FINAL REPORT

Fluorine-free Ionic Liquids for Aqueous Film Forming Foam

SERDP Project WP18-1630

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List of Acronyms

Acronym	Expanded Form
AFFF	Aqueous Film Forming Foam
COD	Chemical Oxygen Demand
DoD	Department of Defense
EPA	Environmental Protection Agency
FFFC	Fire Fighting Foam Coalition
MMI	Materials Modification, Inc.
NMR	Nuclear Magnetic Resonance Spectroscopy
NRL	U.S. Naval Research Laboratory
OECD	Organization for Economic Co-operation and Development
PFAS	Per/polyfluoroalkyl substances
PFOA	Perfluorooctanoic Acid
PFOS	Perfluorooctanesulfonic Acid
PI	Principal Investigator
POC	Point of Contact
SERDP	Strategic Environmental Research and Development Program
SON	Statement of Need
WP	Weapons Systems and Platforms

Keywords

AFFF, Biopersistance, C-8, Fire, foam, fuel, Ionic Liquids, PFAS, PFOA, PFOS, Siloxanes.

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Abstract

Objective:

The Department of Defense is in need of a fluorine-free Aqueous Film Forming Foam (AFFF) fire suppression solution due to the current/pre-existing AFFF technology containing fluorine products that are toxic to both the environment and military personnel. In this project, Materials Modification, Inc. (MMI) investigated and developed a fluorine-free ionic liquid for use in AFFF solutions that can potentially meet the performance and toxicity levels of the MIL-F-24385F standard.

Technical Approach:

Ionic liquids are non-toxic or "green" and can be tailored to various applications based on synthesis procedures and their functional groups. MMI developed a low surface tension, fire quenching, and fluorine-free ionic liquid that produced stable foams when combined with trisiloxane surfactants. MMI assessed the feasibility of using ionic liquid (IL) chemicals for AFFF applications through lab-scale benchtop trials using controlled fire environments. The developed AFFF solution was also be evaluated under standardized conditions according to the MIL-F-24385F standard for fire suppression and toxicity.

Results:

Novel ionic liquid surfactants were synthesized and tested for their AFFF capabilities. Ionic liquid surfactants have the potential to produce AFFF solutions when mixed with trisiloxane surfactants. Ionic liquids enhanced the foam spreading and fire extinction properties of trisiloxane surfactants, possibly through the Marangoni effect. The new ionic liquid surfactant-based formulations were able to quench the benchtop gasoline fuel pool fires <30 seconds. Further optimization of ionic liquid/trisiloxane formulations could yield a fluorine-free formulation that can replace current AFFF.

Benefits:

Ionic liquid-based Aqueous Film Forming Foam (AFFF) system developed in this effort can be used to rapidly quench fires as well as provide an insulating coating on extinguished surfaces for quick recovery action. This system will be particularly useful for military application for recovery of sensitive equipment, materials and will also be useful in the commercial and industrial sector (firefighters, hazmat personnel, and first responders).

Executive Summary

Aqueous Film Forming Foam (AFFF) solutions are water-based formulations that contain fluorosurfactants such as perfluorooctanoic acid (PFOA) and/or perfluorooctanesulfonic acid (PFOS) as critical additives as the fire suppressing agents. Due to the low surface tension properties of the fluorosurfactants, the AFFF solutions can quench the incendiary conditions by producing foam that has high chemical and thermal stability. The fluorosurfactants dubbed as "forever chemicals" have an increased risk for cancer (liver and reproductive), high cholesterol, and thyroid disorders in humans. The U.S. Environmental Protection Agency's (EPA) 2010/2015 PFOA Stewardship Program ended the production of "C-8" and other longer-chain fluoro compounds. Therefore, there is a critical and urgent need for a fluorine-free AFFF solution that meets the performance levels of the MIL-F-24385F standard without toxicity and biopersistence.

Ionic liquids are non-toxic or "green" and are unique in their performance because of their ability to modify with a variety of functional groups. In this project, low surface tension fluorine-free ionic liquid surfactants were synthesized, and their potential to produce firefighting foams with trisiloxane surfactants was demonstrated. Ionic liquids enhanced the foam spreading and fire extinction properties of trisiloxane surfactants. Further optimization of ionic liquid/trisiloxane formulations could yield a fluorine-free formulation that can replace current AFFF.

Introduction

The Strategic Environmental Research and Development Program (SERDP) requires a fluorine-free Aqueous Film Forming Foam (AFFF) fire suppression solution due to the current AFFF technology containing fluorine products that are toxic to both the environment and military personnel. AFFF solutions generally contain perfluorooctanoic acid (PFOA) and/or perfluorooctanesulfonic acid (PFOS), where the inherent chemical structure includes eight (8) fluorinated carbons; this structure has been termed "C-8" fluoro-compound in the industry for short. With the elimination of production of the "C-8" and other longer-chain perfluoro compounds from the EPA's 2010/2015 PFOA Stewardship Program, the industry has transitioned to AFFF solutions with "C-6" technology but still have concerns about the materials' breakdown to other equally toxic materials [1]. Thus, SERDP is in need of a fluorine-free AFFF solution that meets the performance and toxicity levels of the MIL-F-24385F standard.

Ionic liquids are non-toxic or "green" and are unique in their performance because a variety of functional groups, including amphiphilic, can be introduced in their chemical structure. In this project, low surface tension, fire quenching, and fluorine-free ionic liquid surfactants that foam upon application to the incendiary condition were developed.

