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## Determination of Aqueous Surfactant Solution Surface Tensions with a Surface Tensiometer

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# Determination of Aqueous Surfactant Solution Surface Tensions with a Surface Tensiometer

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## Abstract

Surfactant solutions are applicable to engineering systems for cooling equipment for electronics. Surfactants can be added to water to improve heat transfer. An application of using aqueous surfactant solutions can be through microchannel heat sink. Although it is ideal to redesign these systems to reduce heat, it is a costly method. Surfactant solutions at optimal solution concentration can be able to transfer heat quickly and effectively with minimum expense. The surface tension of surfactant solutions is an important parameter for boiling heat transfer and must be taken into consideration. The purpose of this research is to measure surface tension of surfactant solutions at varied concentrations and determine the critical micelle concentration (CMC) point. A surface tensiometer that utilizes the Wilhelmy plate method was used to measure the surface tensions of SLS, ECOSURF™ EH-14, and ECOSURF™ SA-9 of various compositions at room temperature. The measured data for SLS followed a pattern similar to reported data in the literature. There are no reported data for EH-14 and SA-9 in the literature since they are new surfactants. Although each surfactant solution had different surface tension values, it was observed that, as surfactant concentration increased, the surface tension decreased and eventually leveled out at the CMC point.

## Introduction

Surfactants are compounds that lower the surface tension between two liquids or between a liquid and a solid. Surfactants may act as detergents, wetting agents, emulsifiers, foaming agents, and dispersants. Surfactants can be classified as nonionic, anionic, cationic, and amphoteric [1]. Figure 1 shows these classifications.

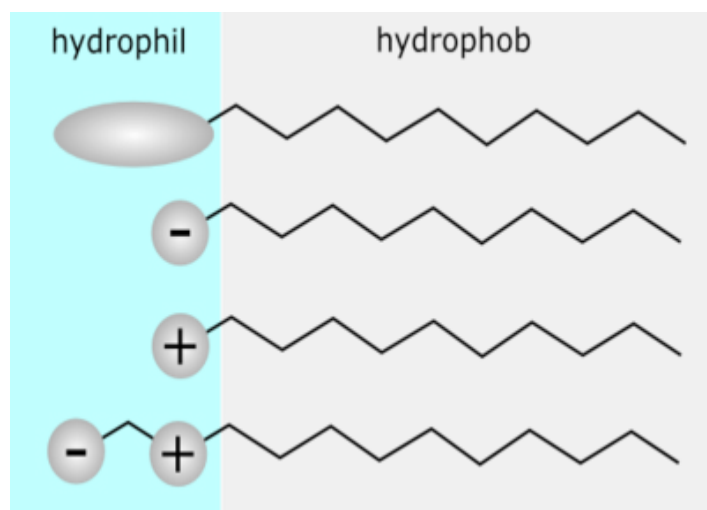


Figure 1: (From top to bottom) Nonionic, anionic, cationic, amphoteric surfactant molecule [2]

Surface tension is a property of liquids. It is defined as the energy, or work, required to increase a liquid's surface area due to intermolecular forces [3]. Liquids with higher surface tension tend to pull on the surrounding

liquid molecules more strongly than those with lower surface tension. Figure 2 shows the differences between high and low surface tension [4].

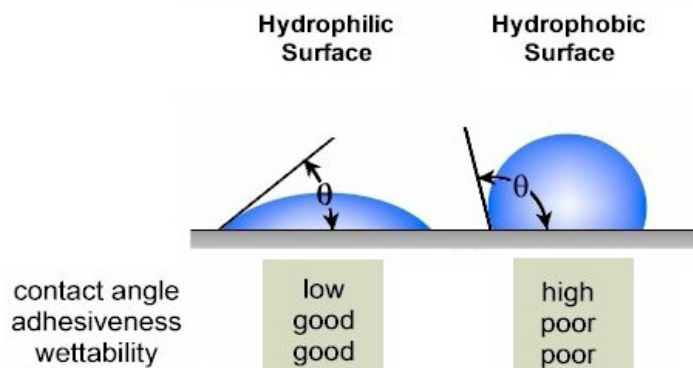


Figure 2: Low surface tension (left) and high surface tension (right)

The proportion of molecules present at the surface of a liquid in the bulk of a liquid depends on their concentration. At low concentrations, surfactants stay on the surface of the liquid. Surface tension decreases as more surfactant is added to water. As the surface becomes crowded with surfactant, additional molecules collect as micelles. This concentration is called the critical micelle concentration (CMC) and can be found by measuring surface tension [5]. At the CMC point, adding more surfactant does not change the surface tension. While it is efficient to use surfactant solutions at their lowest surface tension, it would be inefficient to use them when

they have reached CMC since having additional surfactant in the solution might be wasteful. Figure 3 shows a graphical relationship between surface tension and surfactant concentration and indicates the CMC point.

