Effects of Various Alkaline Materials on the Surface Properties of Aqueous Surfactant Solutions

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ABSTRACT

Alkaline reagents are usually added to surfactant solutions to improve surface properties (surface tension, contact angles). This project aimed to determine if the type of alkaline reagent used, at varying concentrations, significantly impacted the surface properties of the surfactant solution. The surfactant solutions studied in this project are 2 wt.% Paratene®D740 (a zwitterionic surfactant), 0.01 wt.% Dodecylbenzene sulfonic acid (anionic, DDBSA), 0.01 wt.% Sodium dodecylbenzene sulfonate (anionic, SDBS), and 0.1 wt.% RA-600L (anionic). The surface properties of the pure solutions were collected and compared to the values derived when different alkaline reagents (NaOH, KOH, Na_2SiO_3, Na_3PO_4, Na_2CO_3) were present in solution, in varying weight percent concentrations (0.5%, 1%, 2%, 5%). The Young-Laplace surface tension and contact angle values were derived using the pendant drop and sessile drop features on a One-Attension tensiometer. The contact angle experiments were conducted on a carbon steel surface. The results showed a general decrease in surface tension and contact angle with increasing ionic strength within each alkaline series. More importantly, they showed that the type of alkaline used is important. The alkaline reagent's compatibility with the surfactant and the polarizability of the ions present should all be considered when planning a cleaning job.

INTRODUCTION

Our project was sparked by a practical question: What sets the various alkaline substances used in industrial cleaning apart? The typical cleaning process to remove organic deposits combines an alkaline substance and a surfactant (or blend of surfactants). In some instances, alkaline substances alone are used. This may be sufficient in systems of hydrolyzable hydrocarbons, but in asphaltic or paraffinic-based deposits, changing the pH will have little effect on saponifiable or hydrolyzable hydrocarbons. Our research findings, which are of significant importance, provide valuable insights into the selection of alkaline reagents for different cleaning scenarios, enhancing the efficiency and effectiveness of industrial cleaning processes.

Surfactants are chemical compounds added to a liquid that decreases the surface or interfacial tension between two different surfaces: two liquids, a liquid and a gas, or a liquid and a solid.[1] Surfactants are made of a long hydrophobic tail and a polar head group. In aqueous solutions, the polar head group interacts with the water molecules[2] (**Figure 1**), interrupting their strong hydrogen bond framework, while the hydrophobic tail is directed away from the solution bulk. At low surfactant concentrations, the polar head group is adsorbed onto the surface of the solution, with the hydrophobic tails pointing away from the solution.

Increasing surfactant concentration introduces more of the surfactant molecules into the bulk until the critical micelle concentration (CMC) is reached. At this concentration and above, the maximum effect of the surfactant has been reached. Adding more surfactant to the solution would not have any effect. At the CMC, micelles are formed in the bulk solute. The hydrophobic tails are attracted to each other and are shielded from the water molecules by the polar head group.

Alkaline additives such as trisodium phosphate (Na_3PO_4, TSP) are added to aqueous surfactant solutions are included to remove hydrogen sulfide (H_2S).[3] H_2S reacts with the alkaline salts, making aqueous soluble compounds, granted the pH of the solution is greater than 9. Alkaline additives can also further improve the surface properties of aqueous surfactant solutions.

The surface tension and surface contact angle of a cleaning solution are genuine indicators of a surface's cleanliness and how well a given solution will displace substances from the surface. The lower the surface contact angle on a given surface, the higher the wettability of the cleaning solution, and it is controlled by the balance between the intermolecular forces of the liquid and surface. A stronger interaction between the cleaning solution and the surface improves the wettability properties of the solution, which is shown by a decrease in the

surface tension and surface contact angle of the solution. The use of surfactants in aqueous solutions improves their surface tension and surface contact angle by disrupting the hydrogen-bonding framework of water, weakening its intermolecular interactions.

The type of alkaline salt used has yet to be deemed necessary so long as the pH of the solution is greater than 9. There has been little research on the effect of alkaline materials on the surface tension and wettability of aqueous surfactant solutions. However, the type of alkaline material does make a difference in the surface properties of aqueous solutions, especially in the presence of surfactants. The effect of alkaline reagents on the physical properties of a solution is affected by the ion size and polarizability, solution pH, and the amount plus strength of the intermolecular forces present. [4]

The main objective of this project was to investigate the effects of alkaline materials on the surface properties of aqueous surfactant solutions. In the presence of surfactants, alkaline salts are predicted to reduce the surface tensions of aqueous solutions further and improve their wettability in carbon steel (signified as a smaller contact angle). The effect of various alkaline salts on different surfactants is tested on four different surfactants: Paratene®D740, Dodecylbenzene sulfonic acid (DDBSA), sodium dodecylbenzene sulfonate (SDBS), and RA-600L.

EXPERIMENTAL METHODS

Preparation of Solutions

The first half of this project focused on studying the effects of different alkaline reagents at varying concentrations on water's surface tension.

The chosen alkaline reagents are as follows: NaOH, KOH, Na_2SiO_3, NH_4OH, Na_2CO_3, $Na_3PO_4 \cdot 12H_2O$ (TSP), and $Na_2C_6H_5O_7$ (sodium citrate).

The weight percentages (wt.%) used in this study are 0.5 wt.%, 1 wt.%, 2 wt.%, and 5 wt.%.

The densities according to weight percent for each substrate were used to obtain the desired molarity of each solution and, consequently, the required mass. Equation 1 was used to convert to molarity using the density values obtained from 'The Handbook of Chemistry and Physics, 58th edition'.[5] Linear approximations were made for $Na_2C_6H_5O_7$, NH_4OH, and $Na_3PO_4 \cdot 12H_2O$ to obtain the densities corresponding to the desired weight percentages.

The masses of each alkaline reagent were measured using an analytical balance (± 0.0001) and dissolved in a limited volume of de-mineralized water (total dissolved solids = <10 ppm; fluoride content = 0.0 ppm) at or around room temperature (18-20 °C). Each solution was stirred until the solute

was fully dissolved and transferred to a 100 mL volumetric flask for further dilution using a funnel.

$$M\left(\frac{mol}{L}\right) = \frac{weight\ percentage * density\left(\frac{kg}{l}\right) * \frac{1000g}{kg}}{Molecular\ weight\left(\frac{g}{mol}\right)} \quad \textbf{(1)}$$

The second half of this project explored the effect of alkaline reagents (NaOH, KOH, Na_2SiO_3, TSP, and Na_2CO_3) on aqueous surfactant solutions. These reagents were chosen because they are commonly used in industrial cleaning. Four surfactants were studied for this project, and the concentrations used were near or above the critical micelle concentrations (CMC) of each surfactant. The surfactant used, and their corresponding concentrations are as follows: Paratene®D740 (2 wt.%), Dodecylbenzene sulfonic acid (DDBSA, 0.01 wt.%), an anionic surfactant with a sulfate head group, Sodium dodecylbenzene sulfonate, aqueous (SDBS, 0.01 wt.%), the sodium salt version of DDBSA, and lastly, RA-600L (0.1 wt.%), an anionic surfactant with a phosphate ester head group.