Objectives

MMI has developed fluorine-free ionic liquids for use in AFFF solutions for rapid fire suppression. Fluorine-based materials pose extreme health and safety risks for the personnel involved and the surrounding environment. Current fluorine-based AFFF solutions rely on the low-surface tension properties of the materials used to rapidly spread through the incendiary situation and create a barrier between the fire and air (the primary fuel to the fire). The fire is suppressed due to the lack of oxygen due to the seal created by the foams.

The feasibility of using a water-soluble ionic liquid (IL) component for AFFF applications was assessed through lab-scale benchtop trials using controlled fire environments. The ionic liquid foam formulation developed was also evaluated under standardized conditions according to the MIL-F-24385F standard for fire suppression and biodegradability. Future efforts will involve large-scale production of the fluorine-free ionic liquid-based AFFF solution and preparation of delivery methods for field testing.

Technical Approach

<u>Background:</u>

Aqueous Film Forming Foam (AFFF) solutions are water-based chemical solutions that have fluoro surfactant additives (such as PFOA and PFOS) as the fire suppressing agent. Due to the low surface tension properties of the fluorosurfactants [2], the AFFF solutions can quench the incendiary conditions by producing foam that has high chemical and thermal stability [3]. A visual representation of the application of an AFFF system under a controlled environment is provided in Figure 1.

Figure 1. Firefighter extinguishing a controlled fire using AFFF solution

While AFFF solutions have been used for industrial and commercial fire suppression, which must follow National Fire Protection Association (NFPA) 412 protocol, the U.S. military has been using these since the mid-1970s which must follow the MIL-F-24385 specifications on extinguishment time, environmental impact, toxicity, and corrosion rate of surfaces. 3M developed the AFFF technology in 1976, followed by Ansul, National Foam, Angus, Chemguard, and Buckeye in recent years [3,4]].

The critical additive in the currently used AFFF technology is that of fluoro-surfactants such as perfluorooctanoic acid (PFOA) and/or perfluorooctanesulfonic acid (PFOS), where the inherent chemical structure contains eight (8) fluorinated carbons; this structure has been termed "C-8" fluoro-compound in the industry for short. While these fluoro-compounds have excellent low-surface tension properties that allow them to propagate through the fire and create a barrier between the incendiary condition and the combustion fuel (oxygen from the air), they also have undesirable characteristics such as biopersistence and toxicity to the environment [1, 3]. "C-8" has an increased risk for cancer (liver and reproductive), high cholesterol, and thyroid disorders in humans [5]. The U.S. Environmental Protection Agency's (EPA) 2010/2015 PFOA Stewardship Program sought to end the production of "C-8" and other longer-chain fluoro-compounds [1] to reduce biopersistence and health risks.

Ionic liquids are organic cations, such as alkylammonium, alkyl phosphonium, alkyl sulfonium, 1,3-dialkyl imidazolium, alkyltriazolium, alkyl pyridinium, etc. Anions can be classified into two groups: (1) polynuclear, such as Al_2C_{l7}, Al_3Cl_{10}, Au_2Cl_7, Fe_2C_{l7}, $Sb_2F_{11,}$ and Cu_2Cl_3, which are generally water and air-sensitive; (2) mononuclear, which yield neutral stoichiometric salts, such as BF_4, PF_6, CF_3SO_3, $(CF_3SO_2)_2N$, CF_3CO_2 [6]. Some ionic liquids containing non-fluoroanions, such as nitrate, perchlorate, alkyl sulfate, and alkyl oligoether sulfate anions, dinitramide anion ($N(NO_2)_2$), and a variety of organic anions, have been synthesized and studied [7].

According to the MIL-F-24385 standard, the spreading parameter of AFFF on cyclohexane should at least 3 dynes/cm. Using "C-8" compounds, this can be achieved as the surface tension of cyclohexane is that of 25 dynes/cm, the surface tension of ***AFFF (C-8 compound) is around 16 dynes/cm***, and interfacial tension of the AFFF and fuel is that of 2-5 dynes/cm [8]. ***Thus, the developed ionic liquid for AFFF applications must have a similar surface tension in water***.

There has been an extensive investigation of ionic liquids and their applications for anionic surfactants [9, 10] and even a cellulosic/ionic liquid foaming polymer [11]. Specifically, the ionic liquid 1- methyl-3-octlyimidazolium cation and different anions have been able to achieve surface tensions of 31.6 dynes/cm without any fluorine in water [12]. ***Furthermore, 1-Butyl-3-methyl-imidazolium with triple chain (TC) sulfate anion was able to achieve a surface tension of approximately ~25 mN/m [8]. Thus, it is possible to develop a fluorine-free ionic liquid that can achieve the necessary surface tension for applications in AFFF fire suppression solutions.***

Materials and Methods

Materials Procurement

1-Butyl-3-methyl-imidazolium chloride and bis (2-Ethylhexyl) sulfosuccinate sodium salt (Na-AOT) were purchased from TCI chemicals. Dodecylbenzenesulfonic acid, sodium salt (Na-DDBS), Dichloromethane, Triton X-100, and cyclohexane were purchased from Sigma Aldrich.

Synthesis of Fluorine Free Ionic Liquids

Ionic liquids are environmentally friendly due to their low vapor pressure. Also, long chains of common cationic imidazolium-based ionic liquids can self-assemble to form micelles in aqueous solutions [10]. This formation of micelles is the same behavior exhibited by siloxane surfactants. Therefore, there is potential for an ionic liquid to lower the surface tension of water lower than siloxane formulations.

Synthesis of bmim-AOT

Butyl-methyl-imidazolium chloride (bmim-Cl) and dichloromethane (DCM) were added to the Erlenmeyer flask and stirred until they were fully dissolved. Then required amount of Na-dioctylsulfosuccinate (Na-AOT) was broken up into small pieces and added to the solution. This solution was stirred overnight. The resulting mixture was centrifuged at 4000 rpm for 20 min, decanted, and rotorvapped to produce the ionic liquid product with a yield of 89.5%.

