"INVESTIGATING THE EFFECT OF SURFACTANT STRUCTURE ON THE PERFORMANCE AND FOAMING PROPERTIES OF DETERGENTS"

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ABSTRACT

Through the incorporation of a large and electronegative component, bromine, into the unsaturation of sodium oleate, both the surface tension and foaming characteristics of the compound were modified. We tested and analyzed these qualities, then compared them to those of the original oleic soap. It was discovered that sodium oleate had a lower critical micelle concentration (CMC) than any of the brominated surfactants. The bromine moiety has a rate-slowing effect on adsorption, with the doubly brominated surfactant being the one with the most profound effect. Although there was no discernible change in the foamability of the brominated counterparts, it was discovered that the foam was less stable. The coalescence and subsequent bursting of huge bubbles was another effect of bromination.

Keywords: Brominated surfactants, foaming properties

INTRODUCTION

These days, you may find surfactants in a wide variety of items, both commercial and consumer. Their broad use is due to an inherent duality in their molecular features, namely the fact that they comprise of a polar head that is attracted to water and a nonpolar tail group that is repelled by it. Due to the fact that the surfactant has this feature, it is able to self-assemble into a wide range of colloidal structures whether it is present in oil, oil-water, or solid-liquid combinations. Additionally, it enables the surfactant to adsorb at surfaces in an ordered form, so allowing the characteristics of the surfactant to be modified correspondingly. The polar head group may be of a tiny and condensed size, or it may be a lengthy chain of polymeric molecules. They are capable of becoming anionic, The hydrophobic group has also been the subject of a great number of investigations, the most of which have focused on its It was discovered that the critical micelle concentration, abbreviated as CMC, drops in value in a general sense as the number of carbon atoms grows up to roughly 16. Additional enhancements to characteristics with an increase in length to the nonpolar group led to the discovery of Gemini surfactants, with the first paper on them being published by Bunton et al.[8] In spite of the fact that extending the length of the hydrocarbon chain beyond 16 did not result in any appreciable improvements to any of the physical parameters, Gemini surfactants are distinguished by a CMC that is between one and two orders of magnitude lower than the CMC of the analogous monomeric surfactants.

Surfactant qualities have also had their structural characteristics modified by the addition of an aromatic moiety to the hydrophobic group. This alteration has also proven successful. The hydrophobic group underwent still another transformation by virtue of the incorporation of an aromatic side chain, which, as previously mentioned, resulted in an enhanced surface and aggregation. It has been reported that the introduction of double bonds in the hydrophobic

group has a significant effect on the critical micelle concentration. This effect is equivalent to the removal of one to 1.5 CH2 groups from the saturated hydrocarbon chain branching, and it also has the effect of significantly increasing the wetting efficiency. With the addition of a hydroxyl group to the double bond of oleic acid, researchers have also looked at the possibility of lowering the hydrophobicity of the lipophilic group. On the other hand, as a result of this, the surface tension of oleate soaps rose from 29.8 to 37.0 mN=m when they were at the critical micelle concentration. As a result of this change, the surfactant characteristics of the substance were diminished. On the other hand, there have been quite a few efforts attempted to boost the hydrophobicity of surfactants by the process of fluorination.

The smaller hydrogen atom was replaced with the larger and more electronegative fluorine atom, which resulted in major alterations in both the physical and chemical properties of the compound. These surfactants may contain hydrophobic chains that are either completely fluorinated or just partly fluorinated. When compared to other types of surfactants, fully fluorinated perfluorocarboxylic acids have the lowest surface tension. An additional big and electronegative atom, bromine, is added to the hydrocarbon section of a surfactant chain, and the consequence of this addition is presented in this article. Garti et al. conducted research to determine how the incorporation of a dibromo moiety into oleyl would affect the characteristics of the surfactant. There hasn't been a lot of study done on how the middle of an alkyl chain affects things like surface tension and foaming or hydrophobicity, but there has been some. The purpose of this article is to bring more insight to the study that was presented above. It is noteworthy that brominated surfactants have a greater specific gravity since this gives them the capacity to equalize the density of the emulsified phases, which minimizes the risk of phase separation. Due to the fact that bromine is an effective leaving group, further chemical derivatization of these surfactants may be carried out with relative ease.