Paratene®D740 is an aqueous zwitterionic surfactant blend with an amine oxide as the main hydrophilic head group. The length of the hydrophobic chain is unknown. This is one of our products, and it was designed to aid in the removal of hydrocarbons and act as a mild oxidizing agent that removes H_2S and other pyrophoric compounds. The pH of a 2 wt.% Paratene®D740 aqueous solution is 7.857.

DDBSA is a common anionic surfactant with a C12 alkyl chain bonded to benzene and a sulfonic acid functional group as its main head group. 0.01 wt.% DDBSA equates to a molarity of 3.06×10^{-4} M, which is an order of magnitude above the CMC of DDBSA (5.51×10^{-5} M).[6]

SDBS is the sodium salt derivative of DDBSA. For this experiment, a 35% aqueous surfactant solution was used to make a 0.01% standard solution. Since DDBSA and SDBS feature the same surfactant, they are expected to act similarly under basic conditions; hence, the concentrations used for both surfactants were the same. However, at 0.01 wt.%, the molarity of SDBS (1.00×10^{-4} M) is slightly lower than its CMC (1.2×10^{-4} M)[7,8]

RA-600L is a complex, alkyl phosphate ester anionic surfactant. It is used as a detergent hydrotrope in liquid alkaline metal cleaners [3] and is soluble in water and oil. 0.1 wt.% of RA-600L equates to 6.42×10^{-3} M with a pH of 2.833.

The alkaline-surfactant solutions were prepared assuming that 100 wt.% corresponds to 100 g. Hence, 1 wt. % would equal 1 g. The surfactant was added to a 250 mL beaker on an analytical balance, followed by the alkaline reagent. De-mineralized water was then added to reach 100 g. For this set-up, 0.5 wt.% corresponded to 0.5 g of reagent. This also applies to the other concentrations used in this study.

The surfactant solutions were dispensed using the 'ThermoFisher Scientific Finnpipette Variable Volume Pipettes.' All solutions were prepared at room temperature (18-20 °C).

Ionic Strength Calculations

The equation below was used to calculate the ionic strength of the prepared solutions. [9] Complete dissociation was assumed for all solutions. Acid dissociation constants (K_a and K_w)[5] were used to derive the concentrations of the relevant ions in each solution.

$$Ionic\ Strength\ (\mu) = \frac{1}{2}\sum c_i z_i^2$$

$$c = concentration, z = charge \quad \textbf{(2)}$$

pH

The pH of each solution was measured to track how this measurement changes with each surfactant. pH measurements were conducted using an Orion 8107BNUMD ROSS Ultra electrode. It is worth mentioning that the presence of surfactants in solution skews the pH measurements because they easily get caught in the electrode's glass membrane; this prevents more H^+ ions from permeating the membrane, resulting in a higher pH value.

Surface Tension and Contact Angle

The One-Attension Theta tensiometer was used to obtain surface tension and contact angle measurements (dynamic and final). Theta has a camera that can capture up to 60 frames per second (fps). For this experiment, we used 30 fps for both sets of measurements. The pendant drop method was used to record the interfacial tension or surface tension values between water and air. The surface tension values for each solution are a mean of the values obtained from four or five trials. Each trial lasted for 10 seconds, with a surface tension value being measured every second. The average of each trial was calculated, counting for one measurement each. A new droplet was used for each trial. The surface tension values were calculated using the Young-Laplace equation shown below.[10]

$$\Delta p = \gamma \left(\frac{1}{R_{solution}} - \frac{1}{R_{air}} \right) \quad \textbf{(3)}$$

$$\Delta p: change\ in\ Laplace\ pressure$$
$$\gamma: surface\ tension$$
$$R: radii\ curvature\ of\ the\ solution\ or\ air$$

The results are shown by calculating the percent change in the surface tension compared to the pure surfactant solutions (**Equation 4**).

$$\Delta\gamma\ (\%) = \frac{Pure - Alkaline}{Pure} \times 100\% \quad \textbf{(4)}$$

Contact angle measurements were done using the sessile drop feature on the instrument with carbon steel as the surface. Each trial lasted for 25 seconds. The dynamic contact angle was calculated (**Equation 5**)[11] by the instrument using a derivative of **Equation 3**.

$$\gamma_{lg} \cos(\theta_d) = \gamma_{cg} - \gamma_{sl} \quad \textbf{(5)}$$

$$\gamma_{lg} = the\ liquid/gas(air)\ surface\ tension$$
$$\gamma_{cg} = the\ coupon/gas(air)\ surface\ tension$$
$$\gamma_{cl} = the\ coupon/liquid\ surface\ tension$$
$$\theta_d = the\ droplet\ contact\ angle$$

The front and back of two carbon steel coupons were used to get multiple measurements for each solution. Each contact angle run was accomplished using approximately the same spot on the coupons for each alkaline-surfactant solution. After each contact angle run, a Kimwipe and acetone were used to clean the coupon, ensuring it was dry before the next experiment. An average cannot be taken with these values, but the values obtained for each surface were compared to determine a possible trend. The final contact angles within each alkaline-surfactant series were compared to that of the pure surfactant. The % change (**Equation 6**) in contact angle was calculated and used to compare the effect of each alkaline material on the change in the contact angle. A more negative value means a larger percentage decrease, translating to increased wettability.

$$\Delta\theta(\%) = \frac{Pure - Alkaline}{Pure} \times 100\% \quad \textbf{(6)}$$

RESULTS AND DISCUSSION

The effect of salts on the surface tension of a solution is dependent on the ability of the ions to diffuse to the surface layer.[12,13]

Inorganic salts, which include most alkaline reagents, are known to increase the surface tension when compared to pure water due to the depletion of ions at the interface.[14,15] The diffusion of ions to the interface is affected by factors such as the hydrated ion size, electrostatic attraction or repulsion, and ion polarizability. There is a general consensus that anions are preferred at the interface over cations due to the larger hydration radii of cations, especially monovalent cations.[15] Larger and highly polarizable anions are usually preferred at the surface.

The first half of this project focused on the effect of various alkaline reagents that are commonly used in industrial cleaning on the surface tension of pure water. This was done to determine if aqueous alkaline solutions alone make for effective cleaning. For reference, the measured surface tension of the pure water sample used was 78.94 mN/m. The surface tension results were

plotted against the ionic strength (μ) of each alkaline series (**Figure 3**). Sources suggest that the surface tension of electrolyte solutions is supposed to increase linearly with increasing salt concentration.[12-16] This could also apply to alkaline solutions. However, this trend was not observed. No significant trend was observed between the change in ionic strength and the change in surface tensions. For most alkaline reagents in the series, an initial depression in the surface tension was observed, followed by a noticeable increase in surface tension and then another decrease. For most reagents in the series, the spike in surface tension was observed at 1 or 2 wt.%, and the decrease was observed right after.

There is no one explanation for the observed results. Different alkaline reagents have different densities and molecular weights, giving them different ionic strengths for the same wt.% concentrations. Because of this, the strength of electrostatic interactions present in the solution differs. All these, along with the different types of anions present, affect the diffusion of the anions to the surface of the solution.

As stated in the introduction, the surfactant is first adsorbed onto the solution surface, and after the surface is saturated, the surfactant concentration increases in the solution bulk.[2] According to the Stern model, the surfactants are added to the adsorption layer, the outermost layer of the solution. When salts are added, ions that diffuse can also end up in the adsorption layer (**Figure 4**).[13,14] For ionic surfactants, the counterions balance the charge on the surfactant's polar head group along with any counterions that are also at the surface. A larger amount of ions in the at the surface results in an even lower surface tension.