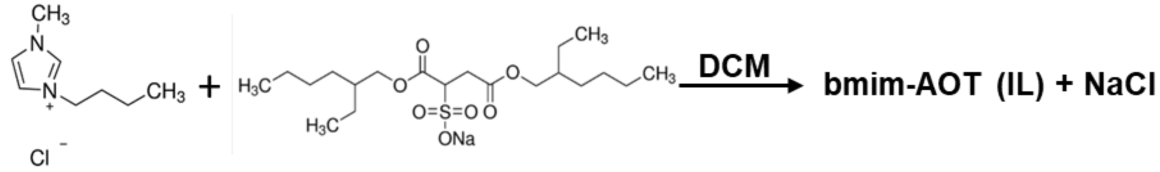

Figure 2. Schematic of the bmim-AOT synthesis reaction

Synthesis of bmim-DDBS

1-butyl-3-methyl-imidazolium chloride and Dodecylbenzenesulfonic acid, sodium salt (Na-DDBS) were added to dichloromethane and left to stir overnight for the ion-exchange reaction to complete. The resulting mixture was then centrifuged, and the supernatant liquid was decanted and then rotovapped at room temperature. The resulting ionic liquid (bmim-DDBS) was viscous and yellow in color.

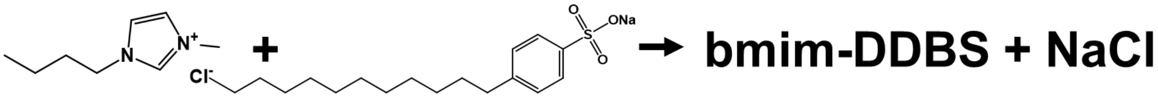

Figure 3. Schematic of the bmim-DDBS synthesis reaction

Chemical and Physical Characterization of Ionic Liquids.

Spreading Parameters

The spreading parameter is an essential tool to use in order to determine the viability of aqueous film formation. The spreading parameter should be positive in order for film formation to be possible. A positive spreading parameter does not guarantee film formation; it only confirms if it is theoretically possible [13]. To ensure film formation, it should be observed optically. The equation of the spreading parameter is:

$$S = \gamma_{LA} - \gamma_{SA} - \gamma_{SL}$$

where,

- γ_{LA} is the surface tension of the fuel in the air
- γ_{SA} is the surface tension of the surfactant solution in air
- γ_{SL} is the interfacial tension between the surfactant solution and the fuel

In order to achieve a positive spreading parameter, the surface tensions of the surfactant solution and interfacial tension between it and the fuel should be sufficiently low. Surface tension values were measured using a model 250 Ramehart goniometer. For each measurement, an amount of siloxane surfactant was dissolved in distilled water at a 1, 3, or 6% concentration. The solution was loaded into a syringe connected to a needle just above the measurement stage. A droplet of the solution was suspended within the field of view of the camera, and a program was initiated to measure the surface tension based on the drop profile. The measurements were calibrated through the surface tension measurement of common liquids such as cyclohexane and oils. Interfacial tension measurements were taken using a contact angle method. In this method, a flat sheet of Teflon is placed at the bottom of a beaker containing cyclohexane fuel. A syringe containing the surfactant solution with a needle attached is immersed in the liquid, and a drop is slowly dispensed onto the Teflon surface. A similar program then evaluated the drop profile to calculate the interfacial tension value.

Aqueous Film Formation

A positive spreading parameter gives the potential for the surfactant to form an aqueous film over a low surface tension hydrocarbon fuel. Formation of such a film can be observed optically or through ignition tests [14]. However, it is not possible to measure the speed at which the film spreads on fuel because of the transparent nature of the fuel and the foam. Therefore, an optical tracking method developed by MMI was used to measure the speed of foam spreading. The proprietary oleophobic powder available from MMI was placed on cyclohexane in a petri dish since the particles can repel low surface tension liquids (even hexane with surface tension 18.43 mN/m at 20 °C) they float on cyclohexane. When the drop of the surfactant is placed on cyclohexane, the surfactant foam pushes the particles as they spread.

Benchtop Fire Testing

The fire extinction performances of the siloxane surfactants were measured using an in-house built benchtop pool fire apparatus (19 cm diameter). This experimental setup was initially developed by the U.S. Naval Research Laboratory (NRL) [15]. The setup for the 19cm diameter pool-fire extinction testing is illustrated in Figure 4 [16].

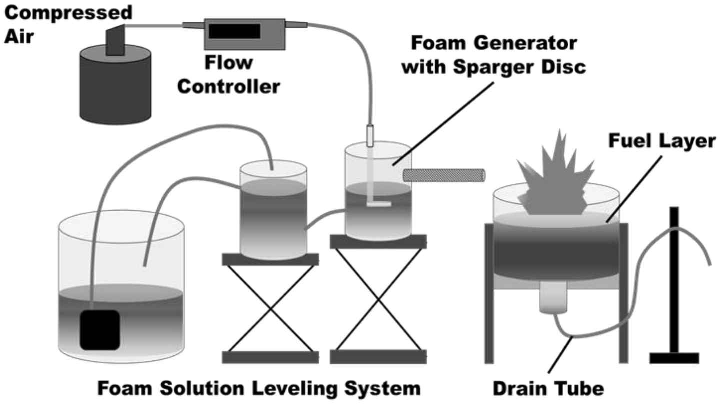

Figure 4. Benchtop foam generation and pool fire suppression [15]

