EXECUTIVE SUMMARY

Innovative Nano-Encapsulated Ionic Liquid Based Surfactants for Fluorine-Free Fire Extinguishing Foams

SERDP Project WP18-1597

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ACRONYMS AND ABBREVIATIONS

AFFF	Aqueous Film-Forming Foam
NEIL	Nanoencapsulated Ionic Liquid
SAIL	Surface-Active Ionic Liquid

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1.0 INTRODUCTION

The management of hydrocarbon fuel fires is relevant to military applications. Current firefighting formulations depend on perfluorinated surfactants. These toxic agents feature exceptionally poor biodegradability. The unique film-forming property of fluorosurfactants is due to the co-existence of hydrophilic, hydrophobic, and lipophobic functionalities. The latter is not found in any other material. Therefore, we have investigated in this project an alternative out-of-the-box pathway to extinguish large hydrocarbon fires that does not rely on film-forming characteristics alone. We have developed a proof of concept formulations based on nano-encapsulated ionic liquids (NEILs), which are green chemistry agents, as alternatives to fluorinated aqueous film-forming foams (AFFFs). Our firefighting foam formulation consists of a mixture of a long-chain surface active ionic liquid (SAIL), magnesium carbonate nanoparticles, and sodium alkyl sulfates, which are fluorine-free and biodegradable. NEIL formulations provide physical and chemical barriers that enhance the AFFF firefighting performance along multiple fronts. First, the NEIL-based formulation would form a film that seals off flammable fuel vapors. Second, the heat of the fire would trigger an endothermic reaction ($MgCO_3 \rightarrow MgO + CO_2$, $\Delta H° = 118$ kJ/mol), which generates a CO_2 blanket that smothers the fire via oxygen deprivation and fuel vapor dilution. Third, the endothermic magnesium carbonate decomposition would serve as a heat sink, and slow down endothermic foam vaporization and/or decomposition. Fourth, nanoparticles and released CO_2 would increase the foam's stability by delaying the coalescence of bubbles. Fifth, the release of ionic liquid from the core upon degradation magnesium carbonate capsules will replenish the surfactant and heal defects in the firefighting film. To our knowledge, no commercial AFFF formulations contain NEILs that have the potential to match and exceed the performance of the current AFFF formulations in use.

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2.0 OBJECTIVES

Any AFFF formulation that substantially decreases or eliminates these environmental risks aligns with the current priorities of the Strategic Environmental Research and Development Program. In this proof-of-concept phase, we aimed to identify formulations based on ionic liquids that meet or closely approach the requirements of the interim amendment 3 to MIL-F-24385F. A metric of success for this proof of concept phase is the number of the key requirements in the interim amendment 3 to MIL-F-24385F that our fluorine-free formulation meets or closely approach. Our ability to identify a potential roadmap to formulations that can be deployed in the real world is another metric of our success.

The requirements that a successful fluorine-free AFFF should satisfy are outlined in the interim amendment 3 to MIL-F-24385F1. The most challenging requirements that we need to address first are the following:

1. The spreading coefficient of formulation over cyclohexane should be at least 3 mN/m.
2. Foam should spread over the fuel and seal off vapor production.
3. The foam drainage time should be at least 2.5 min.
4. The burn-back resistance time should be at least 360 sec.
5. A formulation should be biodegradable, minimally toxic to aquatic life, and harmless to personnel when used as intended.

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3.0 TECHNOLOGY APPROACH

We combined experiments and computational chemistry techniques to identify those surfactants that feature high spreading coefficients over cyclohexane and bind to metal carbonate surfaces. We used molecular dynamics simulations to predict spreading coefficients of surfactants, and density functional theory to quantify the binding of our surfactants to metal carbonate nanoparticle. Based on our in-silico modeling and chemical intuition, we identified, synthesized, and characterized the most promising surfactant-metal carbonate composites.