The contact angle measurements were conducted using carbon steel as a surface. Carbon steel is usually assigned a negative charge. This problem occurs when using anionic surfactants due to the electrostatic repulsion between the surface of the surfactant head group and the carbon steel surface. Increasing the ionic strength of a solution is said to improve the contact angles for anionic and zwitterionic surfactants because the presence of cations reduces the repulsion between the surfactant head groups and between the steel surface and the surfactant. However, this effect is limited to how much surfactant can be adsorbed onto the surface and the limit value; it depends on the surfactant, its concentration, and the hydrophobicity of the surface. [18]

One coupon surface was used to compare the differences in contact angle for all the tested solutions. The trend is the same for all the surfaces used. Increasing the alkali-surfactant solutions' ionic strength improved the surface's contact angle for most alkaline sets. Factors such as the limit value, the surface condition, and the ions' stability in solution play a heavy role in the outcome of the contact angle. Specific ion effects also play a role in contact angle measurements. [18-21]

For the anionic surfactants studied in this experiment, adsorption is mainly controlled by repulsive interactions between the surfactant and carbon steel surface, which is assumed to be anionic for this experiment. Meng et al. showed that adding a salt with increasing ionic strength reduces the repulsion between the anionic surfactant head and the carbon steel surface.[19] This is due to the increased binding of the positively charged counterions to surfactant.

The surface tension of 2 wt.% Paratene®D740 was 29.70 mN/m (±0.13 mN/m), well below the surface tension of the water sample used, 78.94 mN/m. Based on the plot (**Figure 5**), increasing ionic strength did result in a larger percentage decrease in surface tension. Na_2CO_3 had the largest percent decrease. in surface tensions with an approximate 2.4% change at 0.5 wt.%. The percent change in surface tension was higher for Na_2SiO_3 and TSP than it was for KOH and NaOH despite their significantly lower ionic strengths, especially when comparing TSP to Na_2SiO_3, NaOH, and KOH. The difference between the surface tension values for each alkaline reagent at the different concentrations, however, was not significant, likely due to the zwitterionic nature of the surfactant, allowing it to balance its own charges.

The final contact angle of 2 wt.% Paratene®D740 was 12.39° after 13.66 seconds. The initial addition of any alkaline reagent resulted in a percent increase in the contact angle when compared to the pure surfactant solution. However, with increasing ionic strength, a decrease in contact angle was observed (**Figure 6**). The trend observed was opposite to that observed for the surface tension. TSP and Na_2SiO_3 showed the biggest percentage increase in contact angle and poor wettability in the carbon steel surface, with TSP being the worst. At 5 wt.%; however, both alkaline reagents showed a significant percentage decrease in contact angle with Na_2SiO_3 matching 5 wt.% KOH and TSP being even lower than that. NaOH showed the most wettability on the carbon steel surface, with the highest percent decrease starting at 1 wt.%.

DDBSA and SDBS were unstable in alkaline environments, with DDBSA being the most unstable. Precipitation was observed, especially with the highly alkaline (high pH) reagents NaOH and KOH. Since Na_2SiO_3 had the least amount of precipitates formed, precipitation was likely due to oversaturation of the solution. The formation of precipitates made it difficult to be fully certain about the values obtained because the surfactant

concentration was likely lower than what was measured.

The surface tension of 0.01 wt.% DDBSA was 39.68 mN/m ($\pm$0.27 mN/m). Despite the precipitates being observed, each alkaline series still showed a net percentage decrease in the surface tension at all concentrations, as shown in **Figure 7**. KOH started off with the highest percentage decrease and showed promising results as the most effective. A slight percentage increase was observed at 2 wt.%, likely because of precipitate formation. However, at 5 wt.% KOH, the surface tension reduced again. NaOH had the lowest percentage decrease in surface tension, even with a higher ionic strength than the three remaining alkaline reagents. At 2 wt.%, and 5 w.%, Na_2CO_3 had the lowest percentage decrease in surface tension.

The final contact angle of 0.01 wt.% DDBSA was 39.3° after 18.56 seconds. Due to strong electrostatic repulsion between the surfactant head and the carbon steel, most solutions had a higher affinity for the dispensing tube than the surface. **Figure 8** shows that the addition of the alkaline reagents at varying concentrations resulted in a percentage increase in the final contact angle, with NaOH being the exception. KOH started off with a significant percentage decrease. However, an increase in contact angle was observed at 2 wt.% and 5wt.% of KOH. This is likely due to precipitates in the solutions with 5% KOH having the most significant amount. Precipitates in both solutions interfere with the surfactant's ability to interact with the surface, resulting in higher contact angles. Surprisingly, the opposite trend was observed for TSP. Increasing ionic strength still improved the wettability of the cleaning solution for the reagents in the series besides KOH.

The surface tension of 0.01 wt.% SDBS was 51.13 mN/m ($\pm$1.26 mN/m), which is higher than the surface tension of DDBSA. An essential factor to consider when predicting surface tension is the ability of the cations to penetrate the surface to reduce the repulsive force between the anions. More cations at the interface help decrease the surface tension. H^+ has a higher penetrating ability than Na^+, explaining why DDBSA has a lower surface tension than SDBS at 0.01%. The surface tension tests for each solution showed a steady decrease within the 10-second limit, making obtaining a lower standard deviation more difficult. The slow diffusion rate of SDBS is likely due to the ions having a more challenging time getting to the interface.

In the SDBS series, NaOH had the highest percent decrease in surface tension with increasing ionic strength. All alkaline reagents showed a percentage decrease in surface tension compared to the pure surfactant solution (**Figure 9**). At 5 wt.%

NaOH, the observed surface tension was higher than that of the pure surfactant solution, which could be a result of the surfactant precipitating out of the solution. KOH had the second-highest decrease. At 2 wt.% and 5 wt.%, a slight increase in surface tension was observed but was still lower than that of the pure surfactant solution. The trend for the other three alkaline reagents was roughly the same as what was observed for DDBSA. At 5 wt.%, TSP had a higher percentage decrease than all other alkaline reagents at the same weight percent.

The contact angle of 0.01 wt.% SDBS on a carbon steel coupon was 72.33° at 12.30 seconds. The standard solution had a higher affinity for the tube than the surface, skewing the contact angle. Unlike DDBSA and Paratene®D740, adding alkaline salts helped reduce the contact angle for most solutions. The contact angle trends are similar to those observed for DDBSA. All alkali-surfactant solutions had a higher affinity for the dispensing tube than they did for the surface (**Figure 10**). Na_2SiO_3, TSP, and Na_2CO_3 still showed that the contact angle decreases with increasing ionic strength, with TSP showing the most improvement in wettability at 5 wt%. NaOH showed a similar trend; however, at 5 wt.%, a spike in the surface tension was observed. KOH showed an increased contact angle with increasing ionic strength, like in DDBSA, which is likely for the same reason.

