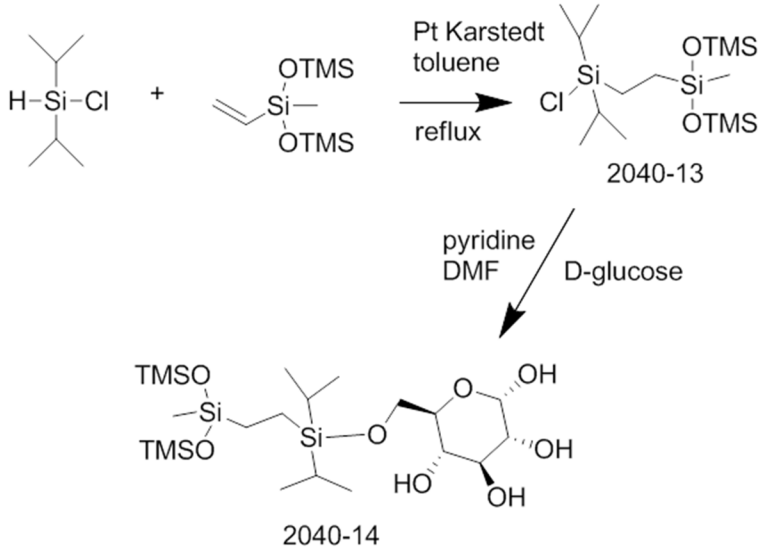


Figure 108 Hydrosilylation of vinylsiloxane and diisopropylchlorosilane and then silylation of glucose.

This reaction worked well and there was no trouble synthesizing the reagent which was an oil. Glucose was chosen as the first sugar to be silylated with 2040-13 in a mixture of pyridine and DMF. We were able to isolate the desired product 2040-14 after chromatography on silica gel eluting with ethyl acetate, Figure 109. The product 2040-14 was a colorless, viscous oil which had no solubility in water. Apparently the other 5 free hydroxyl groups were not sufficiently polar to impart surfactant properties to the compound.

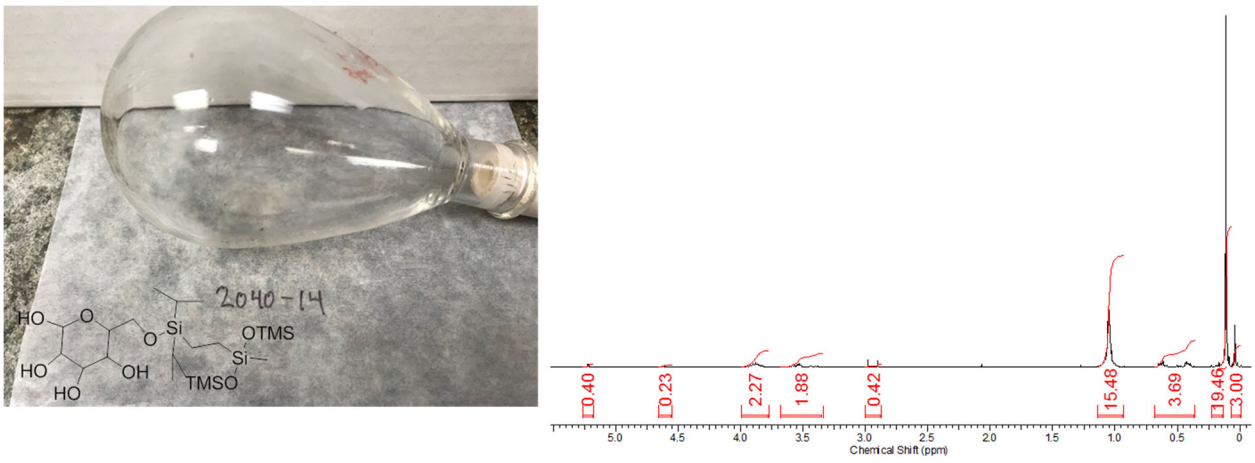


Figure 109 Product from attachment of chlorosilyl linker 2040-13 to glucose, was not soluble in water however.

It was thought that if the silylalkylsiloxane 2040-13 was too non-polar, then the polar head group might have to be much stronger, perhaps an ammonium salt. Choline is a well known natural product that is a quaternary ammonium salt, used by higher organism for cell membrane construction and many other functions. Therefore, it was decided to make a choline-like compound from the silylalkylsiloxane in the manner shown below, Figure 110.

