

|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            |                                                                    |                                                                   |                                                                                        |                                  |
|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------|-------------------------------------------------------------------|----------------------------------------------------------------------------------------|----------------------------------|
| <b>REPORT DOCUMENTATION PAGE</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           |                                                                    |                                                                   | Form Approved<br>OMB NO. 0704-0188                                                     |                                  |
| Public Reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comment regarding this burden estimates or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188,) Washington, DC 20503. |                                                                    |                                                                   |                                                                                        |                                  |
| 1. AGENCY USE ONLY ( Leave Blank)                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          |                                                                    | 2. REPORT DATE                                                    |                                                                                        | 3. REPORT TYPE AND DATES COVERED |
| 4. TITLE AND SUBTITLE                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |                                                                    |                                                                   | 5. FUNDING NUMBERS                                                                     |                                  |
| 6. AUTHOR(S)                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               |                                                                    |                                                                   |                                                                                        |                                  |
| 7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         |                                                                    |                                                                   | 8. PERFORMING ORGANIZATION<br>REPORT NUMBER                                            |                                  |
| 9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)<br><br>U. S. Army Research Office<br>P.O. Box 12211<br>Research Triangle Park, NC 27709-2211                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     |                                                                    |                                                                   | 10. SPONSORING / MONITORING<br>AGENCY REPORT NUMBER<br>XXXXXXX<br>XXXXXXXXX 44547.4-CH |                                  |
| 11. SUPPLEMENTARY NOTES<br>The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.                                                                                                                                                                                                                                                                                                                                                                                                                                                            |                                                                    |                                                                   |                                                                                        |                                  |
| 12 a. DISTRIBUTION / AVAILABILITY STATEMENT<br><br>Approved for public release; distribution unlimited.                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    |                                                                    |                                                                   | 12 b. DISTRIBUTION CODE                                                                |                                  |
| 13. ABSTRACT (Maximum 200 words)                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           |                                                                    |                                                                   |                                                                                        |                                  |
| 14. SUBJECT TERMS                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          |                                                                    |                                                                   | 15. NUMBER OF PAGES                                                                    |                                  |
|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            |                                                                    |                                                                   | 16. PRICE CODE                                                                         |                                  |
| 17. SECURITY CLASSIFICATION<br>OR REPORT<br><b>UNCLASSIFIED</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            | 18. SECURITY CLASSIFICATION<br>ON THIS PAGE<br><b>UNCLASSIFIED</b> | 19. SECURITY CLASSIFICATION<br>OF ABSTRACT<br><b>UNCLASSIFIED</b> | 20. LIMITATION OF ABSTRACT<br><br><b>UL</b>                                            |                                  |

NSN 7540-01-280-5500

**Standard Form 298 (Rev.2-89)**  
Prescribed by ANSI Std. Z39-18  
298-102

Enclosure 1

# Novel Surfactants and Their Applications, Including Mustard Decontamination

Final Report

by

David A. Jaeger

June 30, 2007

U.S. Army Research Office  
Grant No. DAAD19-03-1-0342

Department of Chemistry  
University of Wyoming  
Laramie, WY 82071

## Table of Contents

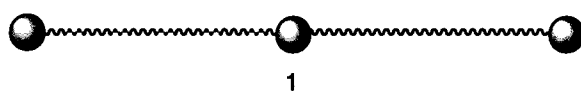
|                                                                                                              | <i>page<br/>number</i> |
|--------------------------------------------------------------------------------------------------------------|------------------------|
| Table of Contents                                                                                            | 2                      |
| A. Statement of the Problem Studied                                                                          | 3                      |
| B. Summary of the Most Important Results                                                                     | 3                      |
| Study 1                                                                                                      | 3                      |
| Study 2                                                                                                      | 4                      |
| Study 3                                                                                                      | 5                      |
| Study 4                                                                                                      | 7                      |
| Study 5                                                                                                      | 9                      |
| Study 6                                                                                                      | 10                     |
| Bibliography                                                                                                 | 12                     |
| C. Publications Submitted Under the Contract                                                                 | 12                     |
| D. List of All Participating Scientific Personnel & Advanced<br>Degrees Earned While Employed on the Project | 13                     |
| E. Report of Inventions                                                                                      | 13                     |

## A. Statement of the Problem Studied.

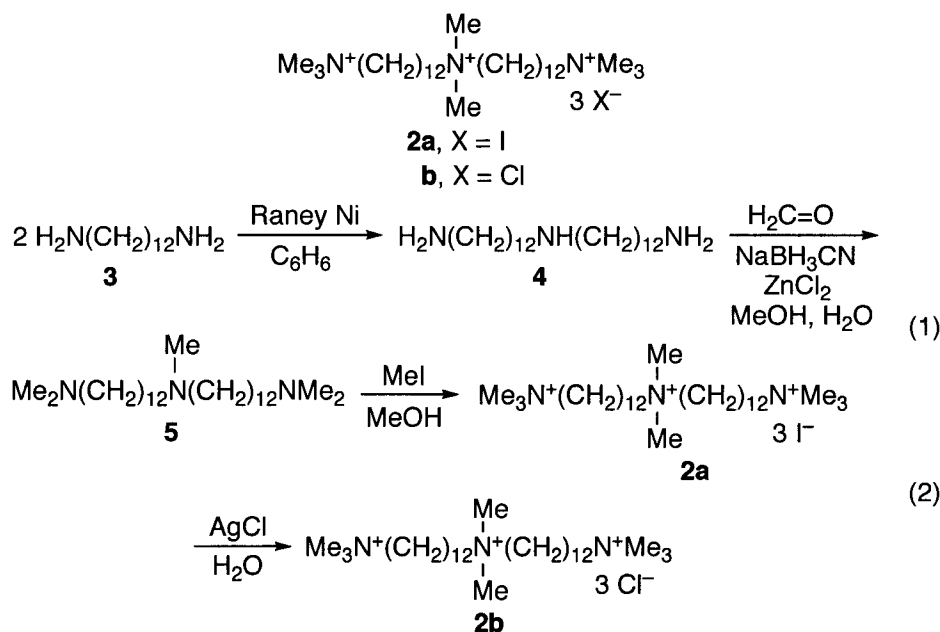
The objectives of the research project included the synthesis and characterization of novel surfactants and the application of their aqueous aggregates. The novel surfactants, known as shamrock surfactants, contain a central headgroup connected to two flanking headgroups by hydrocarbon chains; they do not contain long-chain alkyl groups. The application of some the surfactants in the decontamination of a mustard simulant was evaluated.

## B. Summary of the Most Important Results.

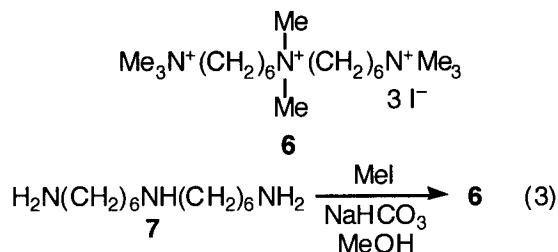
Results were obtained in six studies as summarized below. All of the studies involved novel surfactants with general structure **1**. The darkened circles represent headgroups, and the wavy lines, hydrocarbon chains. Thus the surfactants contain two terminal headgroups connected to a central headgroup by hydrocarbon chains. For ease of discussion, we introduced the term "shamrock" to describe surfactants belonging to class **1**, denoting their triple-headed character and reflecting the fact that shamrocks have leaflets in groups of three.



