

Surfactant Studies of Quaternary Ammonium Compounds: Critical Surfactant Concentration

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ABSTRACT: Quaternary ammonium salts (otherwise known as "quats") commonly form the foundation of formulations in the antimicrobial industry. Although many studies have been conducted on the surfactant and biological aspects of single-component systems, there are few studies concerning the surfactant or biological efficacy of these compounds in multiple-component formulations. Preliminary data using simple emulsion studies with decane were determined to be inadequate. Several inexpensive ways to determine critical surfactant concentrations were developed with limited resources.

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Surfactants constitute a general class of chemical compounds that encompass a myriad of structures, physical properties, and applications (1). This broad applicability has led to surfactants becoming an integral component of many industrial processes and academic endeavors. Quaternary ammonium compounds (quats) are an important branch of surfactants that have unique qualities that make them attractive for investigation. The fundamental distinction between quats and other surfactants lies in their structure. Quats contain a hydrophilic ammonium "head," and a hydrophobic alkyl chain "tail" (2). The presence of the positive charge of the ammonium results in electrostatic interactions between the surfactant and the surface playing the major role. This is in contrast to the vast majority of surfactants, which associate with surfaces as a result of mainly polar and van der Waals interactions (1). Quats have proven to be useful in a variety of applications, including the following: as anti-static agents, conditioners, softeners, and biocides (3,4). Analysis and evaluation of specific structural quats can provide a great deal of insight

into the manner in which this general class of surfactants interacts with a variety of interfaces. The accurate and meaningful measurement of surfactant properties is crucial in determining how a given surfactant will behave within a specific system. The goal of this work is to establish meaningful and affordable methods of evaluation and to move toward a more accurate understanding of the relationship between a surfactant, the interfaces with which it associates, and the system as a whole.

Due to the limited amount of information available for multi-component systems and the inability of surfactant properties to predict biological efficacy, preliminary work was initiated to determine if there were synergistic effects from multi-component systems using a primitive emulsion stability test. The hope was that if some unique properties were seen using simple oil (decane) and water emulsions, other simple tests could be developed using the interfaces of choice (the organism membrane itself). Although the initial studies with two-component systems (5) did show regions of synergy as well as antagonistic effects, the methodology was limiting. Figure 1 demonstrates the interaction between didecyldimethyl ammonium bromide and other dialkyldimethyl ammonium bromides, with alkyl-1 and alkyl-2 represented as the floor of the graph and the height being the difference between the mathematical average of the separate emulsion stability times and the actual measured value. The concentration of 0.05 wt% was determined to be above the critical surfactant concentration (CSC) value, and therefore the mathematical average should represent the case in which no other interaction was involved and mixed micelle formation did not change the measurement. The attempt was made to prove this and other methods.

EXPERIMENTAL PROCEDURES

Three inexpensive methods of indirect surfactant analysis were implemented. These are emulsion stability, drop volume, and a contact area tests. Each method seeks to indirectly evaluate the relationship between a surfactant's concentration and its affinity for a surface via electrostatic, polar, and van der Waals interactions (1). The quaternary ammo-

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Abbreviations: CSC, critical surfactant concentrations; quats, quaternary ammonium salts; CMC, critical micelle concentration.

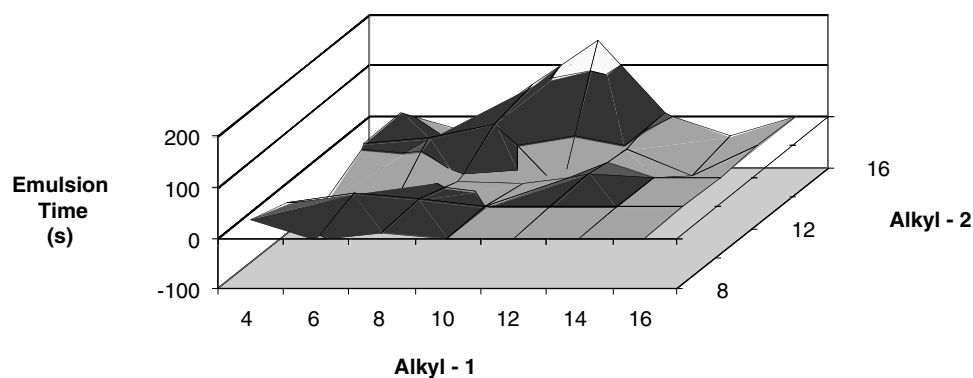


FIG. 1. Emulsion stability of dialkyl quaternary ammonium bromide mixtures with didecyl dimethyl ammonium bromide (50/50 wt/wt at 0.05 total wt%).

nium salts were synthesized using bimolecular nucleophilic substitution (5). The initial results of these single-component systems indicated concentrations at or above the critical micelle concentration (CMC). As the CMC implies a bulk-phase measurement and these primitive tests actually deplete the quaternary ammonium surfactant concentration in the bulk (due to the multiple interfaces), it was believed better to refer to this as cCSC, which can then be classified as being unique for every system.

