Final Report

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Improved Decontamination: Interfacial Transport, and Chemical Properties of Aqueous Surfactant Cleaners

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REVIEW OF EFFORT

Effects of Varied pH on Oil Detachment

BACKGROUND

The aqueous cleaning parameter of interest in this series of studies was the pH of the aqueous cleaning solution. A sessile droplet of industrial quench oil was analyzed to determine the effect of varied solution pH its removal from a stainless steel surface. It can be seen from Young's equation:

$$\gamma_{\text{Oil/Solution}} \cos(\theta) = \gamma_{\text{Solidl/Solution}} - \gamma_{\text{Oil/Solid}}$$

the contact angle of a droplet is a function of the interfacial tension, γ, at the relevant interfaces. Most research has concentrated on modification of the oil/solution interfacial tension to improve detachment. It is known that increasing pH causes a decrease in interfacial tension at the oil/solution interface. Previous research in our group has shown that a decrease in oil/solution interfacial tension corresponds to increases in contact angle and decreases in detachment time. Despite the obvious relevance of the oil/solution interfacial tension on contact angle it is important to consider the changes occurring at the solid/solution interface. It is known that changes in pH affect the adsorption and orientation of surfactant monomers at the solid/solution interface. This phenomenon can be explained by the changes in surface charge due to changes in solution species and the effects such changes have on the structure and orientation of surfactant aggregates. Since pH affects solid surface charge it become imperative to develop an understanding of surfactant surface aggregates and their effect on oil droplet wetting or detachment. The majority of research has concentrated on the effects of ionic surfactant in the presence of pH modification. Since industrial cleaning and degreasing is known to utilize more than just ionic surfactants this study has experimentally analyzed the effects of pH on four different surfactant types (anionic, cationic, zwitterionic, and nonionic). These surfactants are studied using a single type of oil placed on a stainless steel surface. A mechanistic model was proposed to interpret the observed results.

EXPERIMENTAL

Information regarding the materials used in these experiments is presented in the paper titled "Oil Detachment from Solid Surfaces in Aqueous Surfactant Solutions as a Function of pH" which is included in the Appendix. Experiments were undertaken to evaluate the effect of pH changes on single drop detachment, contact angle, zeta-potential, and prototypic surface cleaning using ultrasonication. Solution pH modification was performed through the addition of hydrochloric acid and sodium hydroxide

Droplet detachment and contact angle studies were undertaken in a dedicated apparatus designed to monitor the evolution of droplet shape, contact angle, and droplet detachment when the stainless steel surface was submerged in aqueous surfactant solutions. This apparatus can be seen in Figure 1-1.