The foam solution was placed in a reservoir where an aquarium pump was used to supply the solution into a second reservoir whose height was adjusted relative to a third solution container in which is immersed a glass frit (sparger) to generate the foam by controlled air flow rate passage. These three containers required a volume of about 2.5 L of foam formulation. The foam was supplied through a sidearm in the container cap to a connected glass tube that deposited the flowing foam onto the burning pool. The pool was filled to a level 2cm below its lip with water, followed by a 1cm layer of heptane fuel. The extinction experiments were conducted using a range of foam flow rates between 400 and 2000 mL/min. 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 is conducted by giving the pool a 60-sec pre-burn, then delivering the dispensing nozzle to the tip of the pool fire and observing the times needed for coverage of the pool by the foam and for the extinction of the fire. If extinctions are observed, these data are expressed in a plot of foam flow rate vs. extinction time. A Reference AFFF composed of a fluorosurfactant (Capstone 1157), an alkyl polyglycoside surfactant (Glucopon 215UP), and a solvent (diethylene glycol monobutylether) was used as the reference formulation which has passed MilSpec extinction evaluation [15].

28 ft^2 fire performance

Large-scale fire testing was conducted according to the method described in the MIL-PRF-24385F standard, albeit with heptane as the fuel. This task was performed at Chesapeake Bay Detachment, U.S. Naval Research Laboratory, Chesapeake Beach, MD. The test was performed using a circular pan 6 ft in diameter, as provided in Figure 5.

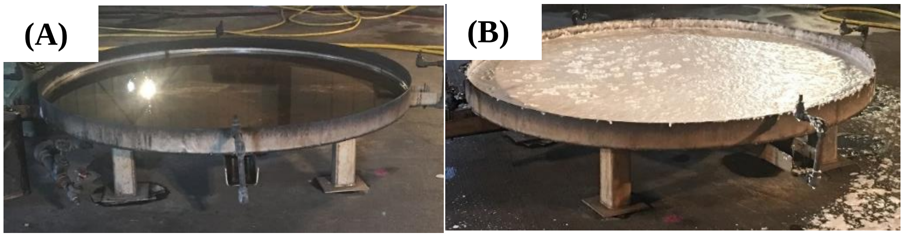

Figure 5. 6 ft diameter pool fire pan with (A) Fuel and (B) Foam on top of fuel after the extinction of fire

The foam produced from the siloxane formulation was sprayed on the heptane fuel using an aspirated nozzle at a rate of 2 gals/min. 10 gallons of heptane was used as test fuel in this task. The fire was started by igniting the fuel. After 10 seconds of a pre-burn period, the foam was sprayed on the fuel, and the fire extinguishing time was recorded using a video camera.

Biopersistance Testing

This task was conducted to determine the biological degradation of the ionic liquid siloxane formulation according to the OECD 301B Ready Biodegradability: CO_2 Evolution guideline [17]. The OECD 301B method is designed to provide a screening of chemicals for ready biodegradability in an aerobic aqueous medium. Samples are required to achieve a threshold of 60% degradation based on the maximum available carbon from a given sample formulation. Total carbon is determined analytically and used as the reference for the determination of the percentage of carbon dioxide (% $ThCO_2$) produced by microbial degradation. Testing of material using the OECD 301B is typically conducted for 28 days with daily analysis of CO_2 production.

Sample testing was conducted following the specification of the laboratory ISO 17025 standards. The total carbon of the test samples was first determined. Test samples were added to 300 ml of mineral medium. 0.5 ml of the original sample was directly added into the sample jar for a final concentration of 20 ppm. Three replicates of the test samples and two of the control samples were prepared. Samples were placed at 23 ± 1 °C in darkness for the duration of the test. Sampling was conducted approximately daily. Measurements of pH were conducted at the end of the test. The bacterial population was enumerated at the beginning and end of the test by plate counting. Degradation of the test sample was followed over 28 days by measuring carbon dioxide production. The maximum theoretical value for CO_2 ($ThCO_2$) was determined analytically for each sample and was used to establish the theoretical biodegradable matter provided by the test sample. The percent degradation was determined for the test sample based on the CO_2 produced in the test system, relative to the maximum ($ThCO_2$) available from the test sample at the beginning of the test.

Results and Discussion

Synthesis of Fluorine Free Ionic Liquids

Two ionic liquid surfactants, 1-butyl-3-methyl-imidazolium dioctyl sulfosuccinate (also labeled as "bis (2-Ethylhexyl) sulfosuccinate") (Bmim-AOT), and 1-butyl-3-methyl-imidazolium dodecylbenzene sulfonate (bmim-DDBS) (Figure 6), were synthesized using the ion-exchange method.

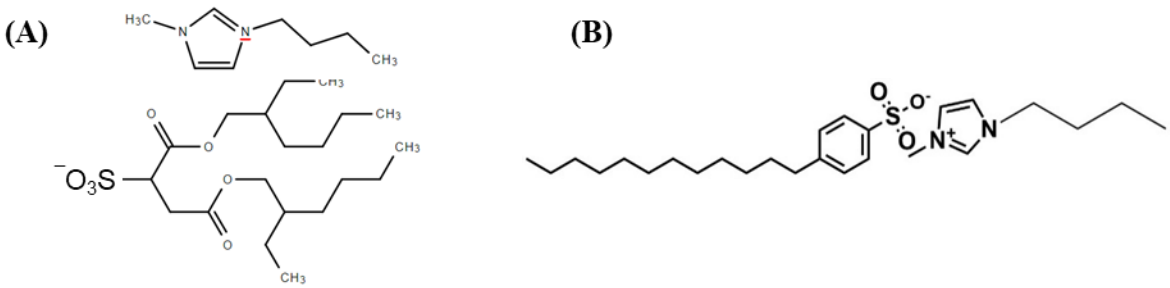

Figure 6. Chemical structure of ionic liquid surfactants (A) bmim-AOT and (B) bmim-DDBS

Chemical and Physical Characterization of Ionic Liquids.