OBJECTIVE

1. The Study Investigating The Effect Of Surfactant Structure.

2. The Study Performance And Foaming Properties Of Detergents.

RESEARCH METHODOLOGY

Single Bromination of Hexenoic Acid

An Erlenmeyer flask with a capacity of 50 ml was loaded with a total volume of 20 ml of the different solvents that were being investigated. After that, 0.5 grams of a model chemical and 1 milliliter of HBr dissolved in acetic acid were added to the flask. In a water bath with temperature control and stirring at 60 degrees Celsius, the reactions were carried out. For the purpose of analysis, samples were taken at a number of different periods. Following the completion of the bromination process, fifty milliliters (mL) of deionized water were poured into the flask in order to remove any acetic acid that had not yet reacted. This process was continued until the sample was deemed to be neutral. After being separated, the organic layer was placed in a conical flask for further analysis. In order to neutralize the sample, 0.5 grams of sodium hydrogen carbonate were added to the organic layer of the mixture. After removing

the supernatant, anhydrous sodium sulfate was then added to the sample in order to dry out the chemical. In a rotary evaporator, the sample that had been brominated to completion was dried up by evaporation. H NMR was used to conduct the analysis on the samples.

Double Bromination of Oleic Acid

A total of 3.7 grams of oleic acid that was 99% pure was put into a flask along with 25 mailliliters of chloroform. To ensure that the contents were uniform throughout, the flask was placed in an ice bath and swirled. The flask received 1 ml of bromine, and the reaction was allowed to continue for a period of 30 minutes. At a temperature of room temperature, the flask containing the reactants was agitated for a further two hours. After that, a condenser was added to the flask, and it continued to be heated under reflux at 85 degrees Celsius for another two hours. After then, the reaction was halted by rinsing the mixture with deionized water until all of the unreacted bromine had been removed. After that, the solvent was rotovaped, and the result was recovered, after which it was dried in a vacuum oven. It was discovered that the level of purity was 97.5%.

Sodium Soaps

After neutralizing the 99% pure fatty acid with an alcoholic solution of sodium hydroxide, sodium soaps were produced from the fatty acid. After the neutral solution had been evaporated to its dry state, the soap was next dried in a vacuum. Dilutions of sodium soap in deionized water led to the production of the solutions, which were then produced in sodium salt buffers provided by Merck. The pH of the solutions is 10, and their ionic strengths are around 0.4. The high pH makes it impossible.

Adsorption

The du Nouy ring was used to take measurements of the dynamic surface tension at the air–solution interface. These results were used to calculate the adsorption rate. The dish had a capacity of around 100 ml, and it was filled all the way to the top with the surfactant solution that needed to be measured. The stock solution was placed inside of a separating funnel that had a flexible tube and a needle at the end of the tube's end. The needle was then inserted into the dish so that it was level with the base. By opening the stop cock of the dish, the solution that was in the separating funnel was allowed to overflow into the dish, which resulted in the creation of a new surface. For the purpose of the experiment, 10 milliliters of solution were poured into the dish, and the surface tension was measured at regular intervals up to the point when equilibrium was established. The concentration of the surfactant solution was the same as the concentration that was used in the process of producing the CMC.

Foam

It was possible to produce foams consisting of sodium oleate (NaOl), sodium 9-bromo stearates (SBO), or its isomer sodium 10-bromo stearate, and sodium 9,10dibromostearates (DBO). According to the literature, the procedure of producing foam is as follows:] The instrument is made up of a glass column that has an internal diameter of 40 millimeters and a G2 fritted glass that ranges from 40 to 100 millimeters at the bottom for gas dispersion. A