0.1 wt.% RA-600L had the lowest surface tension out of all the surfactants used, with a value of 27.35 mN/m ($\pm$0.38 mN/m). The addition of alkaline salts followed the same trend as the other surfactants, decreasing surface tension with increasing ionic strength (**Figure 11**). All salts added followed this trend with a clear linear relationship between ionic strength and surface tension in the presence of a surfactant. The addition of these salts, however, slightly hindered the ability of this surfactant, resulting in a percentage increase for the alkaline reagents at their varying concentrations. This is likely due to a depletion of ions at the solution surface compared to the pure surfactant solution. Unlike Paratene®D740, Na_2SiO_3 and TSP had the highest percent increase, with TSP having the highest increase. In this series, NaOH had the lowest increase in surface tensions for all concentrations, while KOH and Na_2CO_3 were competing for the second spot. At 5 wt.%, the change in surface tensions for all the reagents was not significant. However, the surface tensions were still higher than that of the pure surfactant solution.

The contact angle of 0.1 wt.% RA-600L on carbon steel was 28.43° at 13.16 seconds. RA-600L had a lower contact angle than the other anionic surfactants (DDBSA and SDBS), possibly due to several factors, such as differences in structural properties and a higher ionic strength. No attraction

to the tube was observed, but it was observed in all 0.5 wt.% and 1 wt.% alkali-surfactant solutions. No precipitates or crystals were observed in these solutions. Adding alkaline reagents followed the suspected trend for all salts involved: increasing the ionic strength of the solutions decreased the contact angle (**Figure 12**). Compared to the other surfactants, the relationship between the contact angles and the change in ionic strength was stronger in the presence of RA-600L for most salts (**Figure 12**). The presence of the reagents also caused a significant percent increase in the contact angles compared to the standard solution, with the exception being NaOH. A spike was observed in the contact angle of NaOH at 1 wt.%, followed by a significant drop at 2 wt.%. On the other hand, KOH had the highest percent increase compared to the other reagents and ended up having worsened wettability than Na_2SiO_3 and TSP despite having higher ionic strengths. At 5 wt.%, TSP had a lower contact angle than Na_2CO_3.

The results from this experiment showed that although the ionic strength of a solution plays a role in improving the surface properties of an alkali-surfactant solution, the ions involved play a more important role. As stated earlier, larger and more polarizable anions are preferred at the surface of a solution. Polarizability is affected by the interaction between electrons and the nucleus. The amount of electrons in a molecule affects how tightly held they are to the nucleus. The less pull the electrons have from the nucleus, the more polarizable they are to outside sources, making the molecule more polarizable. The polarizability ranking for the anions used in this experiment is as follows: $PO_4^{3-} > SiO_3^{2-} > CO_3^{2-} > OH^-$. This ranking explains the results observed for Paratene®D740. Since Paratene®D740 is a zwitterionic surfactant, the effect of the anion's diffusion to the diffusion layer is more apparent, especially in relation to wettability. Since the coupon used possessed a negative charge, more anions at the surface resulted in increased repulsion between the coupon surface and the solution. Increasing the ionic strength of each solution increased the number of Na^+ or K^+ ions, allowing any anions at the surface to be neutralized, hence reducing the contact angle. This likely explains the contact angle results for TSP at 5 wt.%.

Another factor affecting the surface properties of the alkali-surfactant solutions is the surfactant-ion relationship, and this is observed with the anionic surfactants. Repulsion between the anions and surfactant polar head reduces the number of anions that diffuse to the surface. The strength of the repulsion is affected by the size of the surfactant's polar head group and the nature of the anions involved, making the results slightly more random.

The nature of the surfactant alkyl chain also affects the surface properties of the solution. Most surfactant hydrophobic tails are a mixture of linear and substituted structures, with the degree of substitution remaining unknown. Linearity allows for better overlap of the hydrophobic tails, creating tighter micelle structures. It also increases the number of surfactant molecules adsorbed onto the solution surface. A substituted hydrophobic tail reduces the potential for overlap, limiting the number of surfactant molecules adsorbed on the surface, hence worsening the solution's surface tension and wettability.

CONCLUSION

The effect of alkaline salts on the surface properties (surface tension and contact angle) of aqueous surfactant solutions was investigated in this study. The surfactants used are Paratene®D740, DDBSA, SDBS, and RA-600L. Alkaline salts improved the surface properties of all surfactant solutions besides RA-600L. Moreover, the results from the experiment showed that increasing a solution's ionic strength improved its surface properties. However, a more important observation is that the alkaline reagent used in the surfactant solution is important to maximize the effectiveness of the surfactant, especially for wettability purposes. The alkaline reagent should be carefully selected to balance strength with the polarizable ions. For the surfactants used, NaOH and Na_2CO_3 were shown to have the best balance with solution stability and improved surface properties.

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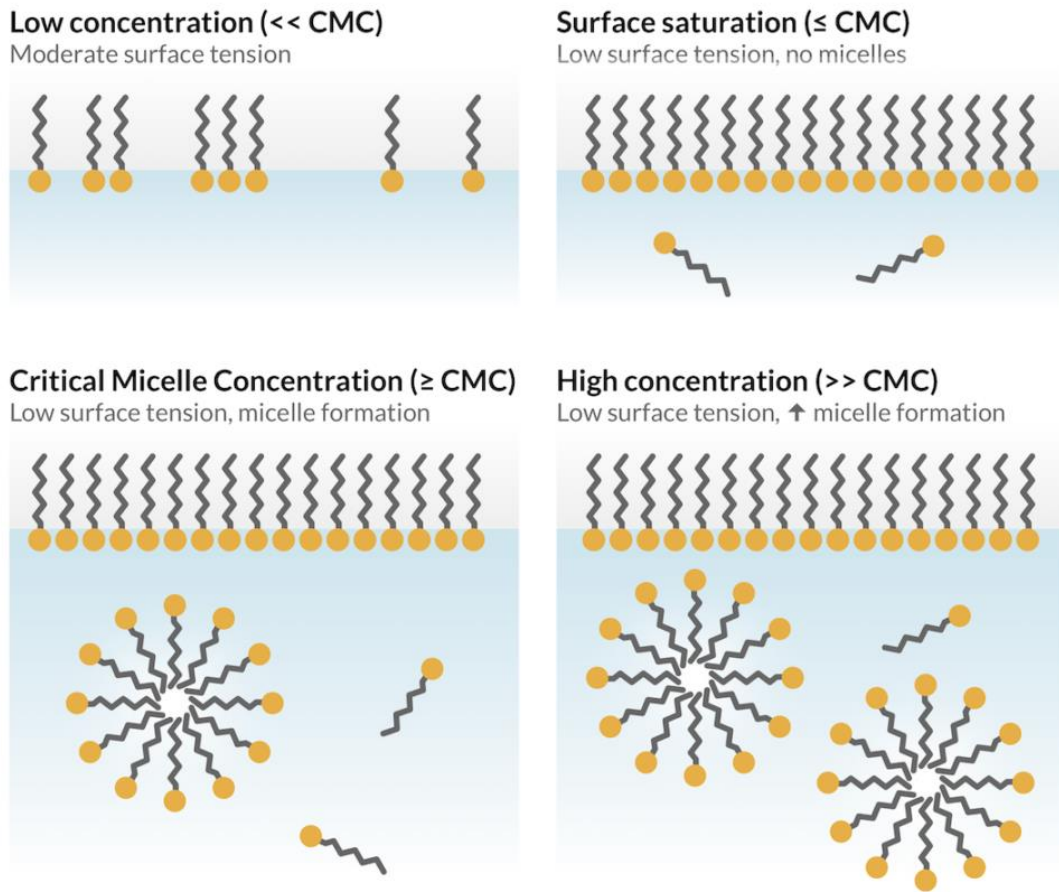
APPENDIX