Solutions of the bmim-AOT and bmim-DDBS ionic liquid surfactants were used in the surface tension measurements on-air and in cyclohexane, and the data are provided in Table 1.

Table 1. Mean Ionic Liquid Surfactant Surface Tension Measurements and Spreading Parameters

Surfactant Solution	**Surface Tension of Surfactant (mN/m)**	**Interfacial Surface Tension (mN/m)**	**Spreading Parameter (S)**
Na-AOT (1wt%)	27.07	-	-
1.5% bmim-AOT	25.56	0.25	-0.25
2.88% bmim-AOT	25.75	-	-
6% bmim-AOT	25.10	-	-
Na-DDBS	29.00		
bmim-DDBS 1%	27.53		

**Mean cyclohexane Surface Tension on air: 25.56 mN/m*

The surface tension of bmim-DDBS was higher than bmim-AOT ionic liquid. This value is higher than required to produce a positive spreading coefficient on cyclohexane. Therefore, it was concluded that ionic liquid surfactants alone would not be able to form a film on top of gasoline fuel and quench the fire. It was decided to mix the ionic liquid surfactants with trisiloxane surfactants to reduce the surface tension and foamability.

Aqueous Film Formation

A positive spreading parameter gives the potential for the surfactant to form an aqueous film over a low surface tension hydrocarbon fuel. Formation of such a film can be observed optically or through ignition tests.

MMI has developed a novel method for observing the movement of an oleophobic powder on top of cyclohexane as the film forms. The powder was placed around the edges of the petri dish that is already filled with cyclohexane. The powder was floating on top of cyclohexane. A drop of the surfactant was placed in the middle, and movement of the powder towards the edges of the petri dish was observed. To compare film spreading between different surfactants, the velocity of the powder movement was measured.

Table 2. Spreading Parameters and Film Formation Tests

Surfactant Solution	**Surface Tension of Surfactant Solution on-air (mN/m)**	**Interfacial Surface Tension (mN/m)**	**Spreading Parameter (S)** *Mean cyclohexane Surface Tension on air: 25.56 mN/m	**Film Formation**
3% bmim-AOT	26.78	0.25	-1.47	No
3% bmim-AOT 1% Triton CG 110	26.56	0.1	-1.1	No
1 % Triton 3 % bmim-AOT 3 % Siloxane surfactant	25.53	0.13	-0.1	Yes
3 % bmim-AOT 3 % Siloxane surfactant	22.15	1.59	1.82	Yes

bmim-AOT with and without Triton CG-110 additive was not able to form an aqueous film. Once the drop was placed, there was no movement in the oleophobic powder. Since bmim-AOT is an anionic surfactant, it is a good foaming agent. The siloxane surfactants alone do not produce foam well. It is possible to add bmim-AOT and bmim-DDBS ionic liquids to the siloxane surfactants as a foaming agent. The mixtures seemed to retain surface tension values that are the average of the surface tensions of individual surfactants. The interfacial surface tension increased in both mixtures when compared to each individual surfactant solution.

The ionic liquid-based foam formulation

Ionic liquids, bmim-AOT, and bmim-DDBS were mixed with a poly(trisiloxane) and tested for foam fill time and fire quenching time. Various formulations (Ionic-n) are provided in Table 3.

Table 3. Ionic liquids-based foam formulations

Sample	Trisiloxane (wt%)	bmim-AOT (wt%)	bmim-DDBS (wt%)
Ionic-1	0.4	0.4	
Ionic-2	0.4	0.8	
Ionic-3	0.6	0.8	
Ionic-4	0.8	0.8	
Ionic-5	1.0	0.8	
Ionic-6	1.5	0.8	
Ionic-7	0.8	1.0	
Ionic-8	1.5	1.0	
Ionic-9	2.0	1.0	
Ionic-10	1.5		0.8
Ionic-11	0.8		1.0
Ionic-12	1.5		0.8

Foam flow rate

The addition of ionic liquids to aqueous poly(trisiloxane) solution increased the foam flow rate on top of fuels several folds **(>300** seconds to **8** seconds). Filling time data for a 19-cm diameter heptane pool is provided in Figure 7 as a function of bmim-AOT ionic liquid concentration. Therefore, there is a potential of using water-soluble ionic liquids in enhancing the foam filling and fire quenching properties of the poly(trisiloxanes). The addition of a higher surface tension liquid along with a low surface tension trisiloxane increases the surface tension gradient, which in turn helps the Marangoni effect.

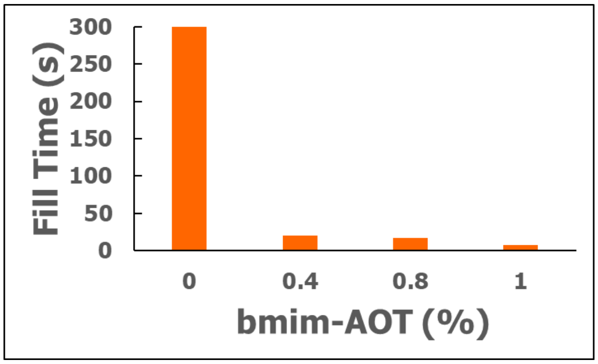

Figure 7. 19 cm diameter pool fill time as a function of ionic liquid concentration

Benchtop Pool Fire Testing

The fire extinction performances of the ionic liquids, bmim-AOT and bmim-DDBS mixed poly(trisiloxane), were measured using a benchtop fire apparatus (19 cm diameter) developed by the US Naval Research Laboratory (NRL). A 25-micron pores sparger was used in foam generation.