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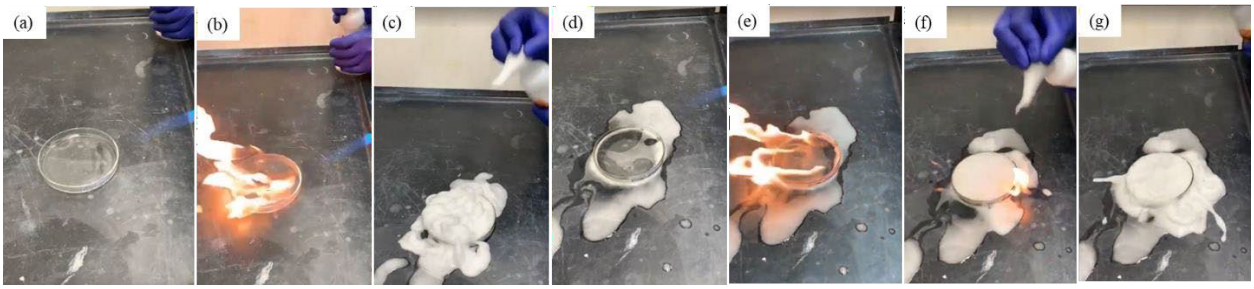
4.0 RESULTS AND DISCUSSION

We have developed a successful AFFF prototype based on ionic liquids as surfactants. We have demonstrated experimentally that a series of alkyl imidazolium-and alkyl pyridinium-based SAILs with a hydrophobic chain length of 10-12 carbon atoms work best for the reduction of water surface tension and foam stabilization. We have shown that molecular dynamics simulations can successfully predict trends in surface and interfacial tensions of aqueous solutions of surface-active ionic liquids. Density functional theory can rank different types of functional groups with respect to their ability to bind to magnesium carbonate surfaces. We have also shown using electrospray ionization-mass spectrometry that ionic liquids are indeed bound to magnesium carbonate nanoparticles as intended. We performed foam stability and small-scale fire tests as the figure below illustrates.



Our fluorine-free AFFF prototype formulations meet or closely approach the key requirements of MIL-F-24385F:

MIL-F-24385F requirement	Our formulation
spreading coefficient > 3 mN/m	as high as 3.3 mN/m
25 % drainage time > 2.5 minutes	as high as 3.9 minutes
Perfluorooctanoic acid and perfluorooctane sulfonate content < 800 ppb	fluorine-free (0)
Foam application time <45-55 s Burn back time>300-360 s	Extinguishes fire, not quantified
Fish toxicity LC_{50}(96h) for Type 3 > 500 mg/L	Estimated LC_{50} as high as 470 mg/L (N-dodecyl pyridinium) 450 mg/L (sodium dodecyl sulfate)
Biodegradability COD, BOD/CODx29	Biodegradable, not quantified
7<pH<8.5	-
Viscosity <20 centistokes at 25C Viscosity <5 centistokes at 5C	-
Refractive index > 1.3630 (Type 3)	-
Corrosion rate limits	-

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5.0 IMPLICATIONS FOR FUTURE RESEARCH AND BENEFITS

In our future work, we will search for ionic liquids and their derivatives that have favorable interfacial properties, firefighting performance, toxicological profile, and compatibility with magnesium carbonate nanoparticles. In particular, it is known that polar groups in the alkyl chains or a change in head groups of ionic liquids can significantly lower the toxicity. The initial screening effort can be accomplished with computational chemistry screening tools, which can be used to predict both toxicity and interfacial properties. Successful formulations identified in *in silico* screening can be further examined experimentally. The costs of *in silico* materials design efforts are significantly lower than those for actual experiments. In this phase, we did not attempt to optimize refractive index, viscosity, pH, and corrosion rate, but we plan to address these factors in the next phase by adding components that do not impact the firefighting performance. Upon completion of the follow-up research to optimize their performance, formulations based on ionic liquids would mitigate risks associated with exceptionally poor biodegradability of perfluorinated surfactants currently used to extinguish jet fuel fires.