Low concentration (<< CMC)
Moderate surface tension

Surface saturation (≤ CMC)
Low surface tension, no micelles

Critical Micelle Concentration (≥ CMC)
Low surface tension, micelle formation

High concentration (>> CMC)
Low surface tension, ↑ micelle formation

Figure 1. A schematic showing the interactions between a surfactant and an aqueous surface at different concentrations of surfactants. The polar head group of the surfactant is shown as a yellow line, and the hydrophobic tail is portrayed as a brown line.
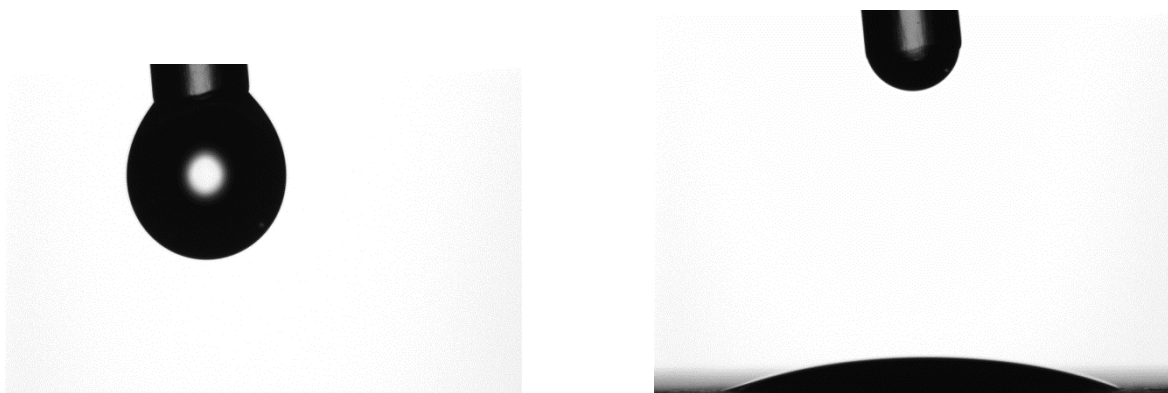
Figure 2. Visuals of the surface tension (left) and contact angle (right) measurements using a OneAttension Theta tensiometer.
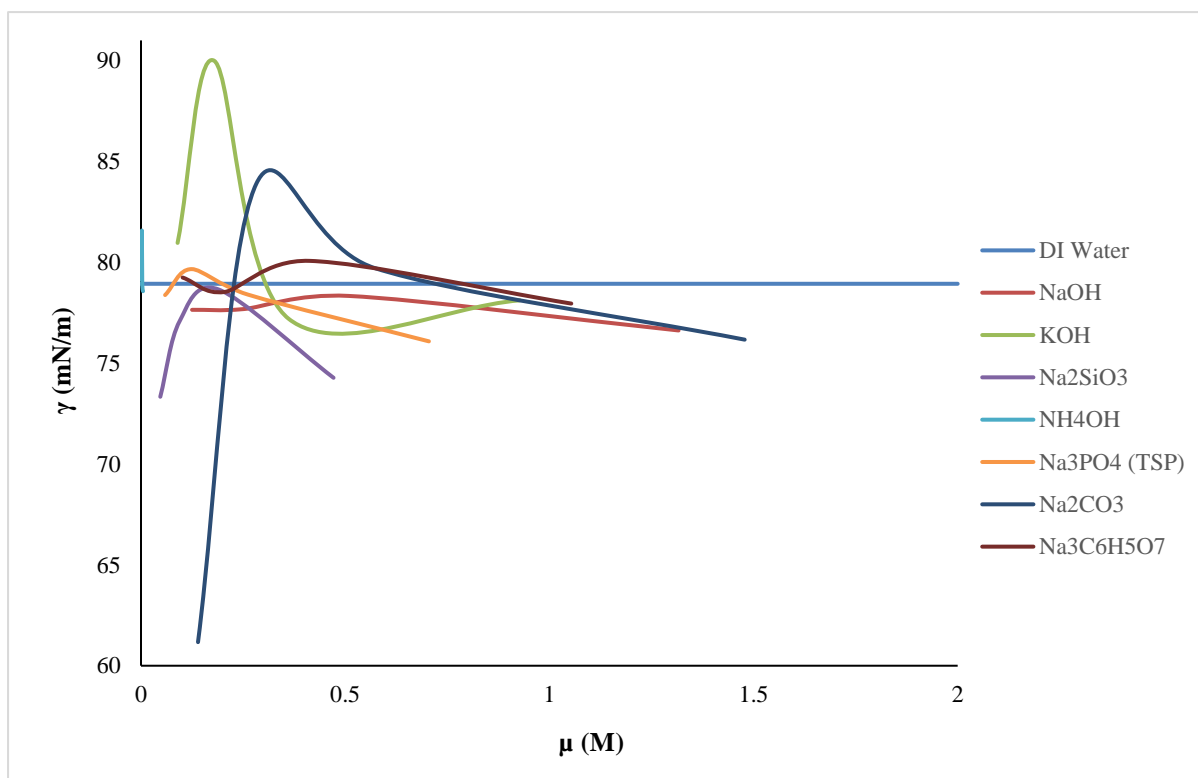
Figure 3. The surface tension (γ, mN/m) of different alkaline solutions with increasing ionic strength (μ, M) compared to deionized water's surface tension (78.94 mN/m). The calculated ionic strength values at all four different concentrations for NH_4OH were about 100 times less than those for the other alkaline solutions.