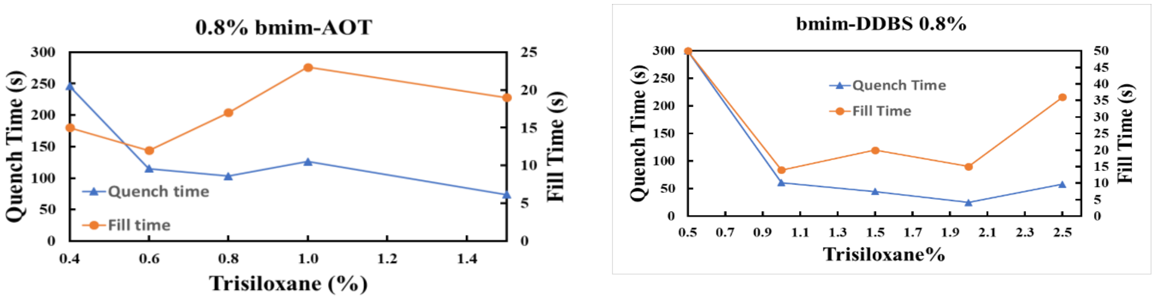

Figure 8. Pool fire test data for bmim-AOT and bmim-DDBS ionic liquids mixed poly(trisiloxane) foams

The fire quench and dish fill time data are provided in Figure 8. Although the fill time was drastically reduced by the addition of bmim-AOT to poly(trisiloxane) solution, it did not translate into effective quenching of fire. This is probably due to the voids or pores on the foam film formed, which allowed the continuous escape of the fuel, resulted in the propagation of fire. The fire was quenched after a sufficient thickness of foams was formed on the fuel, cutting off the fuel vapor. In contrast, the bmim-DDBS ionic liquid was able to reduce the quench time down to 25 seconds. The lowest quench time achieved with bmim-AOT was 62 seconds, with 2% poly(trisiloxane). A most interesting observation is that the surface tension of bmim-DDBS was much higher than bmim-AOT ionic liquid (About 27 mN/m vs. 25 mN/m). However, ***bmim-DDBS performed better in the pool fire testing than bmim-AOT***. The data clearly shows that with the judicious selection of the ionic liquid, it is possible to achieve a fluorine-free formulation capable of meeting the AFFF standard. The major structural difference between these two ionic liquids is the presence of flat-aromatic headgroups in the bmim-DDBS. ***The significance of this structural aspect in quenching the fire will be investigated in future research efforts.***

Fire Testing with Gasoline

According to the AFFF military standard MIL-PRF-24385F, the fuel must be unleaded gasoline. Therefore, 19cm-diameter pool fire testing was conducted using gasoline. The fuel typically contains <10% of ethanol. Based on the heptane pool fire testing, 0.8% of bmim-DDBS ionic liquid was selected for gasoline pool fire testing. The amount of poly(trisiloxane) was varied from 0.4% to 2.5% in the foam solution. The fire extinction time was evaluated using a benchtop fire testing system using these formulations. The data obtained were provided in Table 4.

Table 4. Gasoline pool-fire testing of ionic liquids

Sample ID	**Poly(trisiloxane) (%)**	**bmim-DDBS IL (%)**	**bmim-AOT IL**	**Dish fill time (s)**	**Quench time (s)**
3% C6 Phoschek				5	14
39-2	0.4	0.8		8	300
39-3	0.8	0.8		64	81
39-3	0.8	0.8		58	300
39-5	1.5	0.8		8	37
50-3	1.5	0.8		10	44
48-9	2.5	0.8		12	78
49-4		0.8		13	223
49-7	2.0	0.8		14	72
50-1	2.0			13	122
50-2	2.0		0.8	13	53

The addition of bmim-DDBS ionic liquid reduced the dish fill time dramatically down to 8 seconds. The best fire quench time observed was 37 seconds for the composition poly(trisiloxane) (1.5%) and bmim-DDBS ionic liquid (0.8%). The time-lapse photographs of them taken during benchtop 19-cm diameter gasoline pool fire suppression tests are provided in Figure 9.

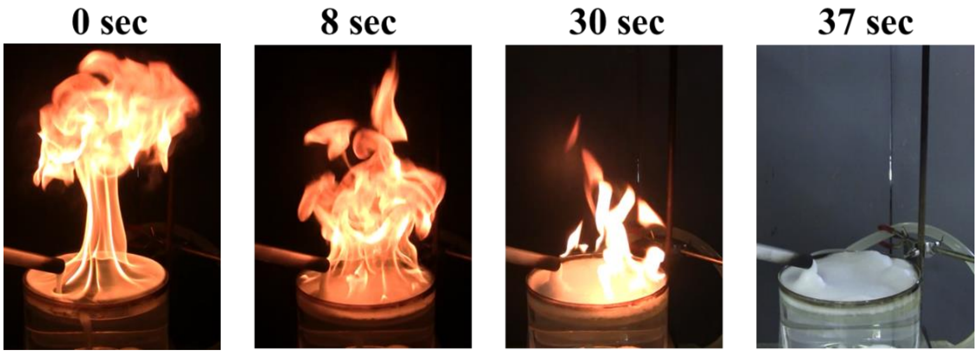

Figure 9. Time-lapse images of gasoline pool fire testing with 1.5% poly(trisiloxane) + 0.8% bmim-DDBS ionic liquid

Ionic liquid/poly(trisiloxane) foam formulation with polysaccharide additive

A foam formulation containing poly(trisiloxane), ionic liquid bmim-DDBS, and polysaccharide was tested for fire quenching performance. This formulation was named "DDX." Plots for quench and fire-dish fill time versus flow rate in a 19-cm diameter gasoline pool fire are provided in Figure 10. The data for AFFF-C6 ("Phoschek") is also included for comparison.