predetermined quantity of air was introduced into the solution that was going to be foamed using a syringe. We used 50 milliliters of the solution and 100 milliliters of air in total. After a period of twenty seconds and at a volumetric gas velocity of eighteen L/hr on average, ambient air was drawn from the syringe and delivered into the solution via the sintered glass. Pipettes were used to carefully introduce the solution into the column, ensuring that no foam was generated and that the solution did not come into contact with the column's sides. Following the addition of air, the stop cock located at the base of the column was closed, and starting heights of both the foam and the solution were determined. The subsequent step was to determine how the height of the foam and the level of the solution changed over the course of time. The measurements were carried out anywhere from two to five times for each concentration of solution, and the results were averaged. A series of trials were carried out. The foaming solutions were prepared at a CMC concentration that was ten times that of the CMC measurements while maintaining the same ionic concentration. Using a digital camera with a Leica D Lux 5 lens, we were able to calculate the bubble size distribution by taking pictures of the foam while looking through the clear wall of the column. Visual inspection was used to determine the sizes of the bubbles at the wall since these bubbles had distinct outlines and were easily discernible in an expanded print format after the contrast had been digitally adjusted. In order to get an accurate representation of the typical size of the foam bubbles, a 10 10 mm slice was taken out of the centre of the foam column. One measurement was taken just after the gas flow was turned off, and another one was taken after the foam had already lived half its life.

DATA ANALYSIS

99% pure oleic acid was used as the starting material in the manufacture of sodium oleate (NaOL), sodium 9-bromostearate (SBO), and sodium 9,10dibromo stearate (DBO). The alkyl halide was produced as a result of the reaction between oleic acid and hydrogen bromide. Because it is a source that is abundant in p electrons, the double bond that is located in position 9 of the hydrocarbon backbone functions as a base. Because of its electrophilicity, the proton of the hydrogen bromide may add to the double bond, which results in the formation of a carbocation intermediate. The reaction is finished off when bromine is added to the carbocation at a later time, which ultimately results in the formation of the product. A model chemical known as trans-2-hexenoic acid was selected for the purpose of investigating the most favorable circumstances for the bromination of the double bond. Because this chemical is pure and only contains a single double bond at position 2, doing 1 H NMR analysis on it is a very straightforward process. In the presence of hydrogen bromide, an alkene may undergo a reaction that results in the formation of the corresponding alkyl halide. It is common practice to carry out this reaction by introducing the dry gaseous hydrogen halide straight into the alkene. The production of hydrogen bromide is accomplished by the reaction of bromine with tetrahydronaphthalene. Because of the volatile nature of the tetralin, this method is time-consuming and requires that the tetralin be in its purest form and completely dry. The use of hydrogen bromide dissolved in acetic acid was chosen since it is significantly less difficult to manipulate. On the other hand, the creation of hydroxides and acetates might result in a conversion rate that is low compared to that of the brominated chemical. In order to determine the optimal conditions for conversion, the bromination was performed at a temperature of 60 degrees Celsius using a variety of solvents. Ether, benzene,

hloroform, and hexane were the solvents that were employed, and each of these solvents has a distinct polarity and capacity for the donation of electrons. The samples were taken at regular intervals, washed, neutralized, and dried before being examined with 1 H NMR.
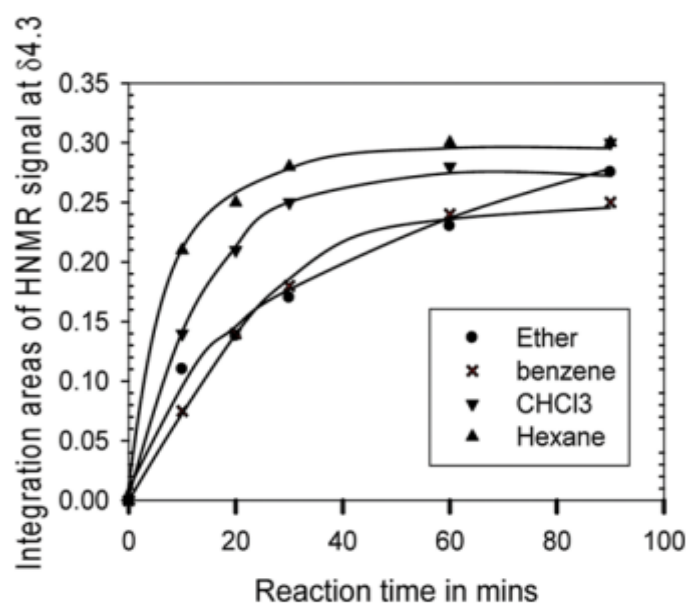

FIG. 1. Graph Of Normalized Areas Of 1 H NMR Spectrogram At D4.3 For Protons Adjacent To Bromine Vs Reaction Time For The Bromination Of Trans-2- Hexanoic Acid Using Various Solvents. (Figure Available In Color Online.)