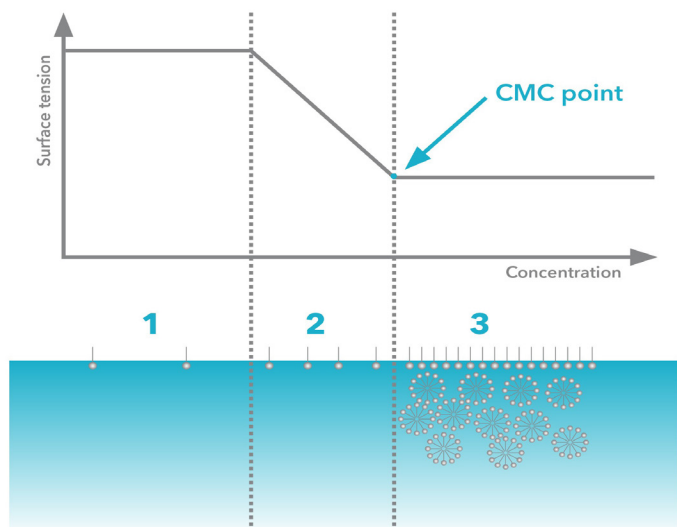


Figure 3: Graph indicating CMC point [6]

There are various methods of measuring surface tension. The Wilhelmy plate method is commonly used to measure surface tension. This method involves using a thin platinum plate to be immersed in a liquid, so that the plate is under surface tension. Obtaining measurements using this method follows Young's Equation;

$$\gamma_s = \gamma_L \cos \theta + \gamma_{sL} \quad (1)$$

where  $\gamma_s$  is solid surface tension,  $\gamma_L$  is liquid surface tension,  $\theta$  is contact angle, and  $\gamma_{sL}$  is solid and liquid boundary tension. A diagram demonstrating the application of Young's Equation is shown in Figure 4.

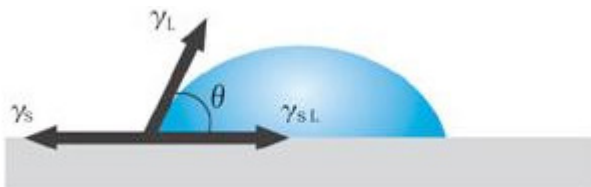


Figure 4: Diagram demonstrating Young's Equation

A surface tensiometer that utilizes the Wilhelmy plate method automatically obtains measurements based on this equation. This device was used in this research to obtain surface tension measurements for surfactant solutions at varying concentrations and to determine their

CMC points.

Three surfactants to be tested are sodium lauryl sulfate (SLS), ECOSURF™ EH-14, and ECOSURF™ SA-9. SLS is an anionic surfactant that is used as a foaming and cleaning agent in detergent, wetting agent in textiles, cosmetic emulsifier, and sometimes in toothpastes [7]. It is synonymously called sodium dodecyl sulfate (SDS). EH-14 is an alcohol alkoxyolate and a biodegradable nonionic surfactant. It has many applications, such as hard surface cleaners, metal cleaners, high performance cleaners, industrial processing and manufacturing, and agricultural formulations [8]. SA-9 is a seed oil surfactant and a biodegradable nonionic surfactant. This type of surfactant provides considerable benefits in handling, processing, and formation. It is used in hard surface cleaners, prewash spotters, and paints and coatings [9].

SLS was chosen for this study because it is a commonly used surfactant. Therefore, the results of this surfactant can be compared to those provided in literature for analysis. On the other hand, EH-14 and SA-9 were chosen because they are biodegradable and environmentally friendly alternatives to SLS. These are new surfactants, and literature does not provide information on them. Experiments were performed to study their surface tensions at various concentrations. The results of these surfactants were compared to those of SLS to observe any differences in trend.