The first method is an emulsion stability test. The emulsion stability in this method is subject to multiple interfaces; a liquid-liquid interface, and a solid-liquid (glass-liquid) interface. Five milliliters of a solution having 0.05 mass percent of surfactant is transferred to a graduated cylinder. This is followed by the addition of 5 ml of decane to the graduated cylinder. Each analysis is recorded in duplicate to eliminate erroneous errors. Each cylinder is agitated once every second for ten seconds. After the ten-second interval, the time of the phase separation is measured using a stopwatch, and the volume of the emulsion is computed. Each analysis is then repeated after diluting the surfactant solution. When high surfactant concentrations are present, the emulsion volume is maximized. However, a positive relationship exists between the concentration and the phase separation time. See Figure 2.

The second method is a drop volume test. In this test, the relationship between surfactant concentration and surface

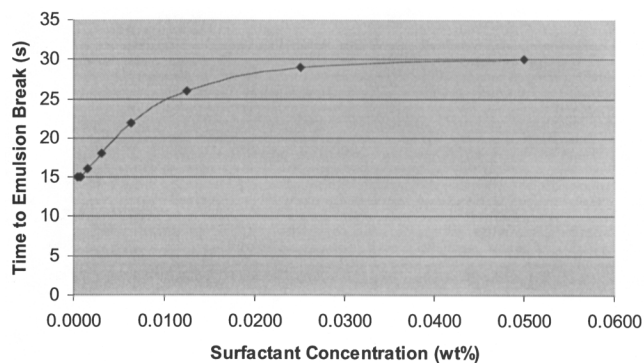


FIG. 2. Emulsion stability of aqueous hexyl tetradecyl dimethyl ammonium bromide and decane.

area (the number of drops per unit volume) is assessed. The drop volume test is subject to both liquid-air and liquid-solid interfaces. A volume of 0.5 ml of surfactant solution is drawn into a 1-cc syringe. The surfactant solution is then gradually forced from the syringe. The number of drops required to fully dispense the solution is recorded. Next, the concentration is diluted by one half and the test repeated. The number of drops of deionized water is used as a baseline (zero activity). The concentration and the number of drops have a positive linear correlation. See Figure 3.

The third method is a contact area test. This method differs from the other two in that only two interfaces are involved and neither is polar. However, during the process of developing the data, the surfactant solution comes in contact with two other surfaces, the syringe glass and the stainless steel needle. The analysis compares the radii of the surfactant solutions at various concentrations. This method involves the solid-liquid interface of the surfactant solution and the parafilm material, as well as the air-liquid interface. A volume of 0.5 ml of a known concentration of surfactant solution is dropped from a 1-cc glass syringe onto the parafilm from a distance of 0.5 in. The radius of the contact area is measured after 5 s. The concentration is then diluted and the test repeated. The data indicate that a positive relationship exists between the surfactant concentration and the radius of the contact area. See Figure 4.

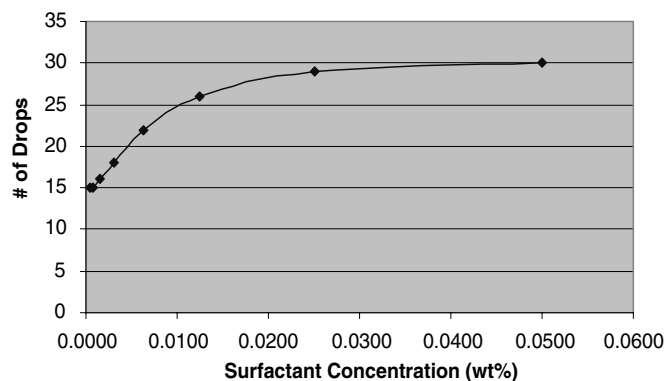


FIG. 3. Drop volume of aqueous hexyl tetradecyl dimethyl ammonium bromide determined by the number of drops from a stainless steel 16-gauge flat needle.

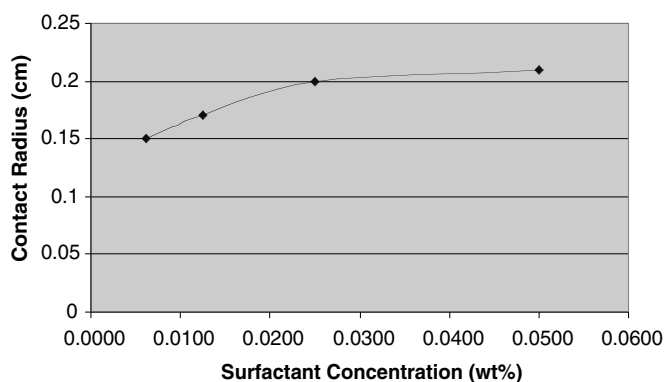


FIG. 4. Contact radius of aqueous hexyl tetradecyl dimethyl ammonium bromide on parafilm.