At a temperature of 25 degrees Celsius, the du Nuoy ring technique with a tensiometer from KSV was used to determine the surface tension (c). The values of surface tension were calculated by taking the average of 7 separate measurements. The equilibrium surface tension measurements led to the determination of the CMC values that are shown in Figure 2 and displayed for sodium, sodium 9 bromo stearate, and sodium 9,10dibromo stearate respectively. It is possible to deduce from the graph that sodium oleate has a CMC that is less than 7.00 105 mN=m, while.
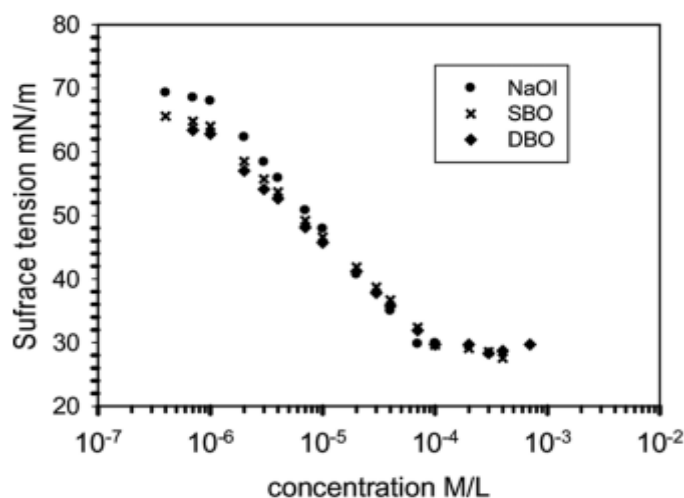

FIG. 2. Graph Of Surface Tension As A Function Of Surfactant Concentration For Sodium Oleate (Naol), Sodium 9-Bromostearate (SBO), Sodium 9,10Dibromo Stearate (DBO).

both of those that are brominated According to research done by Garti and colleagues, brominated ethoxylates have a higher This may be understood with the help of the packing parameter P14 VH=lca0, in which the volume filled by the hydrophobic group is denoted by VH, the length of the hydrophobic core is denoted by lc, and the area covered by the hydrophilic group is denoted by a0. Due to the fact that all three of these surfactants have the exact same amount of carbon atoms and the exact same hydrophilic head, their lc and a0 values are identical. The bulkiness of the bromine group is responsible for the rise in VH that occurs in SBO and DBO. Long, thin hydrophobic groups, such as those found in alkanes, pack tightly and create spherical structures. It is more difficult for surfactants with a big P to pack, which results in cylindrical micelles, and as a result, these surfactants have a higher CMC. This phenomena is also shown by the rise in the CMC=C20 ratio, which went from 8.75 for sodium oleate to 16.6 for SBO and then to 18.8 for DBO. Micellarization is shown to have been suppressed when there is an increase in the ratio of CMC to C20. It has also been shown that the addition of a fluorocarbon chain in lieu of a hydrocarbon chain may significantly boost this. Cmax, which stands for the surface excess concentration at surface saturation, is a measurement that determines how efficient the absorption of the surfactant is at the liquid-gas interface. This was determined by taking into account the connection.