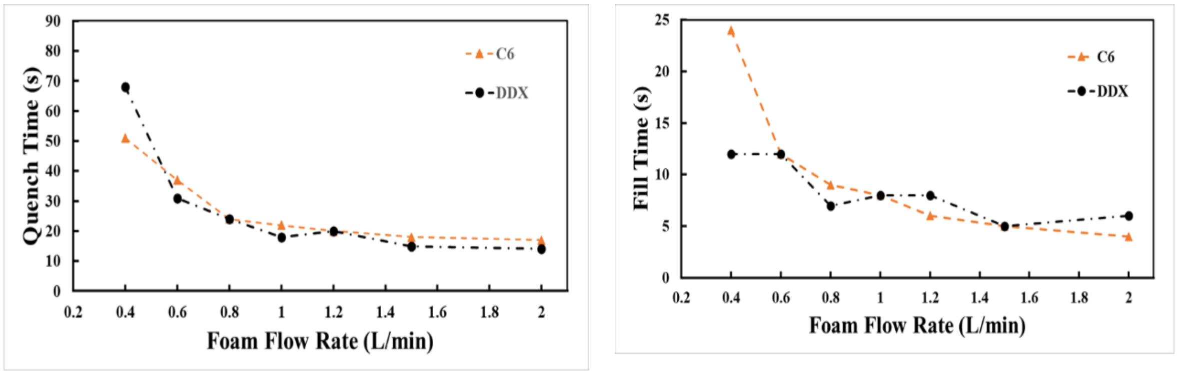

Figure 10. Comparison of AFFF-C6 with DDX foam solution.

From the data in Figure 10, it can be seen that both foams are similar in behavior, and DDX can potentially be a good fluorine-free, environmentally friendly fuel fire suppressant.

Interestingly, when the DDBS anion (with aromatic headgroup) was replaced with long alkyl chain groups (e.g., alkylammonium, non-aromatic headgroup), the firefighting performance was reduced. ***This indicates that benzene-ring-containing ionic liquids performed better than aliphatic chain surfactants***. This is possibly due to the synergistic interaction between the ionic liquid and poly(trisiloxane) surfactants.

28 ft^2 Fire Suppression Evaluation of AFFF Solution

The 28 ft^2 fire suppression evaluation of the AFFF solution was conducted at Chesapeake Bay Detachment, US Naval Research Laboratory, Chesapeake Beach, MD, following the MIL-F-24385 standard. The setup consisted of a circular pan (6 ft. in diameter) constructed of 0.25 in steel with a four on the high side. The nozzle used for the foam application had an 80-mesh range with a two gpm flow rate. The fuel used in the fire suppression test was unleaded gasoline (10 gallons) and was poured onto the test pan over 30 second period, ignited within 30 seconds of pouring, and allowed to burn freely for another 10 seconds. Next, the AFFF solution was applied to the controlled fire for up to 4 minutes. The fire extinguishing time was recorded during this period. The 28ft^2 fire testing data is provided in Table 5.

Table 5. Ionic Liquid/Poly(trisiloxane) Formulations for MIL-Spec 28ft^2 Fire Testing

Composition	Poly(trisiloxane) %	bmim-DDBS %	Polysaccharide Additive %	Fire Extinction time (s)	Expansion Ratio
1-2	2.0	1.0	0.2	234	3.0
1-3	1.5	0.8	0.2	Did not quench	3.5
2-5	2.0	1.0	0	Did not quench	5.7

The ionic liquid compositions failed to quench the gasoline pool fire in the $28ft^2$ testing, though the same compositions were able to quench the fire in the benchtop testing. The burnback procedure was not conducted because the formulations tested were not able to quench the fire.

The reason for the failure of the $28ft^2$ fire testing was analyzed. It was found that the expansion ratio of the foams in the $28ft^2$ was **about 40% less** than the expansion observed in the 19-cm diameter benchtop testing. The foam generating methods in these two tests were different. In the benchtop testing, the foams were generated using flowing air through a porous sparger. In the $28ft^2$ testing, the foam was generated using an aspirated 2gpm Mil-spec nozzle.

Future work will be aimed at mimicking foam generation in the benchtop experiments similar to the mil-spec nozzle. This will be achieved by replacing the sparger in the current benchtop system with a pressure pump unit.

Biodegradation Testing

The determining biodegradability of the ionic liquid – polysiloxane formulation was only 6.2% $ThCO_2$. The test sample did not achieve the biodegradability requirements for Ready Biodegradability by the OECD 301B standard or degradation of 60% ThCO2 within a 10-day window of the test timeframe. The results were similar to the starting polysiloxane [18] The biodegradability of the Heptamethyl-3-(propyl(polyethylene oxide)methyl)Trisiloxane, the main ingredient in polysiloxane, was only 2.5% after an exposure time of 28 days. The biodegradability of the Ionic liquid-Polysiloxane formulation is consistent with the data reported for polysiloxane.