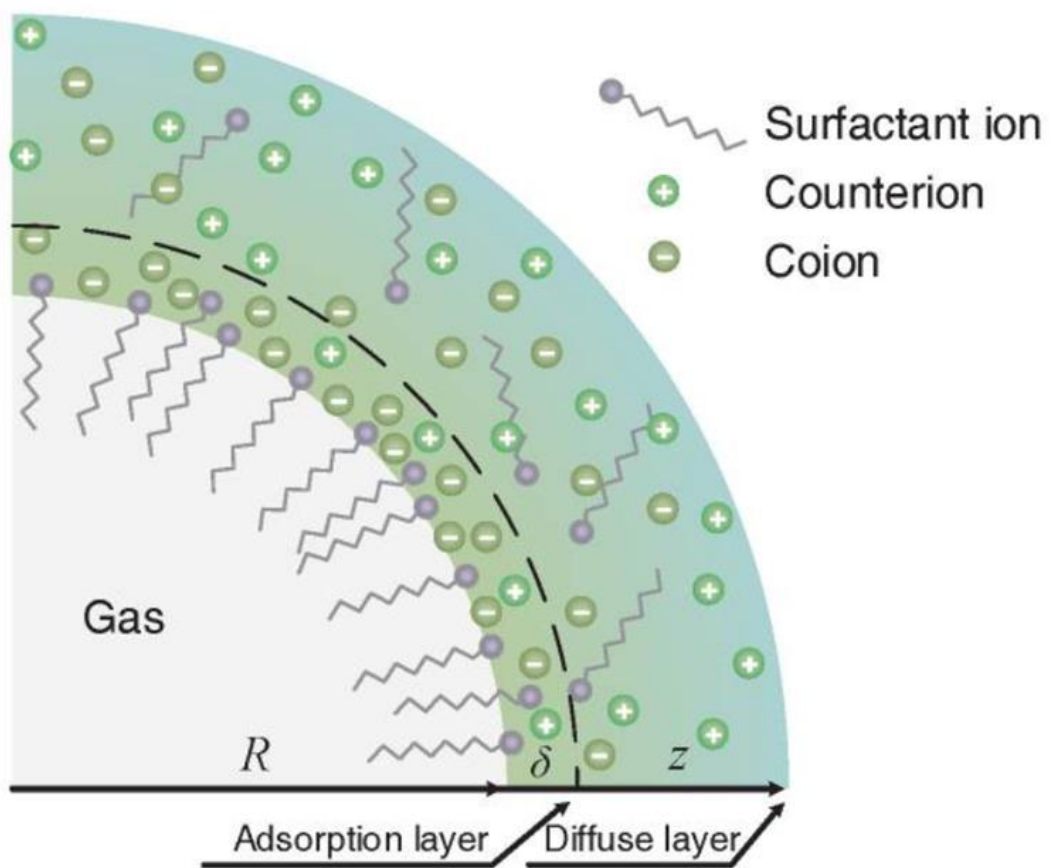
Figure 4. This image shows the interface between an aqueous liquid and the atmosphere, with the surfactant being adsorbed onto the surface of the liquid in its adsorption layer. The polar head group of the surface (grey circle) interacts with the aqueous surface while the hydrophobic tail is directed towards the atmosphere. The adsorption layer also contains some cations and anions. The diffuse layer shows the same and is below the adsorption layer.
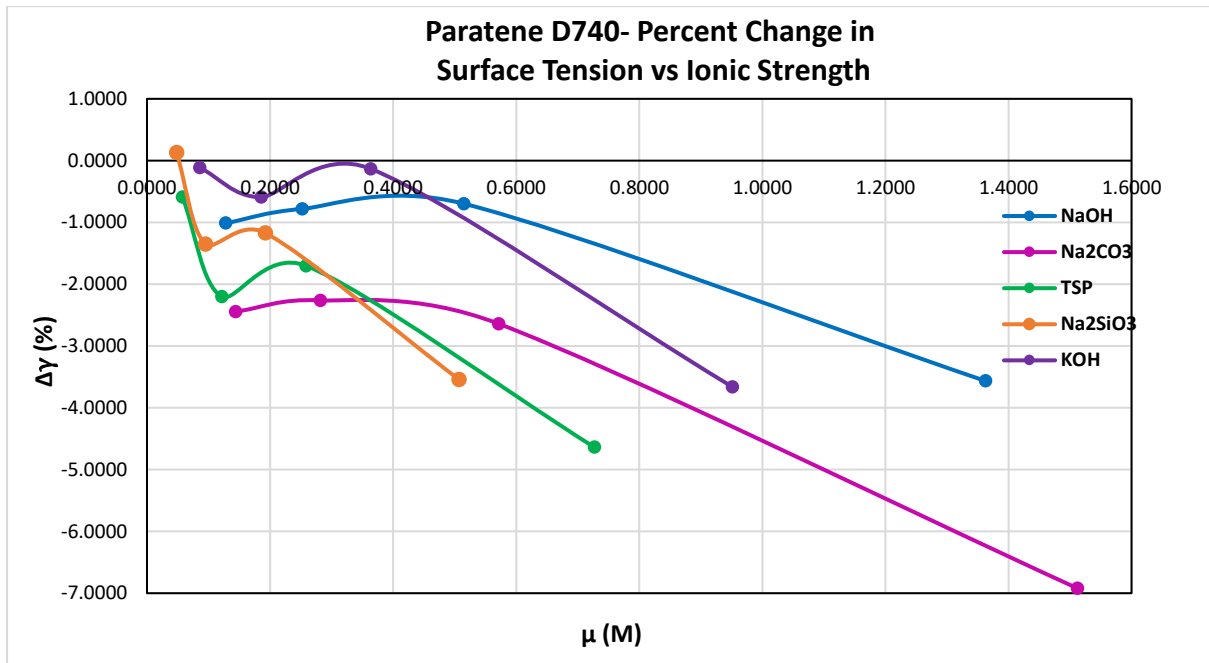
Figure 5. The percent change in surface tension (Δγ, equation 4) plotted against ionic strength (μ) for increasing concentrations of NaOH (blue), Na₂CO₃ (magenta), TSP (green), Na₂SiO₃ (orange), and KOH (purple) in the presence of 2 wt.% Paratene®D740.
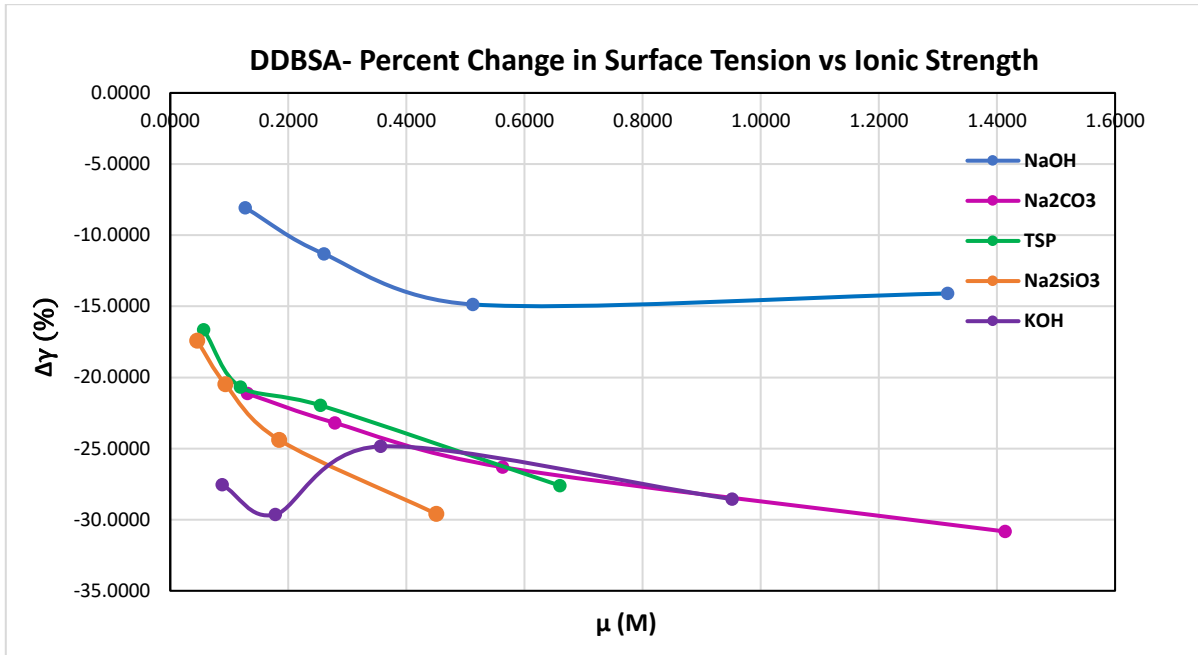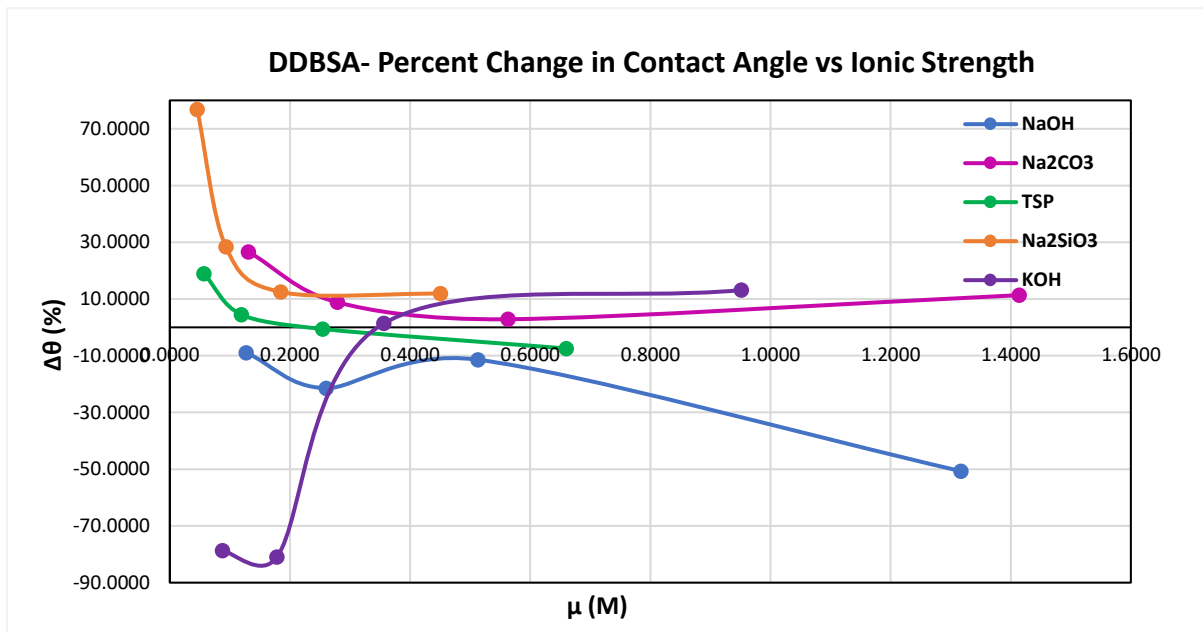