## Methodology

The surface tensiometer used in this study is given in Figure 5. The instrument utilizes the Wilhelmy plate method. Figure 6 shows the platinum plate that accompanies the device.

Before the surfactant solutions were prepared, precautions were taken to ensure that the working environment was clean and safe to prevent injury and equipment damage. A transformer was used to set the voltage to 110 V. This device was connected to the surface tensiometer and an electrical outlet. Once the surface tensiometer was turned on, it was warmed up for exactly 30 minutes to ensure optimum performance in measuring the surfactant solutions. During the warm-up period, the Wilhelmy platinum plate was cleaned to ensure that no contaminants would affect the measurements. A pair of tweezers was used to handle the plate because oil from the hands would contaminate it. The plate was rinsed with distilled water. After that, the plate was cleansed with a flame, which was achieved by using an isopropyl alcohol lamp. The plate was held in the flame until the



Figure 5: BZY-101 automatic surface tensiometer

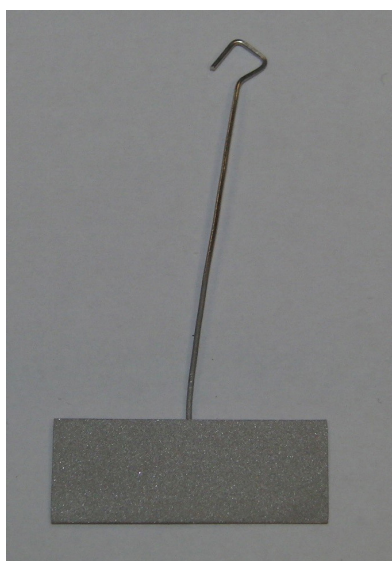


Figure 6: Wilhelmy platinum plate

plate began to appear red. Figure 7 demonstrates this cleansing process.

Once the plate had cooled down and the surface tensiometer had warmed up, the plate was placed on the hook of the device. A series of steps, provided in the instruction manual, were followed to calibrate the surface tensiometer. After calibration, 100 g of distilled water was tested first to ensure that the device was working properly. A beaker containing the water was placed on the platform of the device. With the knob on the side of the platform, the beaker was raised until the plate was completely submerged in the water. Then, the beaker was lowered until the plate was at the point of separation

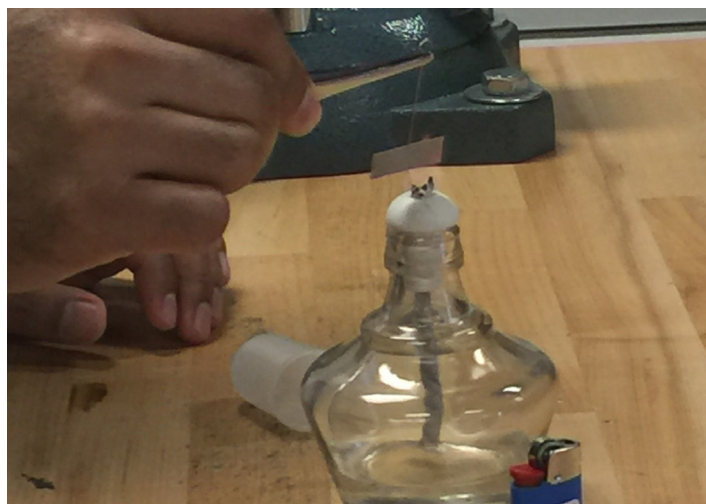


Figure 7: Cleaning the plate with flame

from the water. In other words, only the lower edge of the plate was touching the surface of the water. This procedure was performed, so that the water would apply a pulling force on the plate to achieve surface tension. The surface tension value was immediately recorded. After that, two more measurements were made and repeatability was achieved. For the second measurement, the plate was left at the point of separation for two minutes to observe any changes in surface tension. After two minutes, the value was recorded. For the third measurement, the beaker was lowered to separate the plate from the water, raised to submerge the plate, and then lowered until the plate reached the point of separation from the water. Once the plate reached this point, the surface tension value was immediately recorded.

The recorded measurements were compared to reported data to confirm their accuracy. For distilled water at room temperature (at 25 °C), the surface tension value should be 72 mN/m [10]. If there was a percentage difference greater than 10% between the recorded measurements and reported data, then the distilled water would have to be measured again, or the calibration process would have to be repeated. Otherwise, if the percentage difference was at or lower than 10%, then the next step would be to prepare and measure the surfactant solutions.