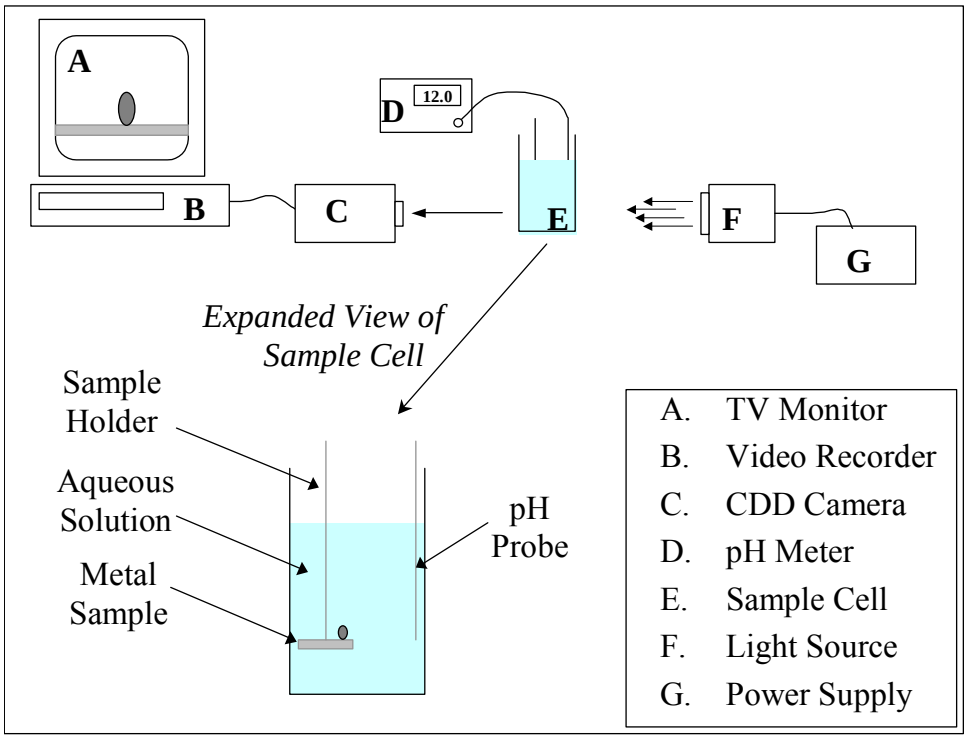

FIGURE 1-1 – Droplet Analysis Apparatus

The stainless steel coupon was cleaned prior to each experiment using a commercial detergent/deionized water mixture and rinsed with deionized water. The surface was allowed to air dry and a two-microliter droplet of Mar-Temp 355 oil was placed on the surface. The droplet was allowed to wet the coupon for five minutes prior to submersion in a square-shaped beaker contain a

pH modified surfactant solution. The coupon was submerged in such a manner as to facilitate the droplet being observed with the imaging camera. Droplet images were then extracted from the imaging system and analyzed to determine contact angle and detachment time for the first portion of the droplet.

Zeta-potential measurements were obtained using a Lazer Zee Meter Model 501. These measurements were taken to provide information relating to the change of oil/solution interfacial charge. This information could be used to infer the effects of pH modification of surfactant adsorption at the solid/solution interface. An emulsion of Mar-Temp 355 oil droplets was produced and analyzed using a Coulter Ls-130 light scattering apparatus to insure constant droplet size. A 5 mL aliquot of this emulsion was diluted with 40 mL of deionized water and analyzed with the zetameter.

Test for cleaning efficiency were undertaken in a Crest bench-top ultrasonic bath. The purpose of these tests was to correlate the observed changes in detachment time with cleaning efficiency for use in industrial cleaning solution parameter selection. The coupon was cleaned and dried in the same manner as previously explained. After cleaning the coupon was weighed to determine the 'clean' weight. The coupon was then submerged in a beaker of Mar-Temp 355 for five minutes after which it was allowed to hang for three hours to drain excess oil from the surface. When this was complete the coupon was weighted to determine the 'dirty' coupon weight after which it was submerged in a 2 L beaker of pH modified surfactant solution and placed in the ultrasonic bath. Following sonication the coupon was removed from the surfactant solution, dried with compressed air, and weighed to determine the 'cleaned' weight. The percent oil removal or cleaning efficiency was determined as follows:

$$\text{Percent Oil Removal} = \frac{\text{Dirty wt - Cleaned wt}}{\text{Dirty wt - Clean wt}} \times 100$$

The experimental methods and conditions, droplet sizes, and surfactant specific concentrations were maintained unchanged for each surfactant type studied. This insured the consistency of the results and reinforced that the results were due to pH modifications.

RESULTS

Since the pH of a surfactant solution is known to have an effect on the dynamics of oil detachment from surfaces the purpose of this investigation was to compare the trends over a range of pH values for the four different surfactant types. The effects of solution pH on detachment times for solutions of each of the four surfactants can be seen in Figure 1-2. It is evident