Figure 6. The percent change in contact angle (Δθ, equation 6) on carbon steel plotted against ionic strength (μ) for increasing concentrations of NaOH (blue), Na₂CO₃ (magenta), TSP (green), Na₂SiO₃ (orange), and KOH (purple) in the presence of 2 wt.% Paratene®D740.

Figure 7. The percent change in surface tension (Δγ, equation 4) plotted against ionic strength (μ) for increasing concentrations of NaOH (blue), Na₂CO₃ (magenta), TSP (green), Na₂SiO₃ (orange), and KOH (purple) in the presence of 0.01 wt.% DDBSA.
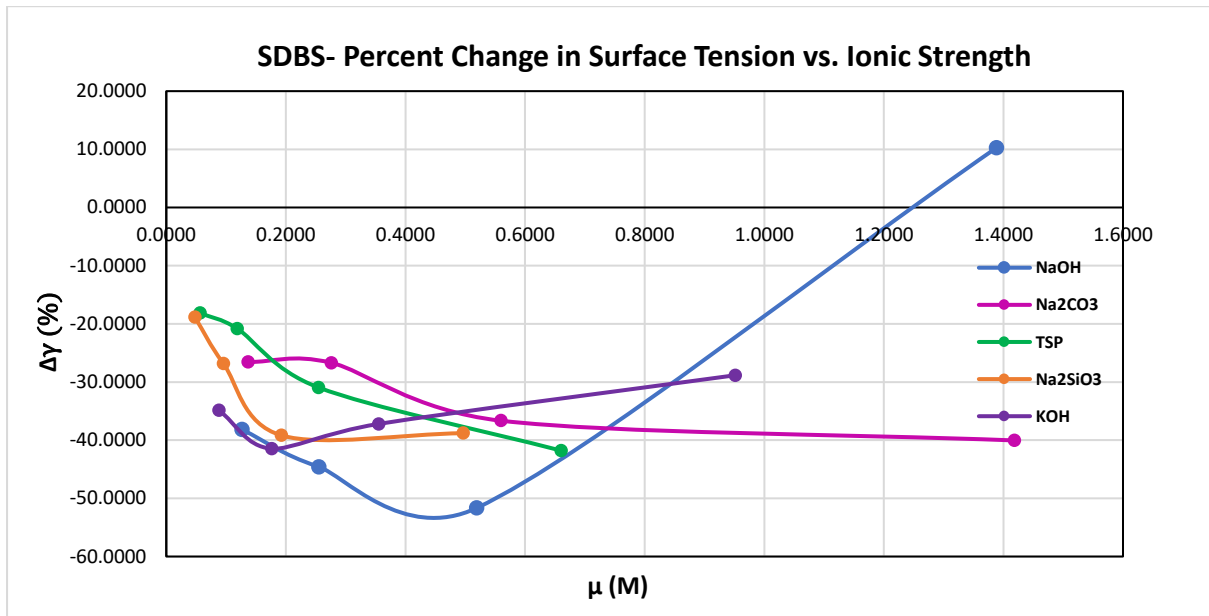