**STUDY 1.** The results of this study have been published.<sup>1</sup> We synthesized and characterized shamrock quaternary ammonium surfactants **2**. Commercially-available diamine **3** was converted (42%) into triamine **4** by treatment with Raney nickel in benzene at reflux. In this unusual reaction, two molecules of **3** combine to give **4**, with the formal loss of ammonia. Then the reductive methylation of **4** gave triamine **5**, followed by its methylation with methyl iodide to give **2a** (eq 1). Surfactant **2a** was converted into surfactant **2b** by a metathesis reaction with silver chloride (eq 2).



For purposes of comparison with surfactants **2**, compound **6** was prepared by the permethylation of commercially-available **7** with methyl iodide (eq 3). It is interesting to note that our initial synthesis of surfactant **2a** followed an analogous route, starting with triamine **4**, but the resultant **2a** was contaminated with sodium iodide, which was difficult to remove due to the similar solubilities of **2a** and sodium iodide in a variety of solvents. Compound **6** could be isolated in pure form, because its solubility characteristics are different than those of sodium iodide.



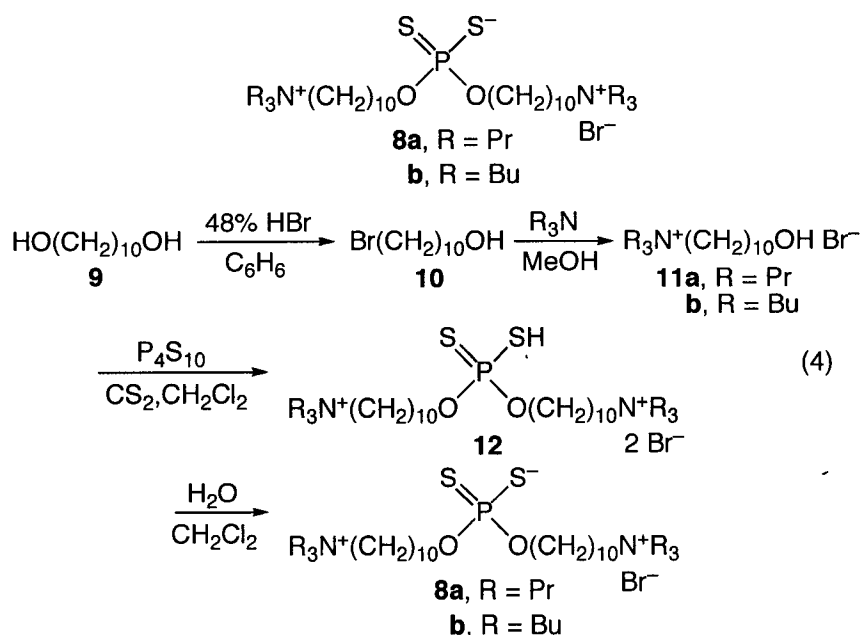
In this study and those below, the characterization of shamrock surfactants generally included measurement of their Krafft temperatures ( $T_k$ ) and critical aggregation concentrations (cac), as determined at 23 °C from plots of surface tension versus log [surfactant]. Aggregated surfactants in water at 23 °C were studied by  $^1\text{H}$  NMR spectroscopy, dynamic laser light scattering (DLS, 90° scattering angle), and phase-contrast optical microscopy. Some were also studied by cryo-etch high resolution scanning electron microscopy (cryo-etch HRSEM).

The  $T_k$  value of surfactant **2b** is  $\leq 23$  °C. Its cac value in water is  $0.016 \pm 0.001$  M, and the surface tension of its aqueous solutions above the cac is ca. 37 mN/m. A  $^1\text{H}$  NMR spectrum of **2b** (0.050 M) in  $\text{D}_2\text{O}$  contained broadened signals, consistent with aggregates larger than micelles. Since concentrations of up to 1.0 M **6** did not lower the surface tension of water, suggesting its lack of aggregation, **6** was not characterized further. By DLS, aggregates of **2b** (0.026 M) in water have a hydrodynamic diameter of  $625 \pm 5$  nm. This size is significantly greater than those of micelles, consistent with the  $^1\text{H}$  NMR above results, and is in the size range of large bilayer vesicles. But the morphology of these aggregates is unknown and not readily predicted. The structural character of shamrock surfactants, i.e., three headgroups connected by two hydrocarbon chains, is not accommodated by recognized correlations between surfactant structure and aggregate morphology.

The hydration of surfactants **2** in water, as followed by phase-contrast optical microscopy, gave coacervate droplets from **2a**, with and without the addition of two molar equivalents of sodium iodide, and from **2b**, with the addition of three molar equivalents of sodium chloride. Coacervates are isotropic colloidal solutions immiscible with their own solvent (generally water), and can be formed from a single surfactant, or, much more commonly, from multiple solutes and water.

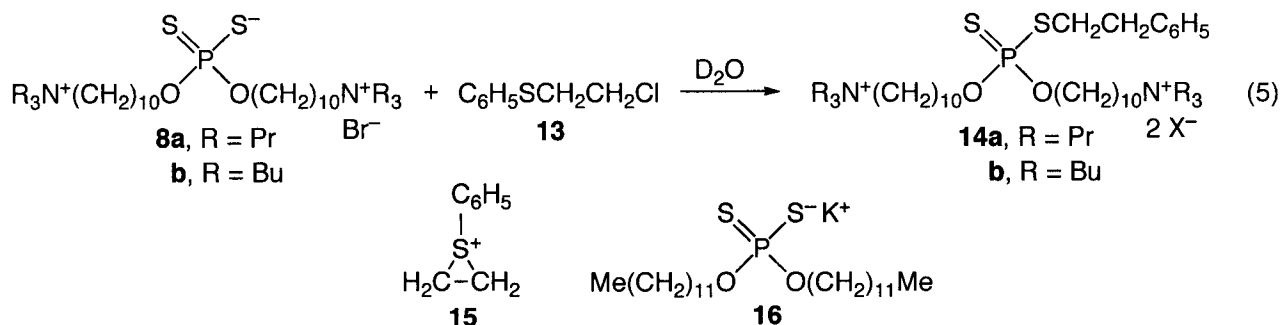
Aqueous 0.052 M (3.3 wt %) **2b** was studied by cryo-etch HRSEM. Micrographs showed cells featuring a complex matrix between walls, which are in part composed of 10-30 nm aggregates. The origin of the observed morphologies is unclear. One possibility is that they correspond to submicroscopic networks of aggregated **2b** that exist before plunge-freezing. But this is unlikely, especially for the cell walls, given the results of a cryo-etch HRSEM study<sup>2</sup> of aqueous sodium chloride and other inorganic salts. Accordingly, the morphologies observed for **2b**, and for the other shamrock surfactants reported below, reflect characteristic segregation patterns formed by the surfactants during the freezing process and/or as ice was sublimed away during the cryo-etch process.

**STUDY 2.** The results of this study have been published.<sup>1</sup> We synthesized and characterized shamrock surfactants **8**. Note that they contain a central dithiophosphate headgroup separated from two flanking quaternary ammonium headgroups by two ten-carbon methylene chains. Surfactants **8** were synthesized in four steps (eq 4), starting with the conversion of commercially-available diol **9** into bromo alcohol **10**. The nucleophilic substitution reaction of tertiary amine  $\text{R}_3\text{N}$  ( $\text{R} = \text{Pr}, \text{Bu}$ ) with **10** gave surfactant **11**, which was converted into compound **12** by reaction with phosphorus pentasulfide. Then a dichloromethane solution of **12** was washed with water to give **8**. In this process, the dithiophosphoric acid unit of **12** ionizes, with the net loss of hydrogen bromide.