Surfactants experiments were started with SLS, so that results can be compared to previously reported literature data. A mass balance was used to ensure consistent measurements of water and surfactant. Before measuring the surface tension, a thermocouple was used to ensure that the water was at room temperature (at 25 °C) because surface tension is a property that can be affected by temperature. To prepare the solution, the surfactant was

dissolved in water, and the solution was stirred for 30 seconds with a hot plate and a magnetic stirrer (Figure 8).



Figure 8: Stirring solution with hot plate and magnetic stirrer

Once the solution was mixed thoroughly, the surface tensiometer was used to measure the surface tension. The procedure for measuring distilled water was followed for the SLS solution. After completing the measurement, the plate was cleaned. The preparation, measurement, and cleansing processes were repeated for various concentrations of SLS. Each concentration was measured in parts per million (PPM). Equation 2 demonstrates PPM,

$$PPM = 1,000,000 \frac{m_c}{m_s} \quad (2)$$

where  $m_c$  is the mass of the component (kg) and  $m_s$

is the mass of the solution (kg). Once all of the measurements were obtained, the results were compared to reported literature data to observe any similarities or differences in trend. After the comparisons were made, the preparation, measurement, and cleansing processes were repeated for the EH-14 and SA-9 solutions. There were important notes that were taken into account when performing the experiments:

- Each lab session started by measuring distilled water to ensure that the surface tensiometer was working properly.
- Any contamination of the plate and solution (including oil from skin) would affect the measurements.
- The temperature of the solution has some effect on the surface tension value. Before measuring surface tension, a thermocouple was used to measure the distilled water and surfactant solutions to make sure that they were at room temperature.
- Surfactant solutions have dynamic surface tensions immediately after mixing. They will reach equilibrium and have static surface tension after sitting for several seconds or minutes.

## Results

For each of the figures shown in this section, the mean surface tension values were plotted. These values can be found in Table 1, 2, and 3 in the Appendix section.

Figure 9 shows the mean surface tension measurements of the SLS solution with the corresponding compositions. Data reported at Cheng et al [10] was plotted for