Figure 8. The percent change in contact angle (Δθ, equation 6) on carbon steel plotted against ionic strength (μ) for increasing concentrations of NaOH (blue), Na₂CO₃ (magenta), TSP (green), Na₂SiO₃ (orange), and KOH (purple) in the presence of 0.01 wt.% DDBSA.
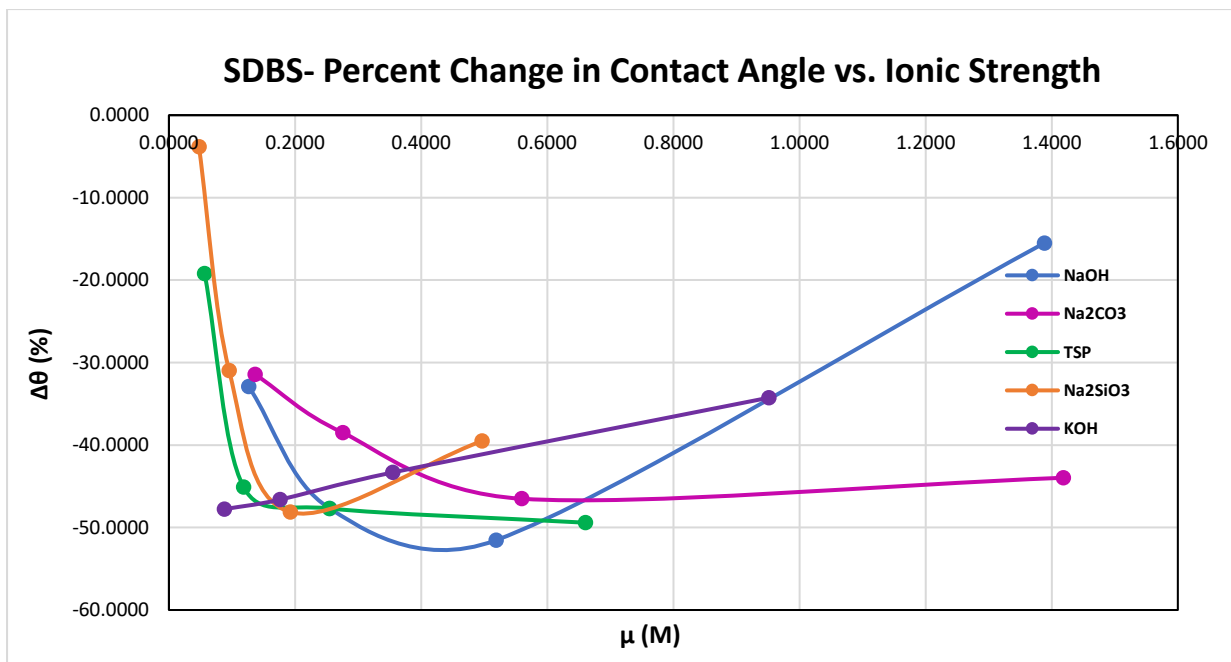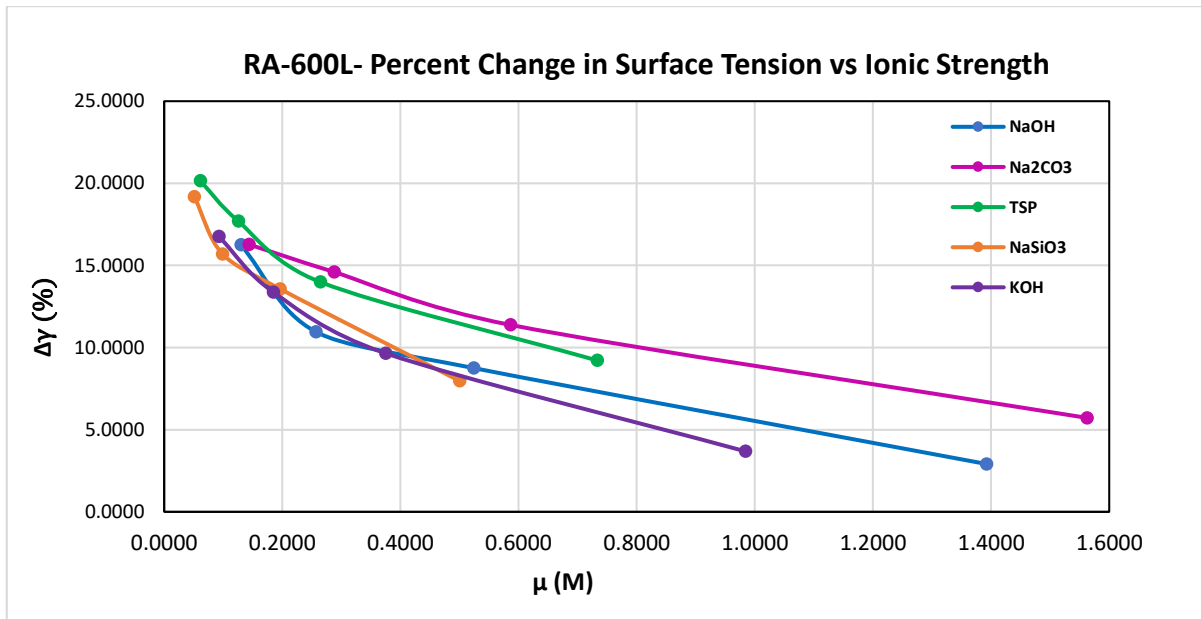
Figure 9. The percent change in surface tension ($\Delta\gamma$, equation 4) plotted against ionic strength (μ) for increasing concentrations of NaOH (blue), Na_2CO_3 (magenta), TSP (green), Na_2SiO_3 (orange), and KOH (purple) in the presence of 0.01% SDBS.

Figure 10. The percent change in contact angle ($\Delta\theta$, equation 6) on carbon steel plotted against ionic strength (μ) for increasing concentrations of NaOH (blue), Na_2CO_3 (magenta), TSP (green), Na_2SiO_3 (orange), and KOH (purple) in the presence of 0.01 wt.% SDBS.

Figure 11. The percent change in surface tension (Δγ, equation 4) plotted against ionic strength (μ) for increasing concentrations of NaOH (blue), Na$_2$CO$_3$ (magenta), TSP (green), Na$_2$SiO$_3$ (orange), and KOH (purple) in the presence of 0.1 wt.% RA-600L.
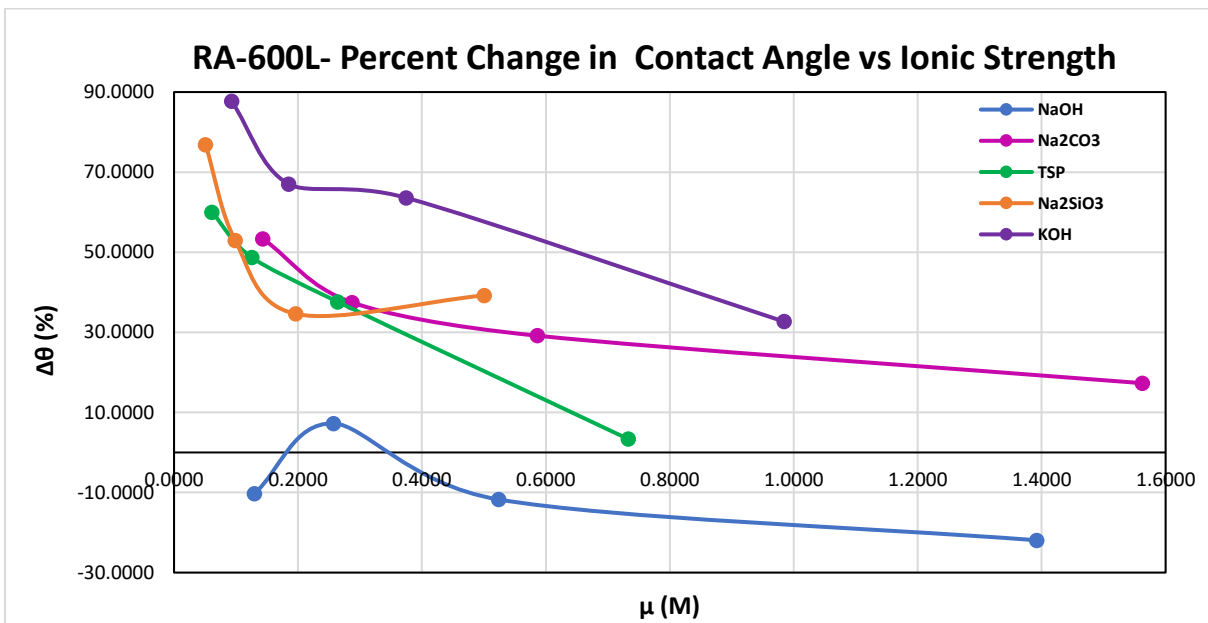

Figure 12. The percent change in contact angle (Δθ, equation 6) on carbon steel plotted against ionic strength (μ) for increasing concentrations of NaOH (blue), Na$_2$CO$_3$ (magenta), TSP (green), Na$_2$SiO$_3$ (orange), and KOH (purple) in the presence of 0.1 wt.% RA-600L.