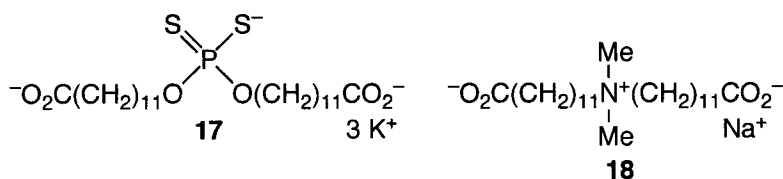


The  $T_k$  values of surfactants **8** are  $\leq 23$  °C. The cac values of **8a** and **8b** in water are  $0.028 \pm 0.001$  and  $0.0064 \pm 0.0006$  M, respectively, and the surface tensions of their aqueous solutions above their cac values are ca. 42 mN/m. The  $^1\text{H}$  NMR spectra of **8a** (0.042 M) and **8b** (0.0096 M) in  $\text{D}_2\text{O}$  contained broadened signals, consistent with aggregates larger than micelles. By DLLS, aggregates of **8a** (0.042 M) and **8b** (0.0096 M) in water have hydrodynamic diameters of  $168 \pm 1$  and  $227 \pm 4$  nm, respectively. The hydration of surfactants **8** in water, as followed by phase-contrast optical microscopy, gave coacervate droplets.

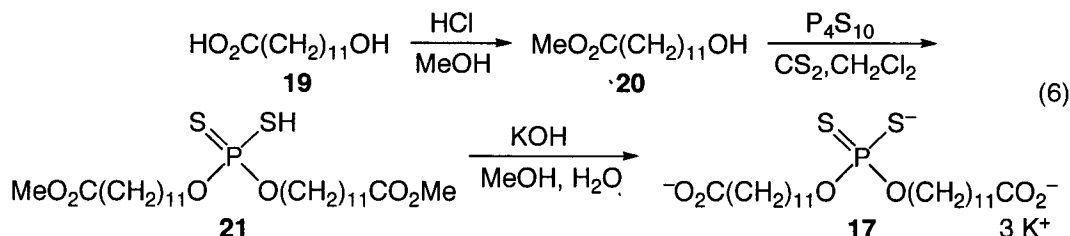
The efficacy of aqueous aggregated **8a** and **8b** in the decontamination of mustard simulant **13** was evaluated. The reaction of **8** with **13** to give **14** corresponds to the decontamination of **13** (eq 5). In this reaction, the nucleophilic dithiophosphate headgroup of **8** most likely captures episulfonium ion **15**, formed by ionization of **13**. Since our results indicated that surfactants **8** are no more effective than the parent dithiophosphate surfactant **16** in decontaminating **13**,<sup>3</sup> we did not pursue this study.



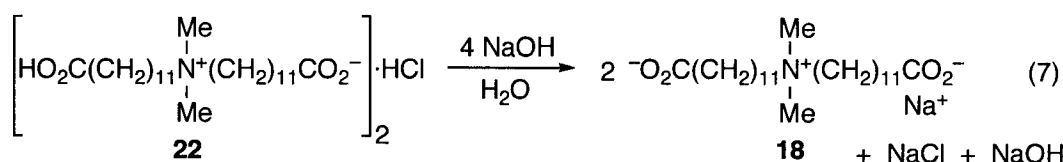
**STUDY 3.** The results of this study have been published.<sup>4</sup> We synthesized and characterized shamrock surfactants **17** and **18**. The former surfactant contains a central phosphorodithioate headgroup and the latter, a central quaternary ammonium headgroup. Both surfactants contain terminal carboxylate headgroups.



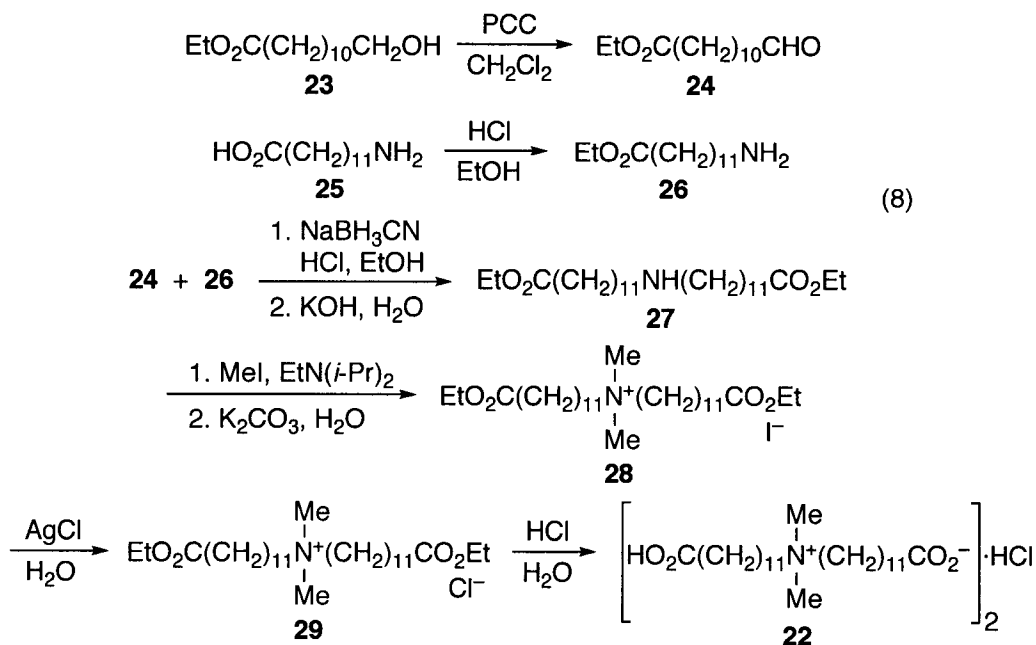
Surfactant **17** was synthesized in three steps (eq 6), starting with the conversion of commercially-available  $\omega$ -hydroxy carboxylic acid **19** into its methyl ester **20**. Then the reaction of **20** with phosphorus pentasulfide gave compound **21**, which was converted into **17** by neutralization of its phosphorodithioic acid group and saponification of its ester groups with potassium hydroxide.



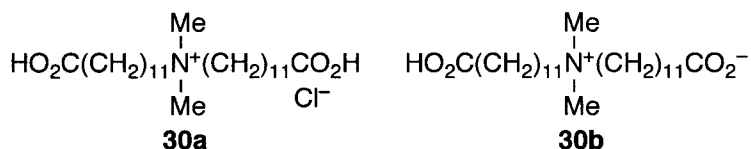
Surfactant **18** was prepared by the addition of four molar equivalents of sodium hydroxide to an aqueous dispersion of surfactant **22** (eq 7), and it was characterized as the resultant mixture with one-half molar equivalent each of sodium chloride and sodium hydroxide.