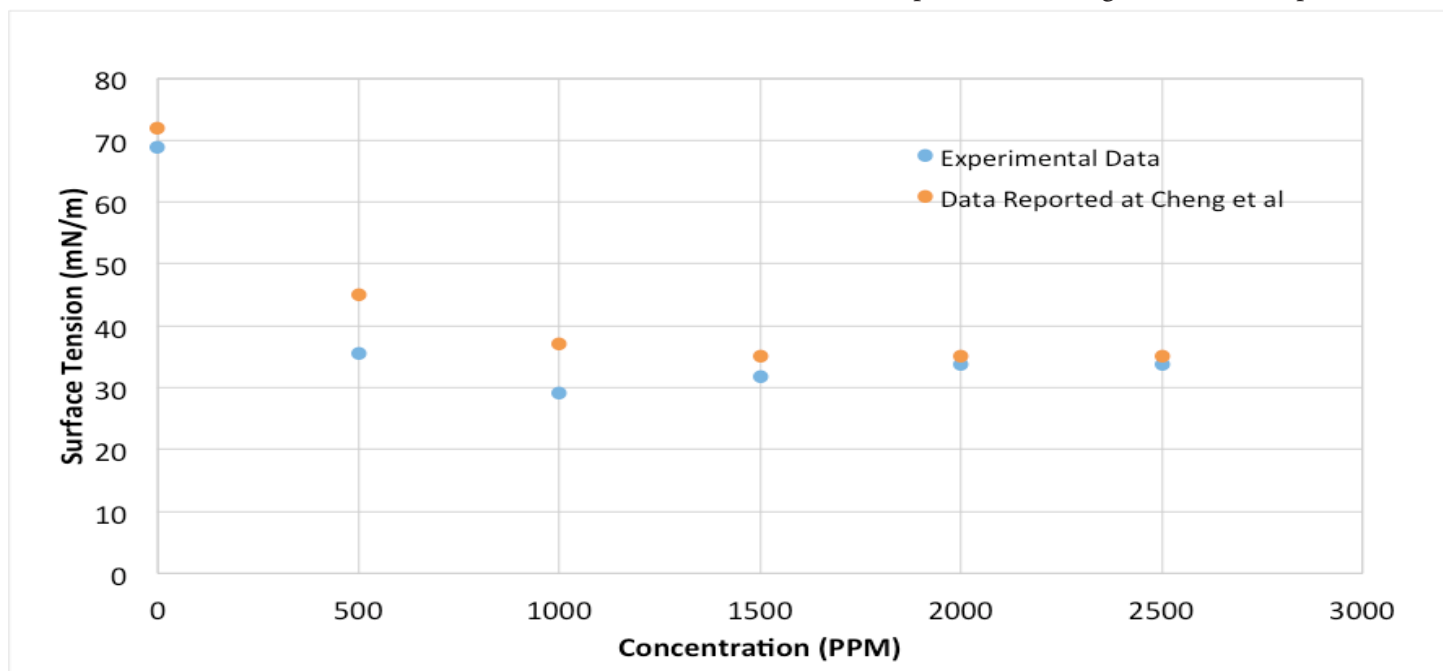


Figure 9: SLS solution surface tensions with increasing composition

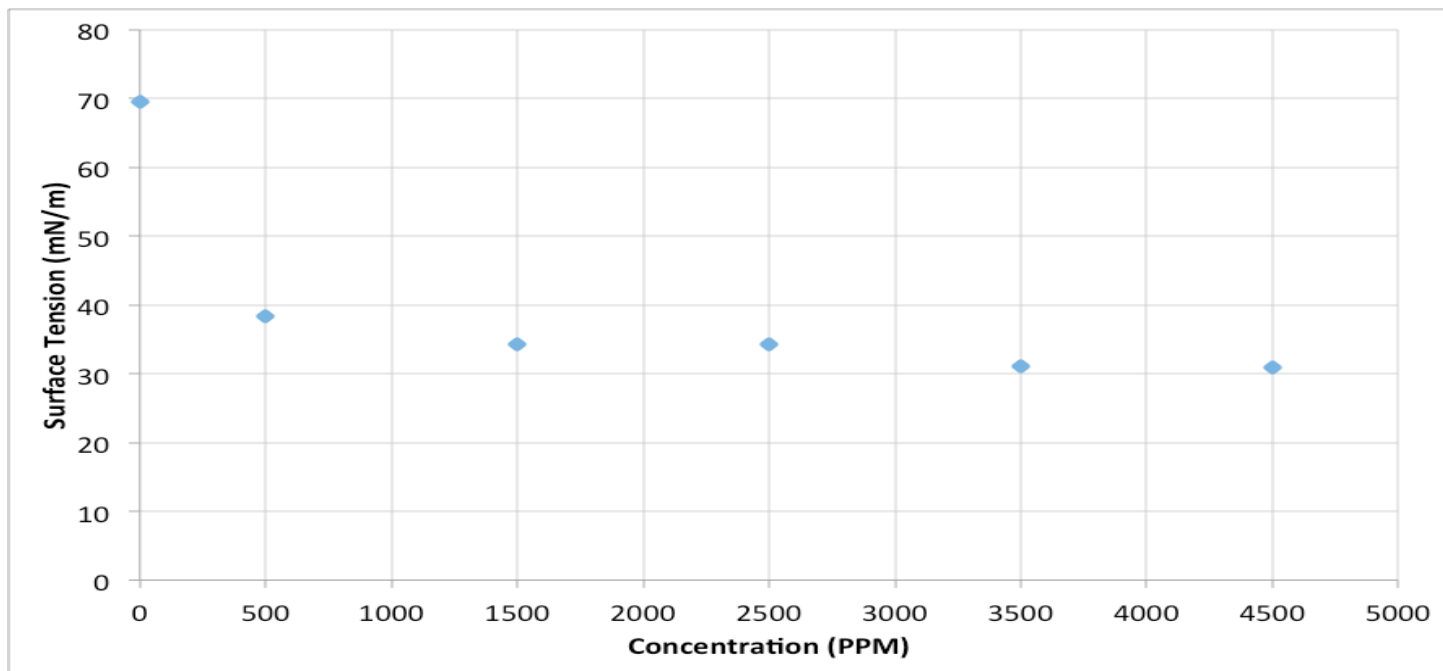


Figure 10: EH-14 solution surface tensions with increasing composition

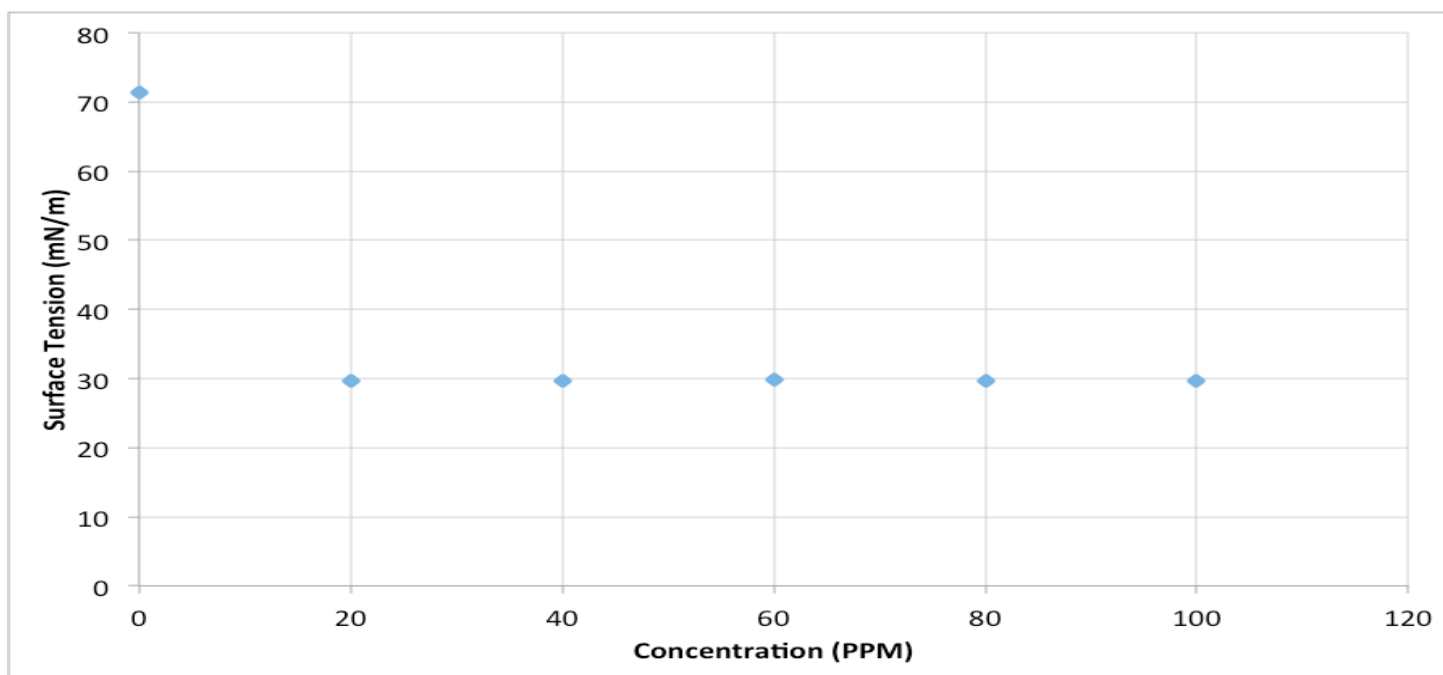


Figure 11: SA-9 solution surface tensions with increasing composition

comparison.

Figure 10 shows the mean surface tension measurements of the EH-14 solution with the corresponding compositions.

Figure 11 shows the mean surface tension measurements of the SA-9 solution with the corresponding compositions.

## Discussion and Error Analysis

All surfactant solutions exhibited a pattern in which

surface tension decreased as concentration increased. Once they reached the CMC point, surface tension remained constant. This pattern is similar to that of Figure 3, which was expected. It was noted that, at the CMC point, the mean surface tension value was 33.7 mN/m for SLS, 31.1 mN/m for EH-14, and 29.6 mN/m for SA-9.