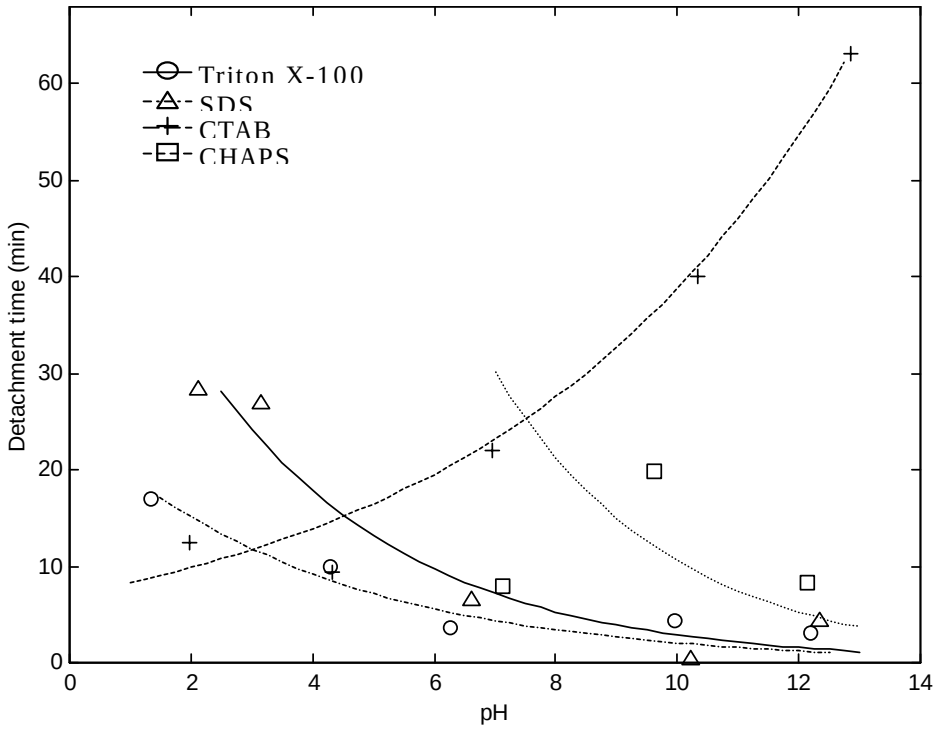

FIGURE 1-2 - Effect of pH on Droplet Detachment Time

that pH has significant effects relative to the surfactant type. For solutions of Triton X-100 (nonionic), SDS (anionic), and CHAPS (zwitterionic) there was a decrease in detachment times for increases in pH. Solutions of CTAB were seen to demonstrate the opposite behavior, increasing detachment time with increasing pH. Over the pH ranges studied oil detachment time decreased 81 percent in solutions of Triton X-100 and 85 percent for solution of SDS. For solutions of CTAB there was an increase in detachment time of about 80 percent. CHAPS decreased with increasing pH, however no detachment was noticed at lower pH (< 7.0) during the maximum test time of 120 minutes. The detachment for CHAPS was noticeably faster for higher pH (> 7.0).

Droplet contact angle changes as a function of time can be seen in Figures 1-3 through 1-6. The effect of solution pH modification of

