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Laboratory Experiment

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# Experimenting with Synthesis and Analysis of Cationic Gemini Surfactants in a Second-Semester General Chemistry Laboratory

Mary E. Anzovino,*[†,§] Andrew E. Greenberg,[‡] and John W. Moore[†]

[†]Department of Chemistry, University of Wisconsin—Madison, 1101 University Avenue, Madison, Wisconsin 53706, United States
[‡]Department of Chemical and Biological Engineering, University of Wisconsin—Madison, 1415 Engineering Drive, Madison, Wisconsin 53706, United States

S *Supporting Information*

**ABSTRACT:** A laboratory experiment is described in which students synthesize a variety of cationic gemini surfactants and analyze their efficacy as fabric softeners. Students perform a simple organic synthesis reaction and two analytical tests (one qualitative and one quantitative), and use the class data to assess the synthesized products. The experiment was based on published research developed in the chemistry department at the institution at which the experiment was developed.

**KEYWORDS:** *First-Year Undergraduate/General, Laboratory Instruction, Hands-On Learning/Manipulatives, Surface Science, Synthesis*

The value of undergraduate research experiences has been documented extensively in the literature. Authentic[1−5] and course-based research experiences[6−12] both yield a variety of positive outcomes for students. For a variety of reasons, integration of research modules into some undergraduate curricula is not currently feasible, so a less complete integration of research ideas is still potentially useful. It is possible to draw inspiration from the topical content of current research and incorporate authentic laboratory techniques in an experiment without it being part of a genuine research framework.

Elliot et al. have suggested[13] that Cognitive Apprenticeship Theory[14] could provide a useful framework within which to design or to revise an undergraduate laboratory curriculum; development of this experiment used this framework. The experiment is part of a larger project evaluating the impact of such experiments on students' awareness of and attitudes toward scientific research; an assessment instrument to address this evaluation will be described in a future manuscript.

The inclusion of this experiment early in the second-semester general chemistry laboratory curriculum served a number of purposes. The schedule allowed the students to conduct this experiment during the organic chemistry unit of the lecture course; this experiment provides practice conducting a basic organic synthesis reaction. The pre-lab and post-lab questions tie in the concept of intermolecular forces, asking students to consider scenarios involving amphiphiles and solvents. Additionally, one of the post-lab questions involves error analysis and prompts the students to consider the reasons why, for example, two groups might get different results in the qualitative assessment for the same synthesized product. Students gain practice using Eppendorf pipettes and volumetric glassware during the experiment; the simplicity of the equipment involved contributes to the wide applicability of this experiment at a variety of institutions. The typical time for a single laboratory section to complete the experiment was usually in the range of 2−2.5 h.

## BACKGROUND

The term *surfactant*, which is a contraction of *surf*ace *act*ive age*nt*, refers to an amphiphilic substance. Surfactants comprise a polar or ionic segment, which is hydrophilic, and a nonpolar segment, which is hydrophobic. Surfactants are classified by the nature of their hydrophilic portion (Figure 1); the four main types of surfactants are anionic, cationic, nonionic, and zwitterionic.[15]

Surfactants are used for a wide variety of applications, generally dictated by the nature of their hydrophilic group. For example, anionic surfactants such as sodium dodecyl sulfate are often used in laundry detergents and personal hygiene products (such as toothpaste). Cationic surfactants find utility in another component of the laundry process: fabric softeners.

A variety of undergraduate laboratory experiments dealing with surfactants have been published in this *Journal*. Those experiments intended for first-year undergraduates primarily involve determining the critical micelle concentration (CMC)