The synthesis of **22** (eq 8) started with the oxidation of  $\omega$ -hydroxy carboxylate ester **23** to give  $\omega$ -oxo carboxylate ester **24**; compound **23** was obtained by the esterification of **19** with ethanol. Then the reductive alkylation of  $\omega$ -amino carboxylate ester **26**, prepared from commercially-available  $\omega$ -amino carboxylic acid **25**, with **24** gave amino diester **27**. Quaternization of **27** with methyl iodide gave **28**, which was converted into **29** by a metathesis reaction with silver chloride. Then the hydrolysis of **29**'s ester groups gave **22**.

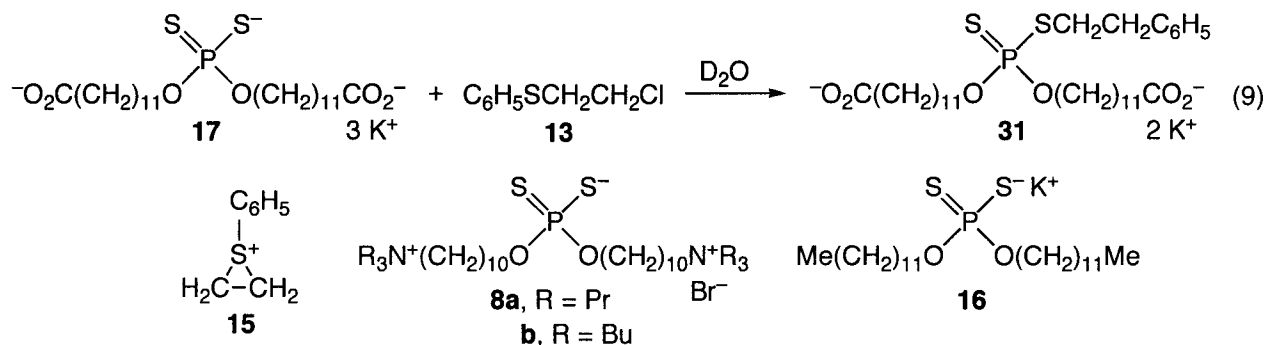


The synthesis of surfactant **22** was included in the Progress Report for August 1, 2004 to July 31, 2005, but its structure was incorrectly shown there as cationic surfactant **30a**. The correct composition of **22** as shown above corresponds to a 1:1 mixture of **30a** and zwitterionic **30b**.

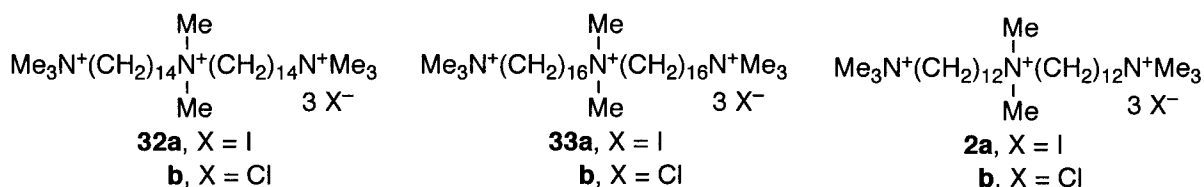


As noted above, surfactant **18** was obtained and characterized as a mixture with one-half molar equivalent each of sodium chloride and sodium hydroxide. The  $T_k$  values of surfactants **17** and **18** are  $\leq 23^\circ\text{C}$ . The cac values of **17** and **18** in water are  $(7.7 \pm 0.4) \times 10^{-3}$  and  $(6.2 \pm 0.1) \times 10^{-3}$  M, respectively, and the surface tensions of aqueous solutions above their cac values are ca. 41 and ca. 36 mN/m, respectively. The  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectra of **17** and the  $^1\text{H}$  NMR spectrum of **18** were recorded in  $\text{D}_2\text{O}$  ([surfactant] = 2.5 its cac value). The  $^1\text{H}$  NMR spectra of **17** and **18** contained sharp, high-resolution signals, and the  $^{31}\text{P}$  NMR spectrum of **17** contained one sharp signal. These results are consistent with the presence of small aggregates such as micelles or small vesicles. By DLLS, the aggregates of **17** and **18** in water ([surfactant] = 2.5 times its cac value) have hydrodynamic diameters of  $123 \pm 9$  nm and  $88 \pm 5$  nm, respectively. These aggregates are significantly larger than micelles, and somewhat larger than small vesicles, but the morphology of these aggregates is unknown. The undisturbed hydration of **17** and **18** in water, as followed by phase-contrast optical microscopy, gave coacervate droplets.

The efficacy of aqueous aggregated surfactant **17** in the decontamination of mustard simulant **13** was evaluated. The reaction of **17** with **13** to give **31** (eq 9) corresponds to the decontamination of **13**. In this reaction, the nucleophilic dithiophosphate headgroup of **17** most likely captures episulfonium ion **15**. In Study 2, we noted that shamrock surfactants **8** are no more effective than the parent dithiophosphate surfactant **16** in decontaminating **13**. Since we found that **17** is no better than both **8** and **16** in decontaminating **13**, we did not pursue this investigation further. We had thought that aggregated **17** would be more effective than **8** and **16**, given the negative charge of the interfacial region of **17**'s aggregates, which might stabilize the transition state leading to the formation of positively-charged **15** from **13** solubilized within the water-aggregate interface.

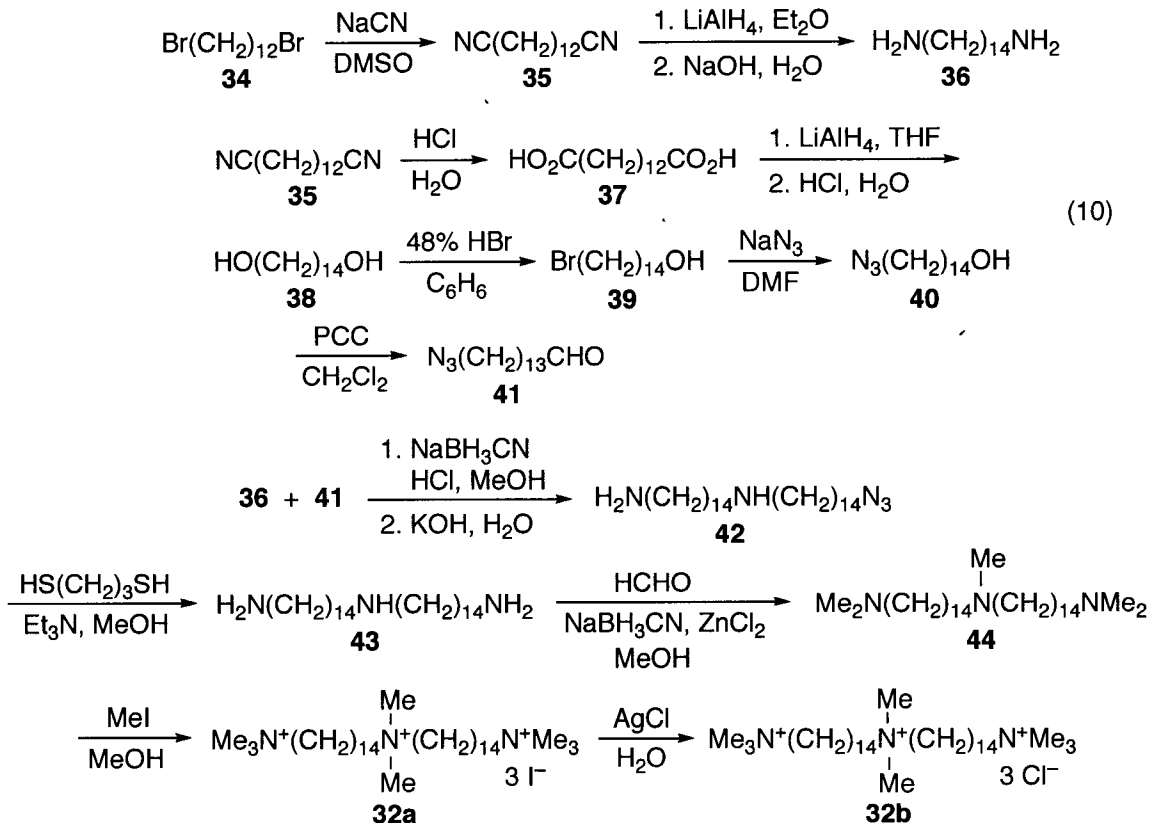


**STUDY 4.** The results of this study have been published.<sup>5</sup> We synthesized and characterized shamrock surfactants **32** and **33**, which are higher homologs of surfactants **2** (see Study 1).