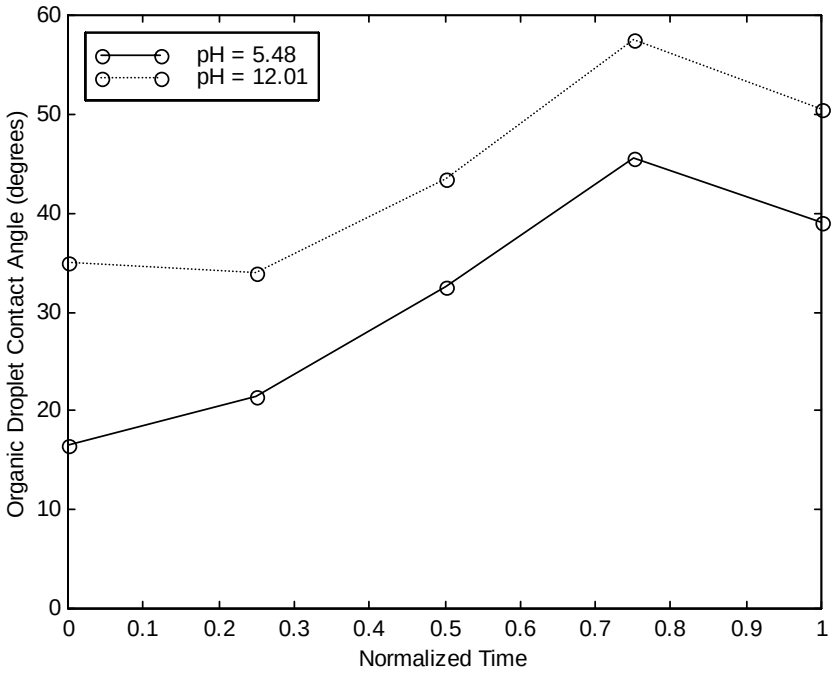

FIGURE 1-3 - Effect of pH for Triton X-100 Solutions

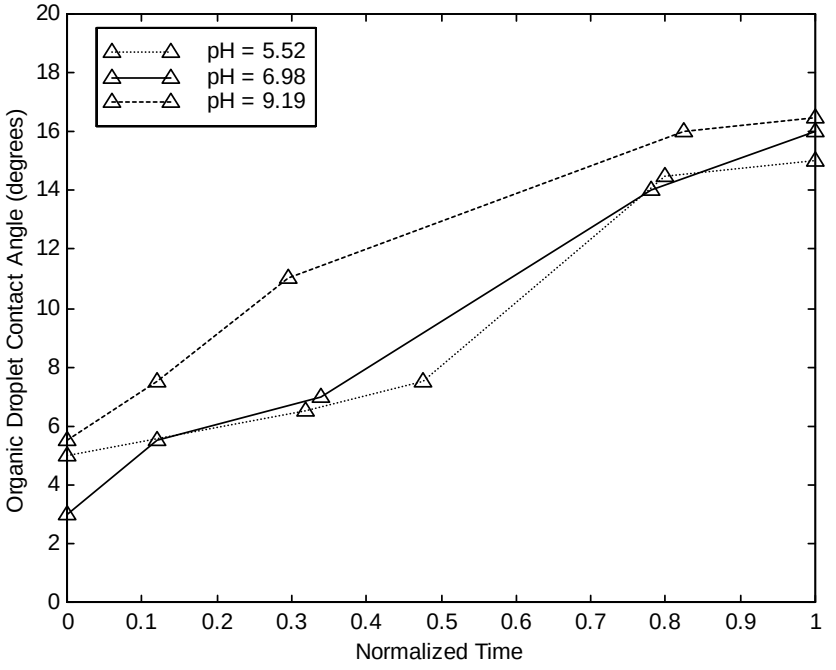

FIGURE 1-4 - Effect of pH for SDS Solutions

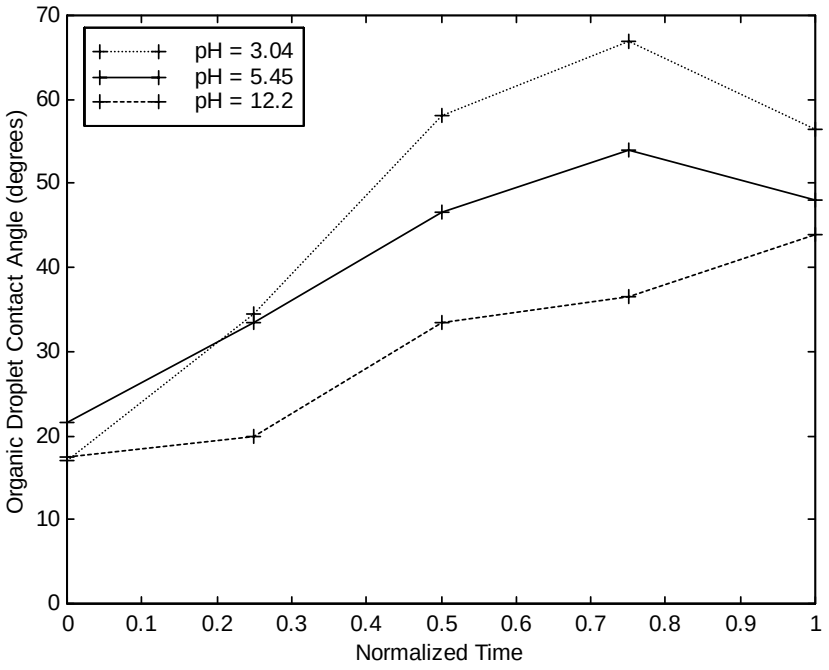

FIGURE 1-5 - Effect of pH for CTAB Solutions

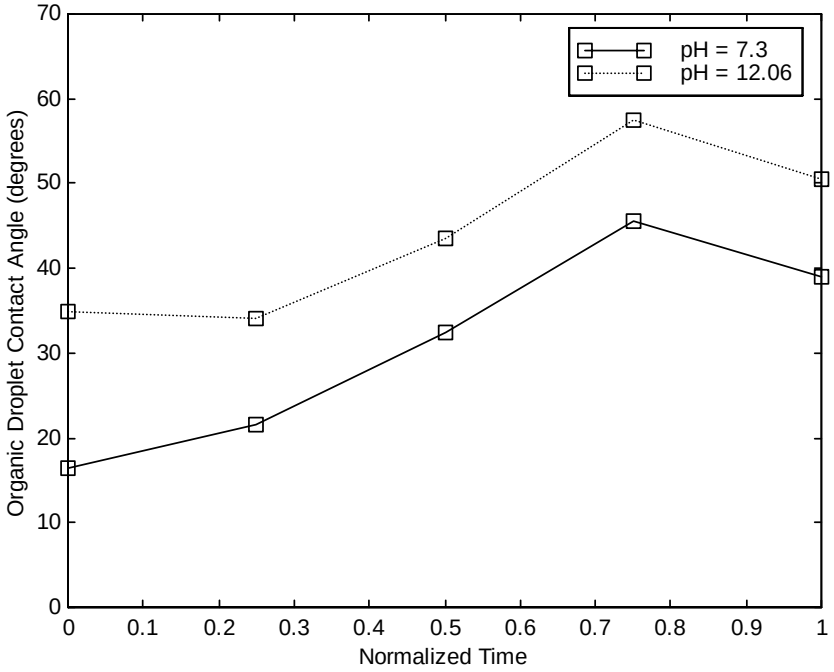

FIGURE 1-6 - Effect of pH for CHAPS Solutions

oil droplet contact angle and consequently oil/solution interfacial tension can be seen. Triton X-100, SDS, and CHAPS solutions exhibited an increase in contact angle for an increase in solution pH. Contact angles decreased for increased CTAB solution pH.