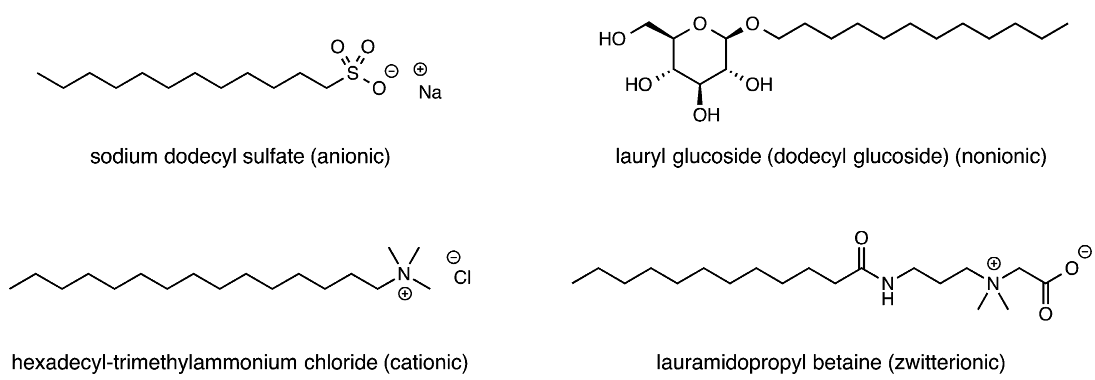
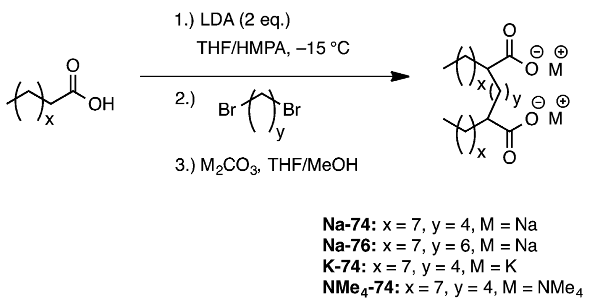



**Figure 1.** Surfactant classifications.

of various surfactants[16−19] or evaluating their detergency (cleaning power).[20,21] Synthetic experiments involving surfactants are less common, mainly involving soaps, e.g., saponification of various oils.[22]

The experiment discussed herein was inspired by published research. Mahanthappa and co-workers have optimized conditions for the synthesis of a new class of anionic gemini surfactants (Scheme 1) that, when dissolved in water, arrange themselves in morphologies (3-dimensional aggregation arrangements) poised to facilitate ion transfer and selective chemical separations.[23]

**Scheme 1. Synthesis of Anionic Gemini Surfactants**

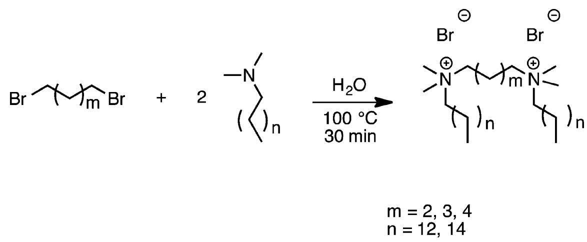



Gemini surfactants are compounds that contain two amphiphilic motifs connected by a short spacer; the gemini nature of these species contributes to the aforementioned aggregate structures. It is not feasible, however, for general chemistry students to replicate the synthesis of these particular compounds, as the reagents required are inappropriate for an introductory laboratory. However, cationic gemini surfactants, particularly bisquaternary ammonium salts, have been synthesized and studied under much milder conditions[24,25] and such compounds seemed a reasonable focus for a new undergraduate experiment.

## ■ EXPERIMENTAL OVERVIEW

Students work in pairs to synthesize one of six possible cationic gemini surfactant products (Scheme 2), arising from one of three starting alkyl dibromides (1,4-dibromobutane, 1,5-dibromopentane, and 1,6-dibromohexane) and one of two starting amines (*N*,*N*-dimethyltetradecylamine and *N*,*N*-dimethylhexadecylamine). The laboratory instructor assigns each pair a target product to ensure that each target product is synthesized by at least one (preferably two, if the number of students allows) groups.

**Scheme 2. Synthesis of Cationic Gemini Surfactants**




The students also perform two analytical tests, one quantitative and one qualitative. A modified version of the Draves test[26] allows them to explore the impact of the surfactant treatment on the absorptivity of denim fabric samples. A qualitative test allows them to assess the impact of the surfactant treatment on the flexibility and softness of the denim fabric samples. The students create a class data table on the chalkboard at the front of the room, and use this information to answer two of the post-lab questions.

This experiment has been conducted by over 1000 students in second-semester general chemistry. Each section met for 3 h and had 20−24 students supervised by a teaching assistant (TA); the students typically completed the experiment in under two and a half hours.