The experimental measurements for SLS was compared to data reported from Cheng et al. When the experimental and reported data were plotted together, as

shown in Figure 9, they followed a similar pattern. For further comparison, percentage difference was calculated for each concentration. This calculation was performed using Equation 3,

$$\%diff. = \left| \frac{\gamma_{exp} - \gamma_{data}}{\frac{\gamma_{exp} + \gamma_{data}}{2}} \right| * 100\% \quad (3)$$

where  $\gamma_{exp}$  is the experimental surface tension and  $\gamma_{data}$  is the reported surface tension at Cheng et al. Table 4, in the Appendix section, shows the percentage difference for each concentration. It shows that surface tension values mostly varied between 500 PPM and 1000 PPM. Unlike SLS, EH-14 and SA-9 are relatively new surfactants, so literature does not provide any information on them. As shown in Figure 10, the EH-14 solution showed the largest change in surface tension between 0 PPM and 500 PPM. After 500 PPM, surface tension gradually decreased as concentration increased. The CMC point occurred after 3500 PPM. On the other hand, the SA-9 solution immediately reached the CMC point when 20 PPM of the surfactant was added to water, as shown in Figure 11.

Although various precautions were taken to ensure that the surface tensiometer would measure the surface tension to the highest accuracy and precision as possible, there might be sources of error. Surface tension is very sensitive to temperature. A small variation in temperature can cause the surface tension measurement to deviate slightly from the liquid's reported surface tension value at a certain temperature. As shown in Tables 1-4 in the Appendix section, the measured surface tension for water at room temperature slightly deviated from the reported value of 72 mN/m. As mentioned in the Methodology section, the percentage difference between the measured and reported surface tensions was calculated to ensure that there was not a significant difference between them. Aside from temperature changes, the Wilhelmy platinum plate could cause some error in measurement as well. The Wilhelmy platinum plate is a very sensitive component; thus, any deviations from its original form would affect surface tension measurements. The wire that is connected to the plate is susceptible to bends, especially when held with a pair of tweezers. The surface of the liquid should be evenly distributed along the lower edge of the plate. If the wire were bent, it would lead to uneven distribution of the liquid, which would

contribute to skewed results. A flat, clean surface and a paper grid were used to ensure that the wire was straight. If the wire was bent, it was straightened manually. While the wire was adjusted with the best ability possible, the presence of a very slight bend was probable since the straightness of the wire was determined by the human eye.

## Conclusion

The following conclusions are made based on the experimental results of this research. The results support the theory that surface tension reaches CMC when there is sufficient surfactant on the surface of water [6]. SLS experimental results show a similar trend to Cheng et al.'s results. The largest variation occurred between 500 and 1000 PPM. It is not known for certain which set of surface tension data is the most accurate as they are both obtained through experimentation. Despite the slight differences, both results showed that the CMC point occurred at 2000 PPM, which is a revealing characteristic for SLS. Comparing the two eco-friendly surfactants, EH-14 presented higher CMC value compared to SA-9. SA-9 is water dispersible, and the solution is not as uniform and homogenous compared to SLS and EH-14. Further experimentation can be done to test the SA-9 solution at concentrations between 0 PPM and 20 PPM and determine whether the solution reaches lower surface tension value before 20 PPM.

The findings of this research provide a better understanding of the relationship between surfactant concentration and corresponding surface tension. In the future, research will be conducted to study how fluid properties of surfactant solutions affect boiling heat transfer. If the results of the eco-friendly surfactants are favorable, compared to SLS, then it is probable that they can serve as alternative sources for boiling heat transfer applications.

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## Authors

### Remelisa Esteves

Remelisa Esteves is an Aerospace Engineering graduate of Embry-Riddle Aeronautical University with a specialization in Aeronautics and a minor in Applied Mathematics. She was involved in school organizations, including The National Honor Society in Aerospace Engineering and The Mathematics Honor Society. She worked on campus as a teaching assistant for Calculus and Analytical Geometry I for Engineers class, a mathematics tutor, and a grader. During her time as an undergraduate student, she studied the fluid properties of surfactant solutions and investigated the application of surfactant solutions to engineering systems.

### Dr. Birce Dikici

Dr. Dikici is an assistant professor at Embry-Riddle Aeronautical University. She obtained both her MSME and Ph.D. from Texas Tech University upon receiving her BSME from Gazi University, Turkey. Dr. Dikici has

numerous journal and conference proceedings on energy generation, boiling, and clean energy systems. She designed various experimental systems and developed several diagnostic methods for characterization of Aluminum nanoparticle burning and brought a number of analytical approaches to model energy propagation.