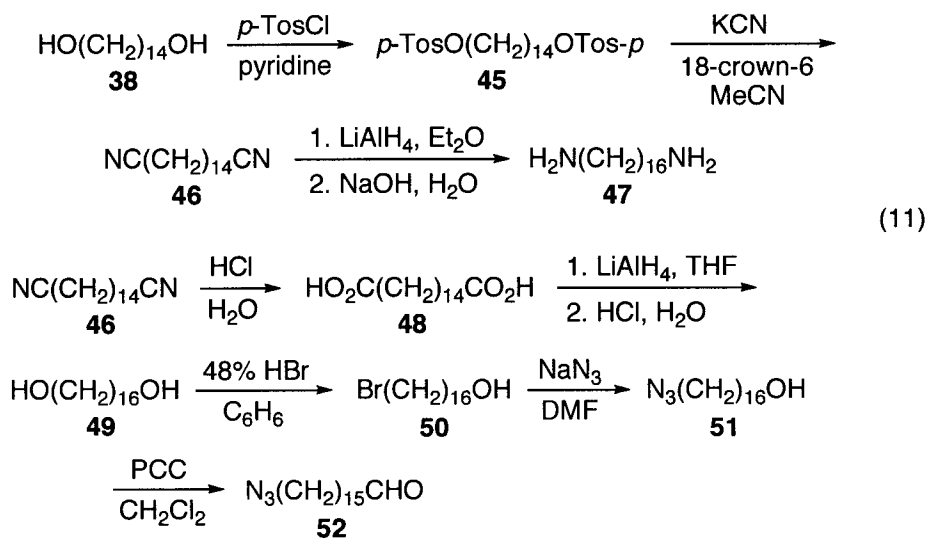


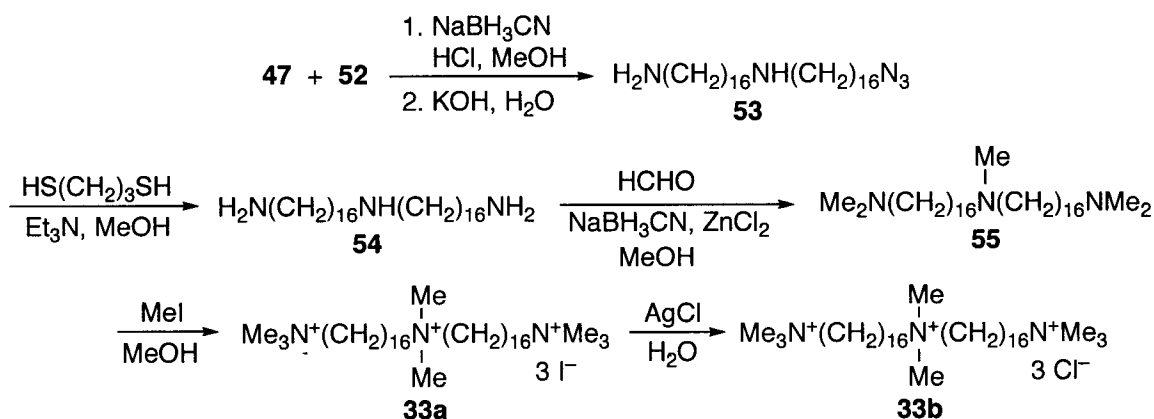
Surfactants **32** were prepared as shown (eq 10), starting with the conversion of commercially-available 1,12-dibromododecane (**34**) into dinitrile **35**. Then the reduction and hydrolysis of **35** gave diamine **36** and dicarboxylic acid **37**, respectively. The reduction of **37** yielded diol **38**, which was converted into bromo alcohol **39**. The nucleophilic displacement of bromide ion from **39** by azide ion gave azido alcohol **40**, which was oxidized to give azido aldehyde **41**. The reductive alkylation of **36**

with **41** yielded azido diamine **42**, which was reduced to give triamine **43**. Reductive methylation of **43** with formaldehyde gave triamine **44**, which was converted into surfactant **32a** by quaternization with methyl iodide. The iodide counterion of **32a** was exchanged for chloride to give **32b**.

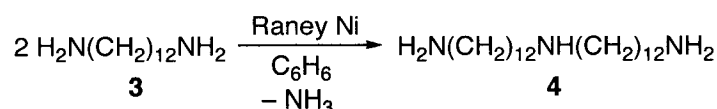


Surfactants **33** were prepared as shown (eq 11), starting with the conversion of diol **38** from above into ditosylate **45**. The nucleophilic displacement of **45**'s tosylate groups by cyanide ion gave dinitrile **46**. From dinitrile **46**, the path to surfactants **33** through compounds **47-55** was analogous to that used to convert homologous dinitrile **35** into surfactants **32**.



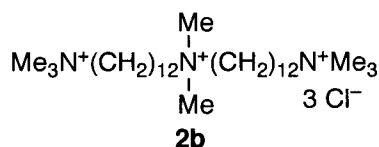


The above synthetic routes to surfactants **32** (C14 homolog) and **33** (C16) were considerably longer than that to surfactants **2** (C12), even though all three routes use the same reactions for the conversion of an intermediate triamine (**43**, **54**, and **4**) into the final products. The difference in length involves the synthesis of the triamine. As noted in **Study 1**, triamine **4** was prepared in one step by Raney nickel-catalyzed dimerization of commercially-available diamine **3**, with the formal loss of ammonia. Since the analogous dimerization of **36** to **43** did not work, the lengthy conversions of **36** to **43** (eq 10), and of **47** to **54** (eq 11) were necessary.

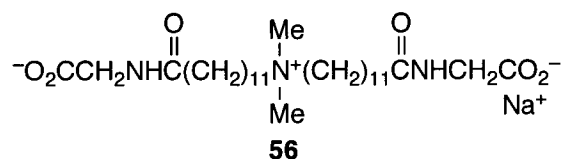


The  $T_k$  values of surfactants **32b** and **33b** are  $\leq 23^\circ\text{C}$ . Their cac values in water are  $(7.2 \pm 0.1) \times 10^{-3}$  and  $(1.8 \pm 0.1) \times 10^{-3}$  M, respectively. The  $^1\text{H}$  NMR spectra of **32b** and **33b** in  $\text{D}_2\text{O}$  ( $[\text{surfactant}] = 2.5\text{--}2.7$  times its cac value) contained sharp or moderately broadened signals. These results are consistent with the presence of small aggregates such as micelles or small vesicles. By DLLS, the hydrodynamic diameters of aggregates of **32b** and **33b** in water ( $[\text{surfactant}] = 2.5\text{--}2.7$  times its cac value) are  $114 \pm 9$  and  $196 \pm 6$  nm, respectively. The aggregates are significantly larger than micelles, and somewhat larger than small vesicles, but the morphology of these aggregates is unknown and not readily predicted. The undisturbed hydration of surfactants **14b** and **15b** in water, each with three molar equivalents of added NaCl, gave coacervate droplets, as followed by phase-contrast optical microscopy.