Rate of Adsorption

For surfactant solutions that are above the critical micelle concentration (CMC), surfactants may be found in solution both as monomers and as micelles. The process of bringing these surfactants to the surface and so decreasing the surface tension is referred to as adsorption. This process takes place at the solution air interface. It has been discovered that this dynamic process is made up of two components. To begin, the molecules of the surfactant move from the bulk toward the interface through convection or diffusion. Second, in order to adsorb at the contact, the molecules need to rearrange themselves. Both the diffusion and adsorption processes are influenced by the structure of the surfactant. For instance, the adsorption rate increases as the length of the hydrocarbon chain decreases. As can be seen in Figure 4, the molecules of oleate adsorb very fast at the contact. The rate of adsorption is slowed down as the bromine moiety is added, with the doubly brominated surfactant being the one with the slowest rate. This is as a result of the changed surfactant's weight as well as its bulkiness.

were extracted from a region of foam with a thickness of 10mm 10mm located in the center of the foam column. Because there is often a gradual rise in bubble size moving up the foam, they were taken to be an accurate representation of the foam bubble distribution. When measuring foam on the surface of a glass wall, some studies have shown that the measures are statistically biased against the inclusion of tiny bubbles [33], while other studies have shown that it discriminates against big bubbles since little bubbles do appear to wedge the large bubbles.
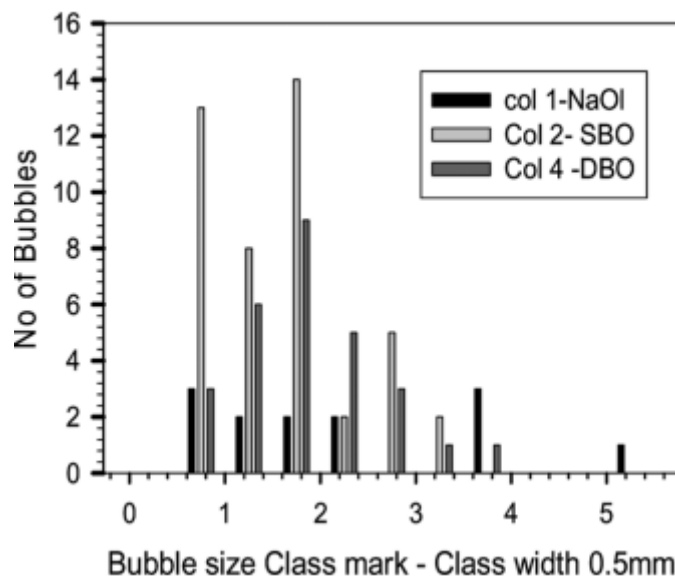
FIG. 3. Foam Bubble Size Distribution At Half-Life For Sodium Oleate (Naol), Sodium 9-Bromostearate (SBO), Sodium 9,10Dibromo Stearate (DBO).

bubbles away from the surface of the The adjustment for this bias is irrelevant in any case, and it is omitted here since the measurements shown above are comparative and are arranged into bins with predetermined class widths rather than real size measurements, which are carried out in the references presented above. The mode of bubble size in the NaOl initial foam distribution is 0.90 millimeters, with the mean bubble size coming in at 1.00 millimeters. The smallest size available is 0.43 mm, and the greatest size available is 2.07 mm. The frequency distribution follows a unimodal pattern that is biased to the right and is characterized by a high degree of homogeneity overall. It is common for distributions to look like this for. The first foam dispersion of SBO has a mean size that is just 0.97 millimeters on average, which is somewhat less than that of NaOl.

The tiniest bubble is 0.41 millimeters, while the biggest measures 2.05 millimeters. The total number of bubbles is the same as it was for the solution containing NaOl. As a consequence of this, the bubble diameters are comparable to those of NaOl, with the exception that it has a bimodal distribution, with two modes located at 0.5 and 1.1 millimeters respectively. The first foam distribution of the DBO has a mean size of 1.29 mm, which is about 30% bigger than the foams described in the previous two paragraphs. The smallest bubble measured 0.58 millimeters, while the biggest measured 2.80 millimeters, indicating that the whole nasurveyed was only around half of the foams in the two categories above. In addition to this, it has a bimodal distribution with modes located at 0.90 and 1.90 millimeters. The consequences of adding the bromine moiety to the hydrophobic chain at this juncture are shown here in the early bubble distributions. It draws attention to the influence on the coalescence of bubbles that occurs before the air flow stops. Because of this, there was a little deviation in the bubble size distribution when NaOl was used. The introduction of a single atom of bromine did not have a significant impact on the total number of bubbles or their size, but it did cause the distribution to take on a bimodal shape. Because of the addition of two bromines, the coalescence rose to such a degree that it pushed the whole bimodal

distribution to the right. Additionally, the bubble size significantly increased, which led to a reduction in the number of bubbles. The decreased intermolecular forces shown by the brominated counterparts are responsible for the expansion of the bubble size.