## ■ EXPERIMENTAL PROCEDURE

Combine starting materials with water in a beaker equipped with a stir bar. Place a watchglass over the beaker to make a crude reflux condenser. Reflux 30 min. One member of the pair watches the reaction while the other prepares a solution of commercially available fabric softener for later use. Allow the solution to cool to near room temperature before diluting it to produce a solution of similar concentration to that of the commercial product.

Obtain six 1 in. x 1 in. squares of denim fabric and treat them by swirling them around in one of the previously prepared solutions for a few seconds and then rinsing. Treat two fabric samples with the commercial fabric softener solution, two samples with the solution of the synthesized product, and two with deionized water as a control. After drying the fabric samples using the heater/stirrer (set on low), perform two analytical assessments. To prepare for the quantitative (Draves') test, deionized water is placed in a beaker. The test is conducted by placing the fabric square flat on the surface of the water and recording the length of time required for the fabric to become completely saturated. For the qualitative tactile assessment, simply rank the fabrics in terms of softness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and flexibility. It is important to use separate fabric samples for the two tests, as the samples will be wet after the quantitative analysis, and it is possible that oils from the skin could be transferred to the samples during the qualitative analysis.

## ■ HAZARDS

All of the chemicals used in this experiment are corrosive and pose a hazard to skin and eyes. Goggles and gloves must be worn at all times while handling them.

## ■ RESULTS AND DISCUSSION

### Components of Cognitive Apprenticeship Included this Experiment

Cognitive Apprenticehip[14] involves four dimensions of the learning environment: content, methods, sequencing, and sociology. Content is the knowledge required to have expertise in a particular area. Methods include the pedagogy employed by the instructor and the authentic techniques performed by the students in the laboratory. Sequencing refers to planning learning activities in order of increasing complexity. Sociology encompasses the social aspects of learning.

This experiment addresses the content, methods, and sociology aspects of Cognitive Apprenticeship. Although some of the details are different from the published research (e.g., nature of the hydrophobic section of the gemini surfactants), the content of the experiment draws from published research in the chemistry department at the institution where the experiment was developed. The procedures involved also feature some authentic practices. The students perform a synthesis reaction by heating a mixture at reflux. The analytical techniques are also modified versions of standard procedures (e.g., the modified Draves test); students obtain data similar to that produced by the tests as originally designed. The sociological components of the experiment reflect authentic scientific practices. The students work in teams (pairs), requiring them to thoughtfully delegate duties throughout the experiment. Both team members are responsible for the data the team produces, so it behooves each student to check his or her partner's work in addition to his or her own work. The pairs in each laboratory section also constitute a larger team since they are required to share and use everyone's data in completing the post-lab assignment.

### Student Data

The students' shared data are necessary to answer some of the post-lab questions. The softness/flexibility ratings and saturation times vary among groups of students, but some general trends were observed across the groups (Figure 2).

Treatment with only deionized water tended to result in the fabric samples being declared the least soft and flexible (dark blue and red bars). Students had more difficulty distinguishing between the impacts of the commercial fabric softener and their surfactants, however, emphasizing the subjective nature of the analysis and/or the variability in the students' products.

The students also examined the class data for saturation times of the fabric samples following the three possible treatments (Figure 3).

One concern when fabric softeners are used is that treated fabrics exhibit diminished ability to absorb water. In this case, however, treatment with the synthesized surfactants (middle, brown) yielded fabrics that had significantly *lower* saturation times (faster absorption) than treatment with the commercial product (left, blue) or water (right, red). It is difficult to

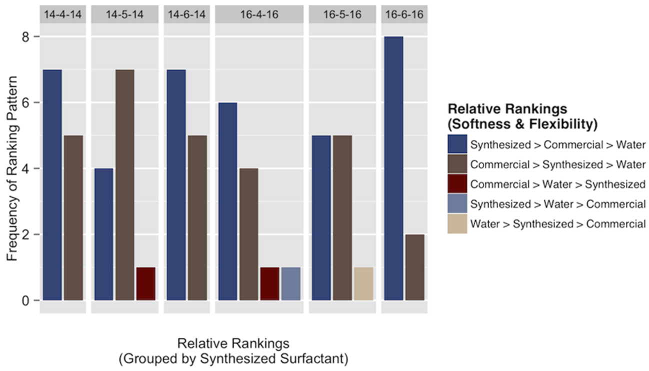


**Figure 2.** Student data: ranking flexibility and softness of fabric samples. Fabric samples were treated with a solution of commercial fabric softener, a solution of their synthesized surfactant, and water. The bisquaternary ammonium salts are typically referred to as *m*−*n*−*m*, where *m* represents the length of the long-chain portion and *n* represents the length of the spacer chain, so, for example, 14−4−14 is the surfactant with a 14-carbon long-chain portion and a 4-methylene spacer.