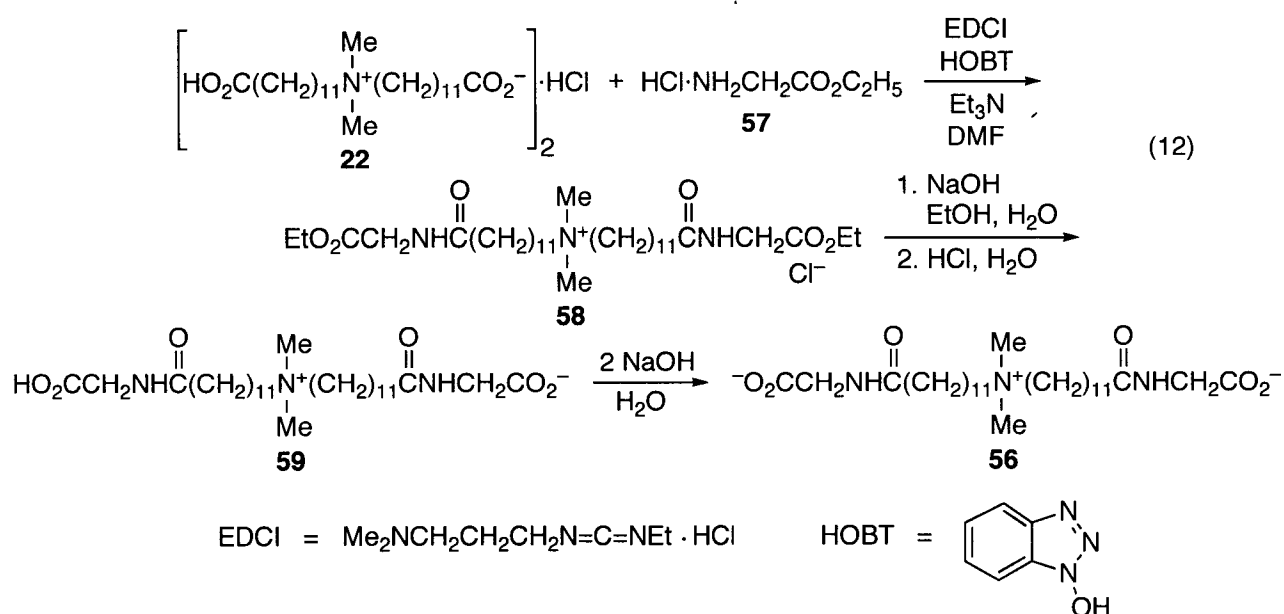
Aqueous 0.052 M (3.3 wt %) **32b** and 0.053 M (3.6 wt %) **33b** were studied by cryo-etch HRSEM. Irregularly-shaped and oriented walls/ribbons connecting to form open compartments were observed for both **32b** and **33b**. These morphologies are similar, but not identical to those observed for **2b**, the C12 homolog of **32b** and **33b** (**Study 1**).



**STUDY 5.** The results of this study have been published.<sup>5</sup> We synthesized and characterized shamrock surfactant **56**. It contains a central quaternary ammonium headgroup and flanking carboxylate headgroups. Surfactant **56** is derived from surfactant **18**. On going from **18** to **56**, the former's carboxylate groups have been converted into amide groups with glycine.

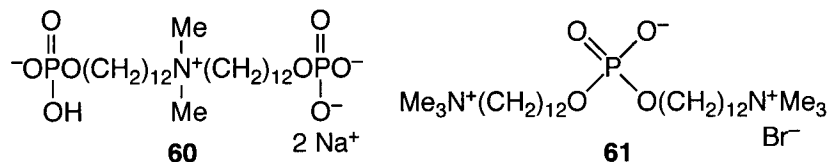


The synthesis of surfactant **56** (eq 12) started with the reaction of surfactant **22** with glycine ethyl ester hydrochloride (**57**) to give surfactant **58**. Then the saponification of **58**'s ester groups gave zwitterionic surfactant **59**, followed by its reaction with two equivalent of sodium hydroxide to give **56** as a mixture with one molar equivalent of sodium hydroxide.

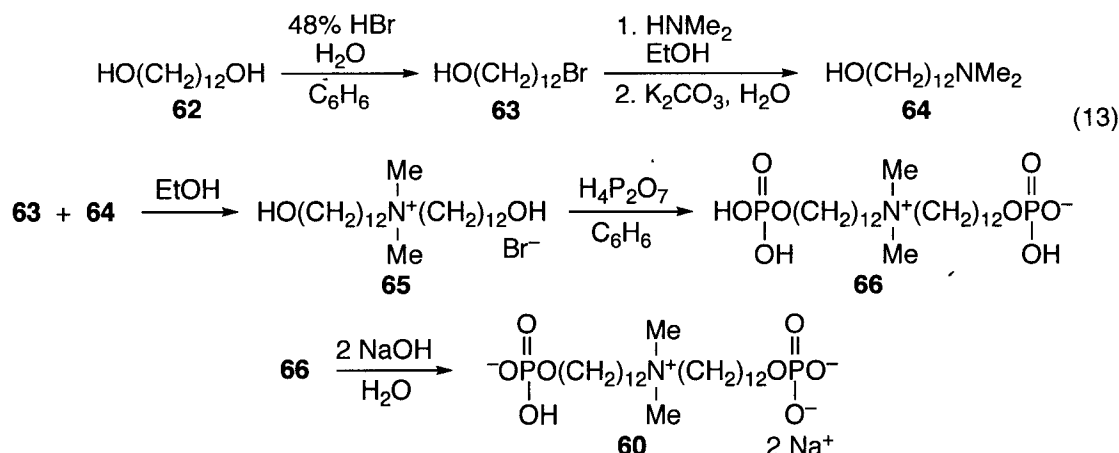


As noted above, surfactant **56** was characterized as a mixture with one molar equivalent of sodium hydroxide. The  $T_k$  value of **56** is  $\leq 23^\circ\text{C}$ , and its cac in water is  $6.7 \pm 0.1 \times 10^{-3} \text{ M}$ . The  $^1\text{H}$  NMR spectrum of surfactant **56** in  $\text{D}_2\text{O}$  ( $[\text{surfactant}] = 2.5\text{--}2.7$  times its cac value) contained sharp or moderately broadened signals. These results are consistent with the presence of small aggregates such as micelles or small vesicles. By DLLS, the hydrodynamic diameter of aggregates of surfactant **56** in water (2.5–2.7 times its cac value) is  $257 \pm 5 \text{ nm}$ , suggesting that the aggregates are significantly larger than micelles and somewhat larger than small vesicles. The undisturbed hydration of **56** in water, followed by phase-contrast optical microscopy, gave coacervate droplets.