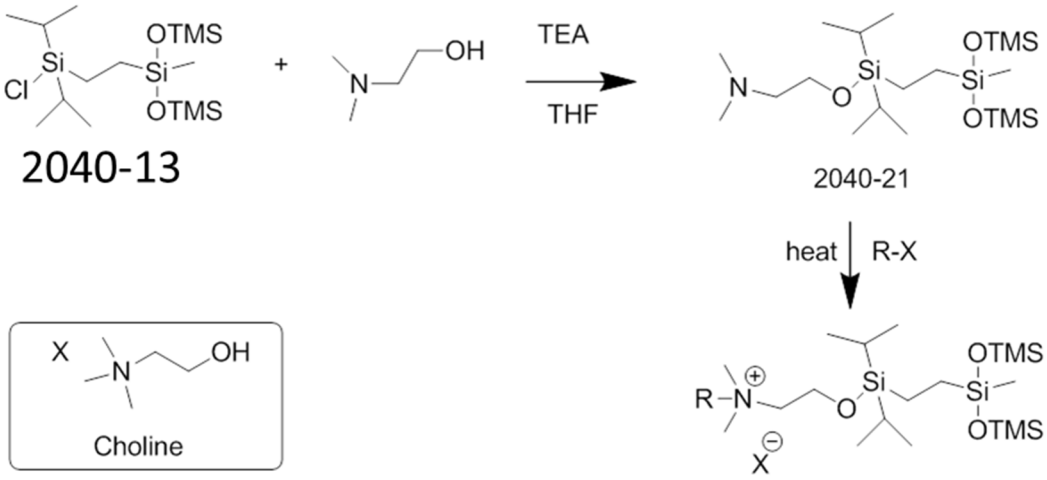


Figure 110 Synthesis of the aminosiloxane 2040-21, a sort of analog of the natural product choline.

There was no problem in the coupling of the dimethylethanolamine with the silyl chloride 2040-13, and the unreported aminosiloxane 2040-21 was obtained as an oil whose NMR looked perfect, Figure 111.

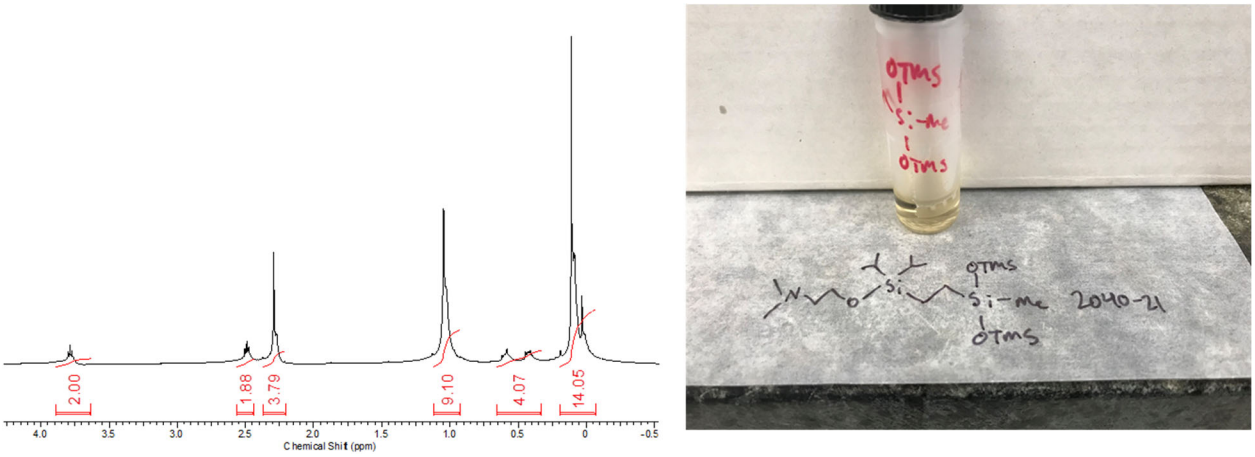


Figure 111 Aminosiloxane 2040-21 and its proton NMR spectra in $CDCl_3$.