RESULTS AND DISCUSSION

Several methods are currently employed for surfactant analysis. Most of these methods work on the presumption that the measurements are taken in a static system, making surfactant concentration the only variable in the analysis. In actuality, this is not the case. For example, in the method known as the “ring test,” a metal ring is slowly withdrawn from a glass vessel containing a surfactant solution in which the ring has been submerged. The ring is mechanically pulled from the solution, and the force required to do so is measured (6). It is assumed that the measurement is static, but in actuality it is not. As the ring is pulled from the solution, the surface area increases. As was demonstrated, this creates a problem because all of the surfaces of a system have an effect on the data obtained. Second, as this surface area increases, the time it takes for the surfactant molecules to migrate to the newly created surface becomes a factor, making the measurement dynamic. Cost may also be a factor. Many of the devices that are used to measure surface tension and other properties of surfactants are very expensive. For these reasons, inexpensive methods of surfactant analysis were developed that do not purport to measure any specific physical property of a surfactant, but instead measure the surfactant’s effect on the system as a whole. See Table 1.

This research has brought to light several practical and affordable methods of measuring the relationship between a quat at a known concentration and its effect on the system. During the initial phase of research, a question arose as to whether the common methods of surfactant analysis are entirely applicable to general surfactant studies. Since surfactants interact with surfaces, it is clear that the system in which a surfactant is measured (surfaces, surface area, etc.) will have a decisive impact on the actual values obtained for measurements such as surface tension. Therefore, the values obtained when implementing methods of surfactant analysis are not absolute, but instead are only relevant to that specific measurement, on a specific machine, under a specific set of conditions. This makes correlating surface tension data that is obtained using the standard

TABLE 1
Method Details

Method 1	Emulsion Stability
Equipment	Two 10-mL graduated cylinders (glass) with base and ground glass stoppers (Septa cylinders were found to add variable contamination, and polymer cylinders were found to cause oil/emulsion to “hang-up” on the sides.) One stopwatch 5 mL of decane per test (Other “oils” were tested, and decane was determined to be the best based on time considerations.)
Training Time	2 h
Cost	\$60
Improving Reproducibility	An automatic shaker set to a specific depth of motion and rate could remove the variations seen between researchers.
Method 2	Drop Volume
Equipment	One 1-mL polypropylene syringe One 316 stainless steel 16-gauge pipetting blunt needle
Training Time	1 h
Cost	\$15.25
Improving Reproducibility	A syringe pump could be used to reduce the number of repetitions and to allow for measuring the dynamic attributes of the surfactant. In this method drops must be formed slowly so that the diffusion rate is not imbedded in the measurement.
Method 3	Contact Area
Equipment	One 1-mL polypropylene syringe One 316 stainless steel 16-gauge pipetting blunt needle One small piece of parafilm
Training Time	1 h
Cost	\$15.35
Improving Reproducibility	A perfectly flat, self-leveling platform would allow the measurement to be made anywhere. It is extremely difficult to find an absolutely smooth and level surface to run this measurement.

means impractical, if not useless, in applying the values to more general properties. To obtain meaningful data on a property of a surfactant, that specific property must be measured using the specific surfaces that are to be investigated. Due to the particular nature of surfactants, measuring a specific surfactant’s interaction with glass will not provide useful information about that surfactant’s interaction with any other surface. It has been demonstrated that, to obtain meaningful data about a specific interface, the specific interface must be used to evaluate and analyze the effect that the surfactant has on a specific system.

Since a surfactant interacts with a surface, it is evident that the system in which a surfactant is analyzed (surface composition, surface area, etc.) will play a critical role in the

analysis and have a direct impact on the data obtained from the analysis (7). This can be inferred from the variation found in the drop volume test and the contact area test. The CSC for the drop volume test is approximately 0.01 wt%, while the CSC for the contact area test is approximately 0.02 wt%; these values were estimated using the first derivatives of the curves. This indicates that the concentration of surfactant may have been depleted to a greater extent when conducting the contact area test. Even though the measurement is dealing with only two interfaces, the solution comes in contact with nearly twice as many surfaces during the experiment. Due to these factors, any analysis performed with a specific device having specific surfaces will not be useful in providing general data that can be applied solely to the surfactant. Therefore, the data obtained from an analysis of a surfactant does not provide absolute data. Instead, the data obtained is a result of the various interfaces and dynamic factors present in the system. This is exaggerated for cationic surfactants, which have an increased affinity for negative surfaces that others do not (6). For these reasons, one could argue that it is necessary to measure the property under investigation in a system that consists of the same interfaces, and, to a lesser extent, conditions, that the application will possess. It has been demonstrated that measurements obtained using a less specific approach than the traditional methods will still yield acceptable data. Furthermore, the data obtained from such analyses provide information that can be used to make inferences about the surfactant's performance in similar systems.

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