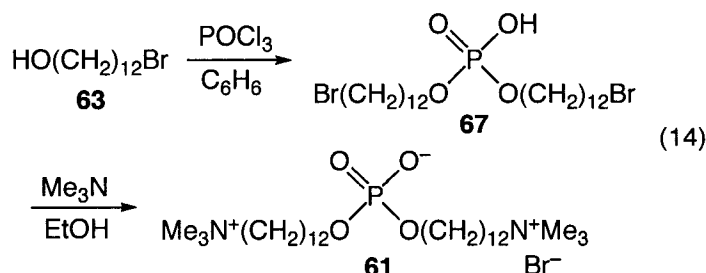
**STUDY 6.** The results of this study have been published.<sup>5</sup> Shamrock surfactants **60** and **61** were synthesized and characterized. Surfactant **60** contains a central quaternary ammonium headgroup and flanking phosphate headgroups. Note that on going from **60** to surfactant **61**, the positions of the headgroups are switched.



The synthesis of surfactant **60** (eq 13) started with the conversion of diol **62** into bromo alcohol **63**. Then the reaction of **63** with excess dimethylamine gave amino alcohol **64**. The  $S_N2$  reaction of **63** and **64** yielded surfactant **65**, which was converted into zwitterionic surfactant **66** by reaction with pyrophosphoric acid. Then **66** gave shamrock surfactant **60** upon reaction with two equivalents of sodium hydroxide.



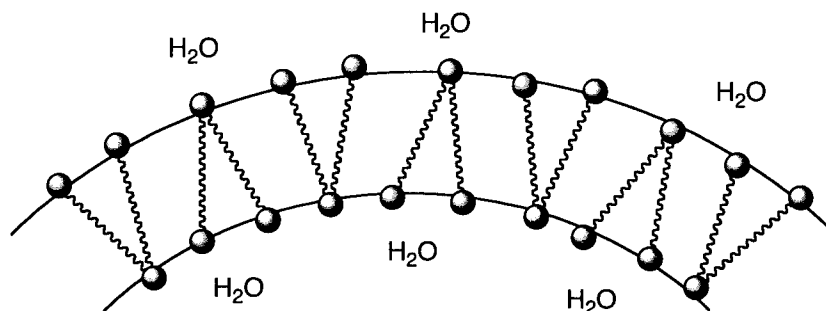
The synthesis of shamrock surfactant **61** (eq 14) involved the reaction of bromo alcohol **63** with phosphorus oxychloride to give diester phosphoric acid **67**, which was converted into **61** by quaternization with trimethylamine.



The  $T_k$  values of surfactants **60** and **61** are  $\leq 23^\circ\text{C}$ . Their cac values in water are  $(3.4 \pm 0.2) \times 10^{-3}$  and  $(1.2 \pm 0.1) \times 10^{-3}$  M, respectively. The  $^1\text{H}$  NMR spectrum of **60** and the  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectra of **61** were recorded in  $\text{D}_2\text{O}$  ([surfactant] = 2.5-2.7 times its cac value). The  $^1\text{H}$  NMR spectra contained sharp or moderately broadened signals, and the  $^{31}\text{P}$  NMR spectrum contained one sharp signal. These results are consistent with the presence of small aggregates such as micelles or small vesicles.

By DLLS, the hydrodynamic diameters of the aggregates of **60** and **61** in water ([surfactant] = 2.5-2.7 times its cac value) are  $242 \pm 11$  and  $278 \pm 2$  nm, respectively. These aggregates are significantly larger than micelles, and somewhat larger than small vesicles, but their morphology is unknown. The undisturbed hydration of surfactants **60** and **61** in water, followed by phase-contrast optical microscopy, gave coacervate droplets.

Coacervate droplets were observed in the hydration of shamrock surfactants in each of the above studies. Perhaps the structural character of shamrock surfactants, with three headgroups separated by two hydrocarbon chains, is favorable for the formation of coacervates. One headgroup of general structure **1** can reside at one of the water-surfactant interfaces of a coacervate membrane, while the other two can reside at the other, as shown below.



### Bibliography

- <sup>1</sup> D. A. Jaeger, X. Zeng, R. P. Apkarian, "Shamrock Surfactants: Synthesis and Characterization," *Langmuir*, **20**, 10427 (2004).
- <sup>2</sup> F. M. Menger, A. L. Galloway, M. E. Chlebowsky, R. P. Apkarian, "Ultrastructure in Frozen/Etched Saline Solutions: On the Internal Cleansing of Ice," *J. Am. Chem. Soc.*, **126**, 5897 (2004).
- <sup>3</sup> D. A. Jaeger, C. L. Schilling III, A. K. Zelenin, B. Li, E. Kubicz-Loring, "Reaction of a Vesicular Functionalized Surfactant with 2-Chloroethyl Phenyl Sulfide, a Mustard Simulant," *Langmuir*, **15**, 7180 (1999).
- <sup>4</sup> D. A. Jaeger, A. Mendoza, R. P. Apkarian, "Shamrock Surfactants with Terminal Carboxylate Headgroups and a Central Phosphorodithioate or Quaternary Ammonium Headgroup," *Langmuir*, **22**, 1555 (2006).
- <sup>5</sup> D. A. Jaeger, A. Mendoza, R. Jose, R. P. Apkarian, "Shamrock Surfactants," *Colloids Surf., A*, **302**, 506 (2007).

### C. Publications Submitted Under the Contract.

#### *Papers Published in Peer-Reviewed Journals*

1. D. A. Jaeger, X. Zeng, "Oxidative Destruction of Vesicles of a Functionalized Surfactant," *Langmuir*, **19**, 8721 (2003).
2. D. A. Jaeger, X. Zeng, "Shamrock Surfactants: Synthesis and Characterization," *Langmuir*, **20**, 10427 (2004).
3. D. A. Jaeger, A. Mendoza, R. P. Apkarian, "Shamrock Surfactants with Terminal Carboxylate Headgroups and a Central Phosphorodithioate or Quaternary Ammonium Headgroup," *Langmuir*, **22**, 1555 (2006).
4. D. A. Jaeger, A. Mendoza, R. Jose, R. P. Apkarian, "Shamrock Surfactants," *Colloids Surf., A*, **302**, 506 (2007).
5. D. Ono, J. Bragdon, D. A. Jaeger, "Synthesis and Characterization of Dithiocarbamate Surfactants," *Colloids Surf., A*, in press (June 25, 2007).

#### *Papers Published in Non-Peer-Reviewed Journals or in Conference Proceedings*

1. D. A. Jaeger, "Synthesis and Characterization of Novel Surfactants," *SCANNING*, **27**, 65 (2005).

*Papers Presented at Meetings, But Not Published in Conference Proceedings*

1. D. A. Jaeger, X. Zeng, A. Mendoza, R. Jose, Z. Li, "A Collection of Novel Surfactants," 8th Annual Meeting of the Swedish Centre for Surfactants Based on Natural Products, Sigtuna, Sweden, September 29 & 30, 2003.
2. D. A. Jaeger, X. Zeng, "Destructible Vesicles of a Functionalized Surfactant," 2003 Joint Services Scientific Conference on Chemical & Biological Defense Research, November 17-20, 2003, Towson, MD.
3. D. A. Jaeger, A. Mendoza, X. Zeng, "Shamrock Surfactants and Mustard Decontamination," 2004 Joint Service Chemical Biological (CB) Decontamination Conference, Tampa, FL, May 16-20, 2004.
4. D. A. Jaeger, X. Zeng, A. Mendoza, R. P. Apkarian, "Shamrock Surfactants," 9th Annual Meeting, Centre for Surfactants Based on Natural Products, Täby, Sweden, September 27 & 28, 2004.
5. D. A. Jaeger, X. Zeng, A. Mendoza, R. P. Apkarian, "Shamrock Surfactants," Workshop on Surfactants and Their Assemblies: Future Opportunities, Jackson Hole, WY, October 6-8, 2004.
6. D. A. Jaeger, "Synthesis and Characterization of Novel Surfactants," SCANNING 2005, the 16th Annual Meeting on Scanning Microscopies, April 5-7, 2005, Monterey, CA
7. D. A. Jaeger, "Shamrock Surfactants and Mustard Decontamination," 2006 DECON Science & Technology Conference, Westminster, CO, October 31-November 2, 2006.