Zeta-potential measurements for the four surfactants studied can be seen in Figure 1-7. For a surfactant free system the zeta

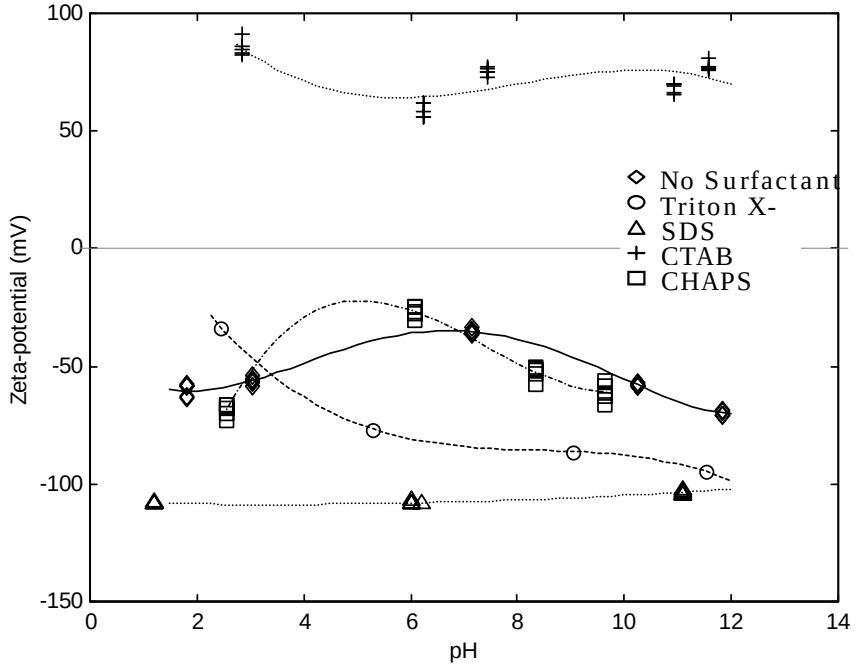

FIGURE 1-7 - Effect of pH on Oil Droplet Zeta-Potentials

potential of an oil droplet varied from -30 mV to –65 mV. This indicates that the oil droplets have a naturally negative surface charge. Solutions of Triton X-100, SDS, and CHAPS exhibited a negative zeta-potential also. This indicates that oil surface exhibits a negative charge also. Zeta potentials in CTAB solutions were found to be positive, indicating a positive surface charge. The curious behavior of the nonionic surfactant Triton X-100 can perhaps be explained by the modification of the organic head and/or tail groups by the pH modifying agents.

Cleaning effectiveness for the four surfactants as altered by solution pH can be seen in Figures 1-8 through 1-11. For solutions