Synergism between the ionic liquid and poly(trisiloxane) surfactants

Trisiloxane surfactants exhibit a unique ability to rapidly and extensively wet hydrophobic surfaces such as leaf tops or general hydrophobic plastics and liquid fuels within seconds and are referred to as "super wetting" or "super spreading" [19]. Trisiloxane surfactant reduced the surface tension (ST) of water to 20 mN/m). The conventional alkyl surfactants, on the other hand, were able to reduce ST to only about 30 mN/m. The reason for the wetting behavior of trisiloxane may be explained as follows and as shown in Figure 11.

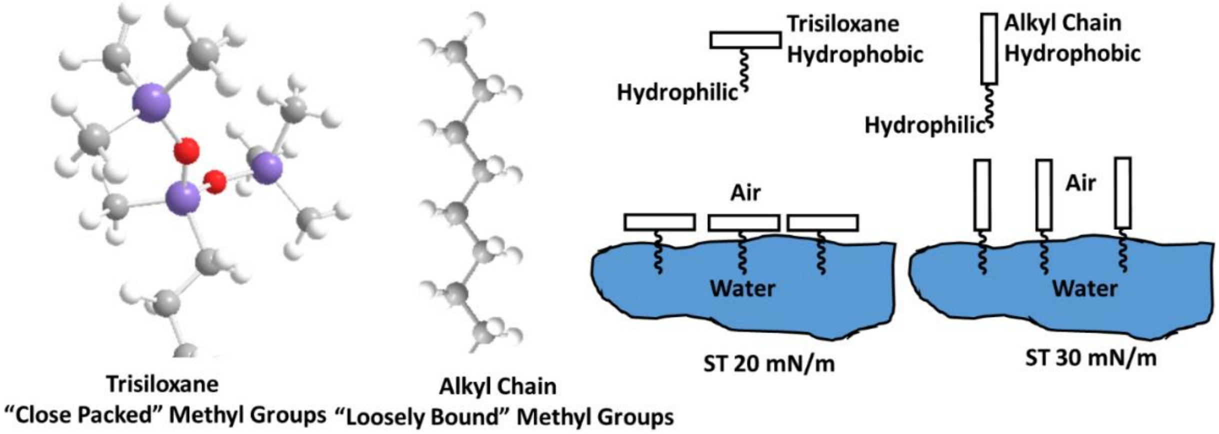

Figure 11. Schematic diagram of the chemical structure of surfactants and their orientation in the water

In superspreading, there has to be a way of transporting surfactant molecules to the newly formed interfaces near the spreading edge of the drop. For the spreading coefficient to remain positive, the contact angle at the advancing contact line must be zero [20]. Ruckenstein [21] proposed that the superspreading of dilute aqueous solutions of siloxane surfactants over a hydrophobic surface is driven by:

1. The spreading at their leading edges of the drop as bilayers of surfactant.
2. The pulling of water (in our case, with ionic liquids) in the hydrophilic environment between the two layers.
3. The displacement of the surfactant and water by a Marangoni effect increased by the formation of bilayers.

The effect of ionic liquid on foam mobility at the top of the gasoline fuel surface can be explained using a bilayer trisiloxane configuration. The proposed mechanism is schematically depicted in Figure 12.

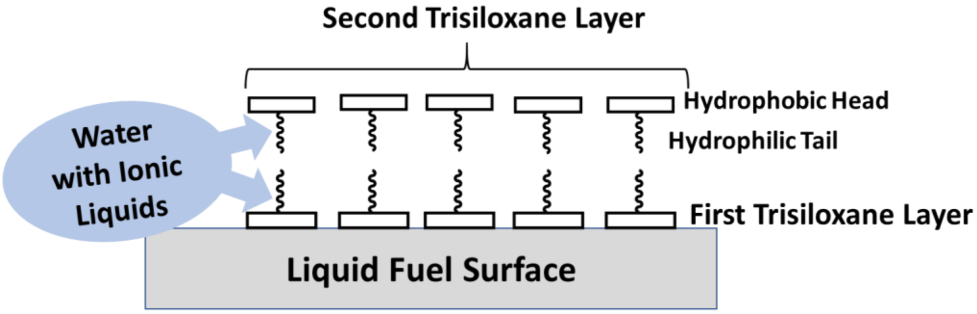

Figure 12. Schematic diagram of the mechanism of ionic liquid action on the fuel surface

The ionic liquid enters the trisiloxane bilayer and drives the foam over the gasoline layer due to the difference in the surface tension gradient. ***The presence of aromatic head groups presumably assists the formation of lamellar surfactant micelles.***

The earlier study led to the following understanding:

- The addition of a liquid with higher surface tension (bmim-DDBS) to a low surface tension poly(trisiloxane) increased the surface tension gradient, which in turn helps the Marangoni effect of fast-spreading of foams on the fuel layer. The time for foam spread was reduced from 360 seconds to 8 seconds to fill 19 cm diameter gasoline fuel.
- Ionic liquid surfactants containing aromatic head groups exhibited higher firefighting capacity than long alkyl chain surfactants.
- Further optimization of ionic liquid/poly(trisiloxane) formulations could yield shorter times for fire extinction under 28ft^2 testing.

In future work, ionic liquid/poly(trisiloxane) formulations could be modified to increase the foam expansion ratio to about 7 from the current value of ~3 using a MilSpec aspirated nozzle. Further, with the foam expansion, the stability of foams on hot gasoline fuel should also be improved with selective additives. Future studies should include understanding the mechanism of the synergetic effect of ionic liquids (ST 26 mN/m) with the lower surface tension-poly(trisiloxane) surfactants

(ST 20 mN/m) and the significance of ionic liquids with aromatic headgroups containing anions in the fire quenching performance.

Understanding the effect of ionic liquid surfactants on the foamability of the poly(trisiloxane) formulations and their interaction with the fuel could help in the preparation of better-quality firefighting foams.

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