*Manuscripts Submitted But Not Published*

None

*Technical Reports Submitted to ARO*

None

**D. List of All Participating Scientific Personnel & Advanced Degrees Earned While Employed on the Project.**

David A. Jaeger, PI  
 Robin Jose, Ph.D., 2006  
 Alvaro Mendoza, Ph.D., 2006

**E. Report of Inventions.**

None

# REPORT OF INVENTIONS AND SUBCONTRACTS

(Pursuant to "Patent Rights" Contract Clause) (See Instructions on back)

The public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing the burden, to the Department of Defense, Executive Services Directorate (9000-0095). Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.

## PLEASE DO NOT RETURN YOUR COMPLETED FORM TO THE ABOVE ORGANIZATION. RETURN COMPLETED FORM TO THE CONTRACTING OFFICER.

|                                                                                                       |  |                                        |  |                                           |  |                          |  |                                                                                                               |  |
|-------------------------------------------------------------------------------------------------------|--|----------------------------------------|--|-------------------------------------------|--|--------------------------|--|---------------------------------------------------------------------------------------------------------------|--|
| 1. a. NAME OF CONTRACTOR/SUBCONTRACTOR<br>David A. Jaeger                                             |  | c. CONTRACT NUMBER<br>DAAD19-03-1-0342 |  | 2. a. NAME OF GOVERNMENT PRIME CONTRACTOR |  | c. CONTRACT NUMBER       |  | 3. TYPE OF REPORT (X one)<br>a. INTERIM <input type="checkbox"/> b. FINAL <input checked="" type="checkbox"/> |  |
| b. ADDRESS (Include ZIP Code)<br>Department of Chemistry, University of Wyoming,<br>Laramie, WY 82071 |  | d. AWARD DATE (YYYYMMDD)<br>20030915   |  | b. ADDRESS (Include ZIP Code)             |  | d. AWARD DATE (YYYYMMDD) |  | 4. REPORTING PERIOD (YYYYMMDD)<br>a. FROM 20030915<br>b. TO 20070630                                          |  |

### SECTION I - SUBJECT INVENTIONS

| 5. "SUBJECT INVENTIONS" REQUIRED TO BE REPORTED BY CONTRACTOR/SUBCONTRACTOR (If "None," so state) |                       |                                                                                     |                                             |        |             |        |                                                                                  |        |    |  |
|---------------------------------------------------------------------------------------------------|-----------------------|-------------------------------------------------------------------------------------|---------------------------------------------|--------|-------------|--------|----------------------------------------------------------------------------------|--------|----|--|
| NAME(S) OF INVENTOR(S)<br>(Last, First, Middle Initial)                                           | TITLE OF INVENTION(S) | DISCLOSURE NUMBER,<br>PATENT APPLICATION<br>SERIAL NUMBER OR<br>PATENT NUMBER<br>c. | ELECTION TO FILE<br>PATENT APPLICATIONS (X) |        |             |        | CONFIRMATORY INSTRUMENT<br>OR ASSIGNMENT FORWARDED<br>TO CONTRACTING OFFICER (X) |        |    |  |
|                                                                                                   |                       |                                                                                     | (1) UNITED STATES                           |        | (2) FOREIGN |        |                                                                                  |        |    |  |
|                                                                                                   |                       |                                                                                     | (a) YES                                     | (b) NO | (a) YES     | (b) NO | (a) YES                                                                          | (b) NO | e. |  |
| None                                                                                              |                       |                                                                                     |                                             |        |             |        |                                                                                  |        |    |  |

| f. EMPLOYER OF INVENTOR(S) NOT EMPLOYED BY CONTRACTOR/SUBCONTRACTOR |  |                                                        |  | 9. ELECTED FOREIGN COUNTRIES IN WHICH A PATENT APPLICATION WILL BE FILED |  |                                             |  |
|---------------------------------------------------------------------|--|--------------------------------------------------------|--|--------------------------------------------------------------------------|--|---------------------------------------------|--|
| (1) (a) NAME OF INVENTOR (Last, First, Middle Initial)              |  | (2) (a) NAME OF INVENTOR (Last, First, Middle Initial) |  | (1) TITLE OF INVENTION                                                   |  | (2) FOREIGN COUNTRIES OF PATENT APPLICATION |  |
| (b) NAME OF EMPLOYER                                                |  |                                                        |  |                                                                          |  |                                             |  |
| (c) ADDRESS OF EMPLOYER (Include ZIP Code)                          |  | (c) ADDRESS OF EMPLOYER (Include ZIP Code)             |  |                                                                          |  |                                             |  |

### SECTION II - SUBCONTRACTS (Containing a "Patent Rights" clause)

| 6. SUBCONTRACTS AWARDED BY CONTRACTOR/SUBCONTRACTOR (If "None," so state) |                                  |                                |                           |                      |                                                                   | SUBCONTRACT DATES (YYYYMMDD) |                             |
|---------------------------------------------------------------------------|----------------------------------|--------------------------------|---------------------------|----------------------|-------------------------------------------------------------------|------------------------------|-----------------------------|
| NAME OF SUBCONTRACTOR(S)<br>a.                                            | ADDRESS (Include ZIP Code)<br>b. | SUBCONTRACT<br>NUMBER(S)<br>c. | FAR "PATENT RIGHTS"<br>d. |                      | DESCRIPTION OF WORK TO BE PERFORMED<br>UNDER SUBCONTRACT(S)<br>e. | f.                           |                             |
|                                                                           |                                  |                                | (1) CLAUSE<br>NUMBER      | (2) DATE<br>(YYYYMM) |                                                                   | (1) AWARD                    | (2) ESTIMATED<br>COMPLETION |
| None                                                                      |                                  |                                |                           |                      |                                                                   |                              |                             |

### SECTION III - CERTIFICATION

| 7. CERTIFICATION OF REPORT BY CONTRACTOR/SUBCONTRACTOR (Not required if: (X as appropriate))                                                                                                                             |                                                   |                                            |  |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------|--------------------------------------------|--|
| I certify that the reporting party has procedures for prompt identification and timely disclosure of "Subject Inventions," that such procedures have been followed and that all "Subject Inventions" have been reported. |                                                   | X SMALL BUSINESS or NONPROFIT ORGANIZATION |  |
| a. NAME OF AUTHORIZED CONTRACTOR/SUBCONTRACTOR<br>OFFICIAL (Last, First, Middle Initial)<br>Roger Wilmot                                                                                                                 | b. TITLE<br>Associate Vice President for Research | c. SIGNATURE                               |  |
|                                                                                                                                                                                                                          |                                                   | d. DATE SIGNED                             |  |