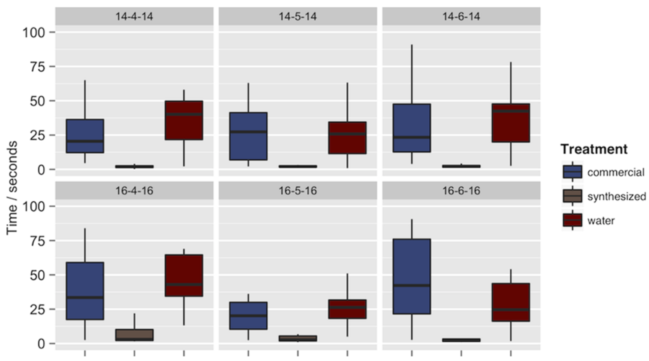


**Figure 3.** Student data: saturation times of fabric samples. (Outliers have been removed for clarity.) Fabric samples were treated with a solution of commercial fabric softener, a solution of their synthesized surfactant, and water. The bisquaternary ammonium salts are typically referred to as *m*−*n*−*m*, where *m* represents the length of the long-chain portion and *n* represents the length of the spacer chain, so, for example, 14−4−14 is the surfactant with a 14-carbon long-chain portion and a 4-methylene spacer.

determine the reasons for these differences, because the precise composition of the commercial product is unknown. It is possible that the fabric (which was used as purchased with no pretreatment) initially has some kind of coating that inhibits water absorption, and the surfactants synthesized by the students have sufficiently high detergent behavior that treatment with those products removes that coating.

In a post-lab question, the students are asked "Based on the absorbency criterion, which of the surfactants synthesized in class today would you most want to use as a fabric softener in your next load of laundry? Explain your choice." Answering this question requires them to look at the class data and identify the synthesized product that result in the lowest saturation time. In each laboratory section, there were only two sets of data for each product, and sometimes those data did not agree with each other. Consequently, students had to evaluate the quality of the data in order to provide a good response to the question.

Another post-lab question explicitly asks the students to consider data quality by comparing their own results to those of the other group that synthesized the same product. If the data are not similar, the students are asked to provide possible reasons for the differences, of which there are a variety. The most common reason for differences in data involves a difference of opinion between students about what constitutes the fabric being "completely saturated", despite clear directions in the laboratory manual.

### Student Feedback

Student feedback was collected each time this experiment was conducted. Two five-point Likert-scale items were used to assess student perceptions about how enjoyable and how difficult the experiment was, as compared to the other experiments in the course. Overall, students enjoyed this experiment as least as much as, and felt it was no more difficult than, the other experiments they had conducted. A more detailed description of the student feedback results is available in the Supporting Information.

## CONCLUSION

A new laboratory experiment involving the synthesis and authentic analysis of cationic gemini surfactants has been designed and performed by more than 1000 second-semester general chemistry students. The experiment has everyday relevance for the students and is straightforward to complete. Additionally, there exists a variety of possible extensions for this experiment. For example, deionized water was used in the synthesis and analysis phases of the experiment; students could explore whether differences in test results arise if tap water is used. Anionic surfactants are more commonly used as cleaning agents than are cationic surfactants. It is possible that the students could explore why this is so by assessing the detergent behavior of the two categories of surfactant using other experimental procedures featured in this *Journal*.[21]

## ASSOCIATED CONTENT

### Supporting Information

Instructor notes; student handouts; student feedback results. This material is available via the Internet at http://pubs.acs.org.

## AUTHOR INFORMATION

### Corresponding Author

*E-mail: anzovime@miamioh.edu.

### Present Address

[§]Department of Chemistry and Biochemistry, Miami University, Oxford, OH 45056, United States.

### Notes

The authors declare no competing financial interest.

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