Unfortunately, we ran out of time to run quaternization reactions of 2040-21 with alkyl halides, similar to reactions with APS. Although 2040-21 was not soluble in water, after adding one equivalent of ascorbic acid, a surfactant solution was generated with good foam, Figure 112. So,

2040-21 appears to behave in much the same manner that APS does in the presence of AA. So the hypothesis that ammonium ion would be strong enough to cancel out the effect of the non-polar diisopropylsilyl moiety appeared valid. We did not have time to collect interfacial surface tension on the 2040-21/AA surfactant mixture. We also wanted to try to attach 2040-21 onto choline itself but ran out of project time.

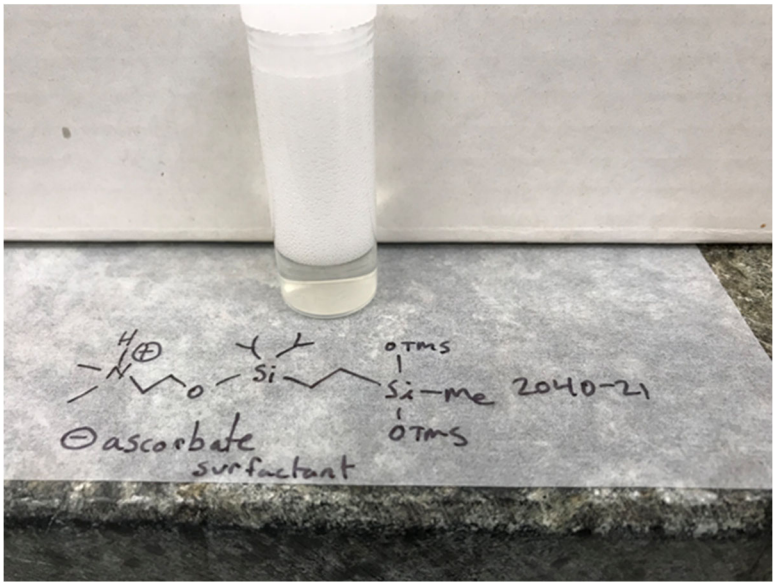


Figure 112 Good foaming behavior in water from the ascorbic acid salt of the new aminosiloxane 2040-21.

It was thought that a second generation derivative with only methyl groups on the silylchloride linker might be even better since it would be less non-polar. This idea was based on the theory that that two diisopropyl groups of 2040-21 had too much non-polar character. There was also no difficulty in the coupling reaction of the vinyl trisiloxane with dimethylchlorosilane to make the new derivative (2040-20), Figure 113. However, the project came to a close before we had the opportunity to attach 2040-20 to carbohydrates or the 2-N,N-dimethylaminoethanol.

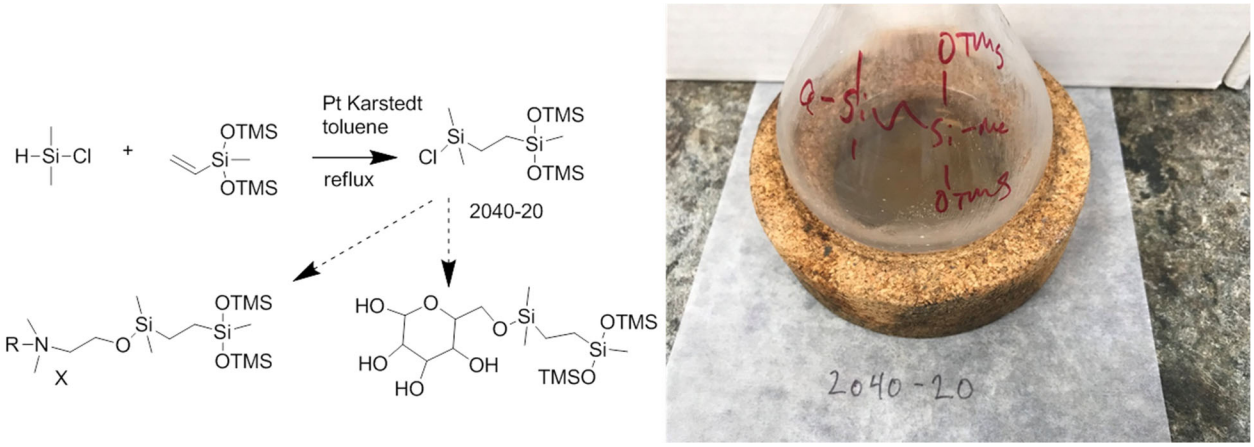


Figure 113 Successful hydrosilylation of vinylsiloxane to make 2040-20 with the smaller, dimethylchlorosilane; further planned syntheses.