The bubble size distribution at half-life is distinctive and fascinating to look at. The size distribution of the NaOl bubbles shifted from being unimodal to multimodal throughout time. The lowest mode is 0.75 millimeters, and there is a collection of smaller bubbles ranging from 0.50 to 2.5 millimeters around it. One class was located at 5.25 mm, with the higher modes having a central point of 3.75 mm. This indicates that the distribution split into three groups, with one group being quite tiny and the other two groups being somewhat big. The SBO foam initially had a bimodal distribution, but over time it developed into a multimodal distribution. While the size of the bubble with the lowest diameter stayed stable at around 0.75 millimeters, another mode emerged at 1.75 millimeters, and the mode with the largest diameter was 3.25 millimeters. The distribution of the DBO foam went from being bimodal to being unimodal, and the mode was determined to be 1.75 millimeters (the class mark). We made the observation that it is challenging for the SBO and DBO foam to maintain huge bubbles since the size of their largest bubbles is inferior to that of the NaOl foam. In addition to this, the foam of the DBO is one of a kind since it has several big holes all over the
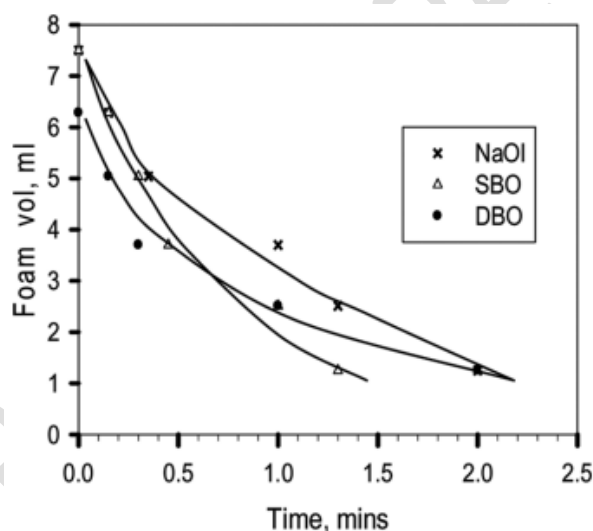

FIG. 4. Liquid Drainage For Wet Foam For Sodium Oleate (Naol), Sodium 9-Bromostearate (SBO), Sodium 9,10Dibromo Stearate (DBO).

CONCLUSION

One or two bromine atoms were introduced into the structure of the hydrophobic region of sodium oleate in order to bring about the desired structural change. The CMC of the oleate soap went raised from mN=m to 1.00 10 4 mN=m as a result of this change. When compared to sodium oleate, the CMC=C20 ratio was 8.75, but when compared to SBO and DBO, it was 16.60 and 18.80, respectively. This demonstrates that the insertion of a big and electronegative molecule, bromine, to the midst of a surfactant's hydrophobic region prevented micellization. However, there is not much of an effect on adsorption at the solution interface since all of the analogues have the same surface tension when measured at CMC. In point of fact, bromination enhanced the efficacy of a surfactant in lowering surface tension, as can be inferred from the values of Pc20 NaOL (Pc20 of 5.09), which led to a reduction in

surface tension that was 2 units lower than it had been before. The addition of a second bromine brings the total number of moles to 5.27. As a result of the kink in its molecular structure, sodium oleate is an excellent foaming agent. The addition of a big hydrophobic bromine may have the same effect as the kink in expanding the surface area of each molecule, allowing the substance to keep its excellent adsorption capabilities and, as a result, its capacity to foam. On the other hand, this has a negative impact on the stability of the foam. Because of the bulky structure of bromine, there is a rise in bubble drainage, coarsening, and coalescence. This is because the weaker intermolecular interactions, greater permeability of gases, and lower rate of adsorption are all produced by the same thing. It is interesting to note that this causes the bubble size of oleate soaps to become coarser while at the same time the bubble size of brominated surfactants becomes smaller.

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