Dr. Dikici is also ASME student section advisor at Embry-Riddle Aeronautical University. She encourages mechanical engineering students to become involved in their ASME student section by arranging activities.

### Matthew Lehman

Matthew Lehman is an Aerospace Engineering graduate student at Embry-Riddle Aeronautical University specializing in aerospace and propulsion. He obtained a Bachelor of Engineering in Mechanical Engineering at Youngstown State University in May 2014. He is currently completing a study on surfactants ability to suppress water evaporation. He has performed zinc-oxide thin film research funded by the National Science Foundation at North Carolina State University and material characterization research funded by Catacel Corp. at Youngstown State University. He has interned at Delphi Automotive, Inc. working with electrical terminal crimp technology and Florida Turbine Technologies, Inc. working with heat transfer and combustion.

### Qayyum Mazumder

M A Qayyum Mazumder is a master's student in aerospace engineering at Embry-Riddle Aeronautical University with a concentration in aerodynamics and propulsion. He is an alumnus of Daniel Webster College where he obtained his Bachelor of Science degree in aeronautical engineering. Throughout his undergraduate career he was involved in student senate as a senator, and as the treasurer of Engineering Advisory Board. He also worked on campus as a tutor in math and science where he tutored calculus, linear algebra and trigonometry. Currently he is studying fluid properties of surfactant solutions and carrying out experiments with surface tensiometer apparatus.

### Nonso Onukwuba

Nonso Onukwuba is a graduate of Embry-Riddle Aeronautical University, who graduated in the spring semester of 2016. He pursued a Bachelor of Science degree in Aerospace Engineering with a focus on the Aeronautics track. He was a member of AIAA, Catholic Students Association as well as the African Students Association,



where he served dutifully as the financial secretary. In addition to Aerospace Engineering, Nonso was very much involved in the Mechanical Engineering Department, where his interests in Fluid Mechanics could be observed through the research projects he was an active participant.

## APPENDIX

**Table 1: Summary of SLS solution surface tension tests**

PPM	H <sub>2</sub> O mass (g)	SLS mass (g)	First initial surface tension (mN/m)	Surface tension after 2 min. (mN/m)	Second initial surface tension (mN/m)	Mean Surface Tension (mN/m)
0	100	0	68.9	69	68.9	68.9
500	100	0.05	36.5	35.1	35.1	35.6
1000	100	0.10	29.7	28.9	28.9	29.2
1500	100	0.15	31.6	31.7	31.7	31.7
2000	100	0.20	33.8	33.6	33.6	33.7
2500	100	0.25	33.9	33.7	33.8	33.8

**Table 2: Summary of EH-14 solution surface tension tests**

PPM	H <sub>2</sub> O mass (g)	SLS mass (g)	First initial surface tension (mN/m)	Surface tension after 2 min. (mN/m)	Second initial surface tension (mN/m)	Mean Surface Tension (mN/m)
0	100	0	69.6	69.6	69.6	69.6
500	100	0.05	38.6	37.8	38.8	38.4
1500	100	0.15	34.7	33.8	34.4	34.3
2500	100	0.25	34.5	34.1	33.9	34.2
3500	100	0.35	31.2	30.8	31.2	31.1
4500	100	0.45	30.9	30.7	31.0	30.9

**Table 3: Summary of SA-9 solution surface tension tests**

PPM	H <sub>2</sub> O mass (g)	SLS mass (g)	First initial surface tension (mN/m)	Surface tension after 2 min. (mN/m)	Second initial surface tension (mN/m)	Mean Surface Tension (mN/m)
0	100	0	71.4	71.4	71.4	71.4
20	100	0.002	29.9	29.4	29.6	29.6
40	100	0.004	29.8	29.5	29.7	29.7
60	100	0.006	30.0	29.6	29.8	29.8
80	100	0.008	29.9	29.4	29.6	29.6
100	100	0.010	29.7	29.5	29.7	29.6

**Table 4: Comparison between experimental and reported experimental SLS surface tension values**

PPM	Experimental Surface Tension (mN/m)	Reported Surface Tension at Cheng et al (mN/m)	Percentage Difference
0	68.9	72.0	4.40%
500	35.6	45.0	23.3%
1000	29.2	37.0	23.6%
1500	31.7	35.0	9.90%
2000	33.7	35.0	3.78%
2500	33.8	35.0	3.49%