Conclusion and Implications for Future Research

A POSS surfactant was made by PEGylation of an incomplete isobutylPOSS, having three PEG chains of 550 molecular weight on three corners of the silicate cage. Indeed, the compound was water soluble but had only weakly decreased the surface tension in air (48 mN/m). The PEGlyated POSS had an interfacial surface tension versus cyclohexane of 18.49 mN/m. These data were used to calculate its spreading coefficient which was –49.8 mN/m which was well below +3 mN/m specified by MIL-F-24385F. If the hydrocarbon content of the POSS cage could be decreased by starting with the incomplete methylPOSS, then a PEGylated POSS with better surfactant character would likely by realized. However, such a starting POSS compound was not commercially available and it was difficult to synthesize although it is known in the literature. In addition, the platinum-catalyzed hydrosilation reaction was somewhat challenging, at least when a POSS was involved. Owing to these issues and the short duration of the project, other chemistries within the purview of silicon-containing compounds were explored.

A high-risk idea came up during the project which was a perfluoromethyl POSS compound made into a surfactant, Figure 114. Such a compound would have 21 fluorine atoms and may behave with omniphobicity in the same manner as PFOS or PFOA. However, perfluoromethylPOSS could eventually undergo hydrolysis in the environment to small trifluoromethylsilanetriol molecules. The latter might have low persistence unlike the long-chain perfluoroalkyl AFFF compounds.

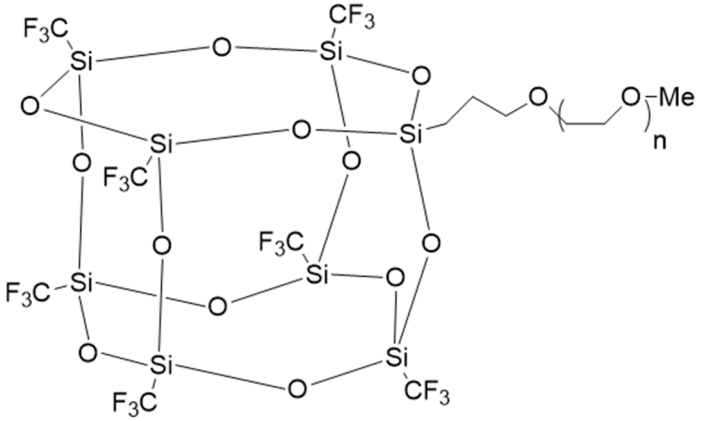


Figure 114 A perfluoromethyl-PEGylated-POSS might be a good fire-fighting surfactant that could breakdown to less hazardous trifluoromethylsilanetriol ($CF_3Si(OH)_3$).

AminopropylisobutylPOSS was successfully derivatized with gluconic acid lactone but the product was not soluble in water. This also demonstrates that there must be a large hydrophilic groups to overcome the very non-polar character of the heptaisobutylPOSS cage. Again, if the isobutyl could be replaced with methyl groups water solubility may have been better. Not surprisingly, the aminopropylisobutylPOSS did not form a water soluble salt with weakly acidic ascorbic acid. We were able to obtain metathesis products from reaction of the water soluble octa(tetramethylammonium)POSS (OTMAP) with other tetraalkylammonium salts in water. The lowest surface tension in air (37.5 mN/m) from the three salts we tried was a 1:1 mixture of OTMAP and dodecyltrimethylammonium bromide. We also were able to do a similar exchange with of OTMAP with phosphonium salts, tetrakis(hydroxymethyl)phosphonium chloride

(THMPCl) and tetrabutylphosphonium hydroxide (TBPOH). Unfortunately, the reaction with THMPCl gave immediate generation of hydrogen gas from decomposition of the phosphonium salt. When OTMAP and TBPOH were mixed in a 1:8 ratio, respectively, a solid precipitate formed which was likely the completely exchanged octa(tetrabutylphosphonium)POSS complex which did not have good solubility in water. The corresponding tetramethylphosphonium salt might have better solubility in water however, the tetramethylphosphonium hydroxide was not a commercial product.

Two sugar acid amides from 3-aminopropylmethylbis(trimethylsiloxy)silane (APS) and gluconic and gulonic acid lactones, the latter from L-ascorbic acid reduction. The APS gluconamide was water soluble and made a foaming solution but interestingly the isomeric APS gulonamide had very poor water solubility and did not make any foam. This inadvertently demonstrated that the structure of the sugar can have an enormous impact on the physical properties of a surfactant.

Strong surfactants could be made from stoichiometric neutralization of APS with simple carboxylic acids. The salt of APS and ascorbic acid was measured by pendant drop tensiometry and had a positive spreading coefficient on cyclohexane of + 4.6 mN/m and CMC of 0.05 M. The surfactant also had a spreading coefficient of +0.74 mN/m on heptane by de Nüoy tensiometry. Unfortunately, this surfactant system was not stable and slowly deteriorated over 7 days, resulting in a two-phased mixture with water on top or bottom depending on the original concentration of the surfactant. Nevertheless, the surfactant was tested against a 19 cm heptane pool fire but no extinction occurred at any flow rate (400–1500 mL/min). This result was disappointing since tensiometry seemed to suggest the surfactant would form a layer. It might be that the hot heptane vapors could have increased the rate at which the surfactant decomposed. It should be noted that APS/ascorbic acid surfactant was not mixed with other ingredients (e.g. hydrocarbon surfactants, solvents, buffers) to help increase foamability and perhaps stability of the system. Our NRL colleagues agree that more study of the APS-type surfactants could lead to some fire-fighting foam hits.

We had been under the impression that surfactants with positive spreading coefficients on cyclohexane, would likely be able to extinguish hydrocarbon pool fires. This hypothesis was incorrect at least as far as the APS/AA system showed. Considering all the careful experiments and expensive instruments that are necessary for collecting tensiometry data, maybe a simple empirical test of a large sample of various surfactants against pool fires might be a useful method to identify new lead surfactants. There are so many more surfactants available since the early days of foam fire-fighting research that a cheap and fast screen might uncover surfactant phenomenon that one could not predict beforehand.

The quaternary alkyl ammonium salts made from APS also appear to be lead compounds for low surface tension surfactants. For example, we found that 3-trimethylammoniumpropyl-methylbis(trimethylsiloxy)silane iodide salt had a surface tension in air of 32 mN/m. These compounds were very easy to synthesize from commercial reagents without having to carry out the platinum-catalyzed hydrosilation. By the synthetic method described here, a wide range of derivatives could be made in a ‘foam’ discovery screen (e.g. high-throughput screen) for optimal properties targeted for fire-fighting foams. Similar salts were taught as fire-fighting foam agents in a patent however time ran out before we could evaluate a few ourselves against hydrocarbon pool fires. However, because they contain the siloxane head group, they may also suffer from stability issues in water solution. To continue research with siloxanes for fire-fighting foams, it

would be prudent to develop a water stability test to ensure these materials do not hydrolyze rapidly. However, the hydrolysis of siloxane surfactants over a longer period of time would actually be beneficial from an environmental health perspective.

The chlorosilane-siloxane functionalizing group unfortunately did not make a surfactant when attached to glucose, but there are many other sugars or disaccharides to try. However, an apparent surfactant was made by ascorbic acid neutralization of the chlorosilane-siloxane covalently attached to N,N-dimethylaminoethanol. The latter compound has structural similarities with the natural product choline, used by organism as an osmoregulator. One could imagine that the chlorosilane-siloxane group, or even siloxanes, could be reacted with choline to make surfactants with low surface tensions, and possibly useful as fire fighting foams.

Blunk et al. have patented carbosilanes for use in fire-fighting foams, Figure 115.[46] It is highly likely that such compounds may have been designed so that the hydrolytic instability of siloxanes could be avoided.

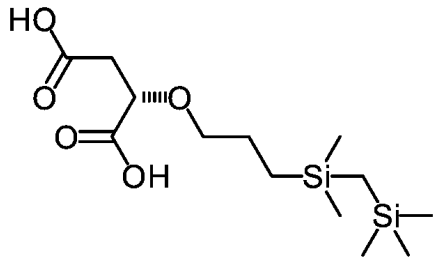


Figure 115 Chemical structure of interesting carbosilane patented for use as fire-fighting foam.

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