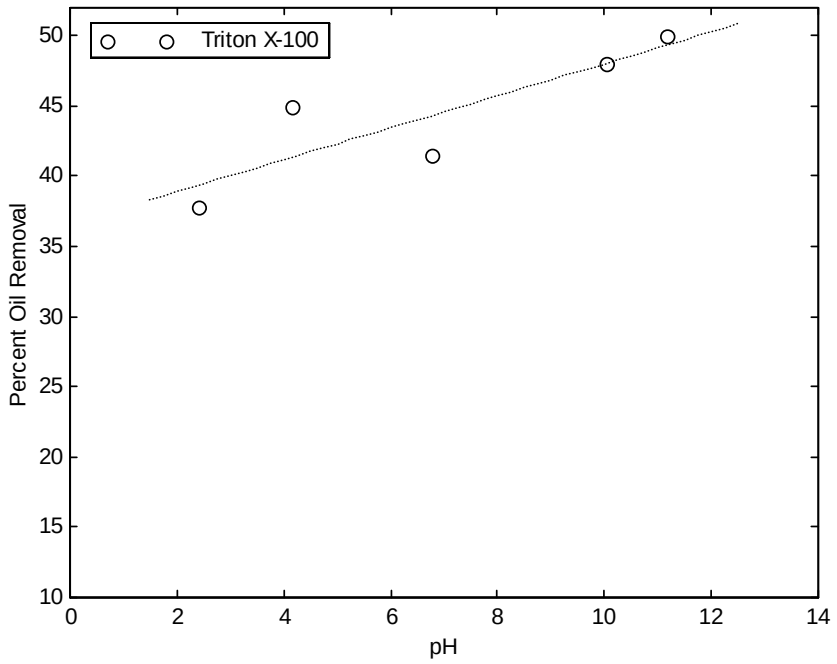

FIGURE 1-8 - Effect of pH on Cleaning in Triton X-100 Solutions

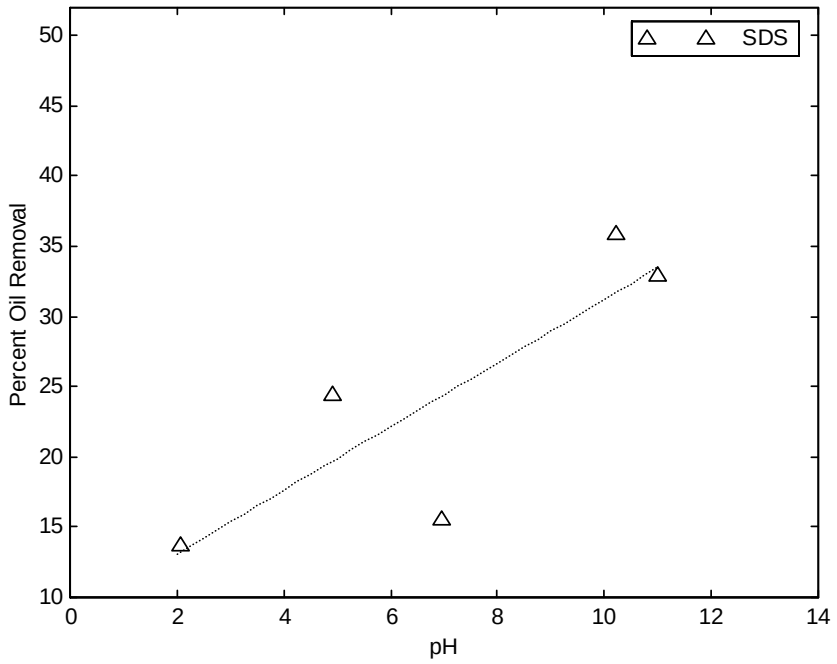

FIGURE 1-9 - Effect of pH on Cleaning in SDS Solutions

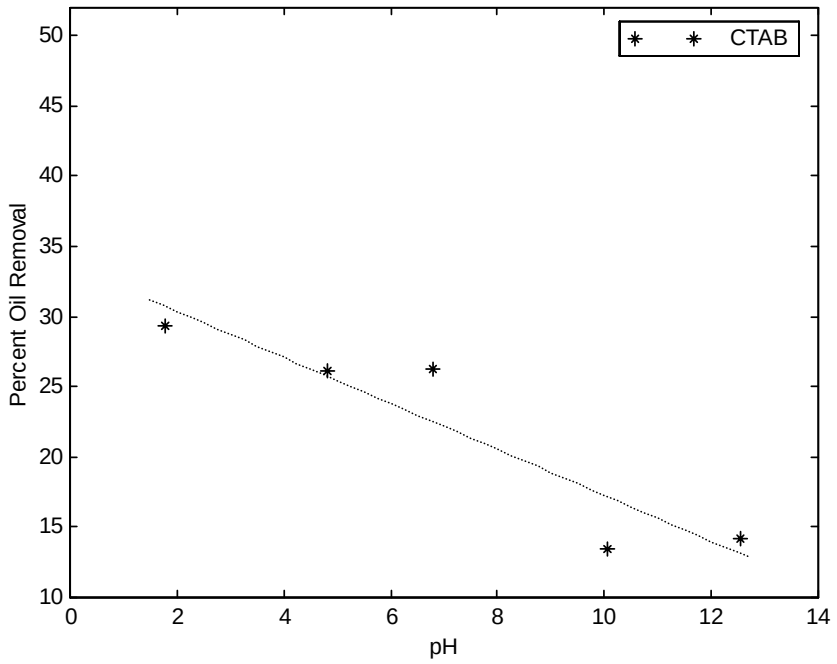

FIGURE 1-10 - Effect of pH on Cleaning in CTAB Solutions

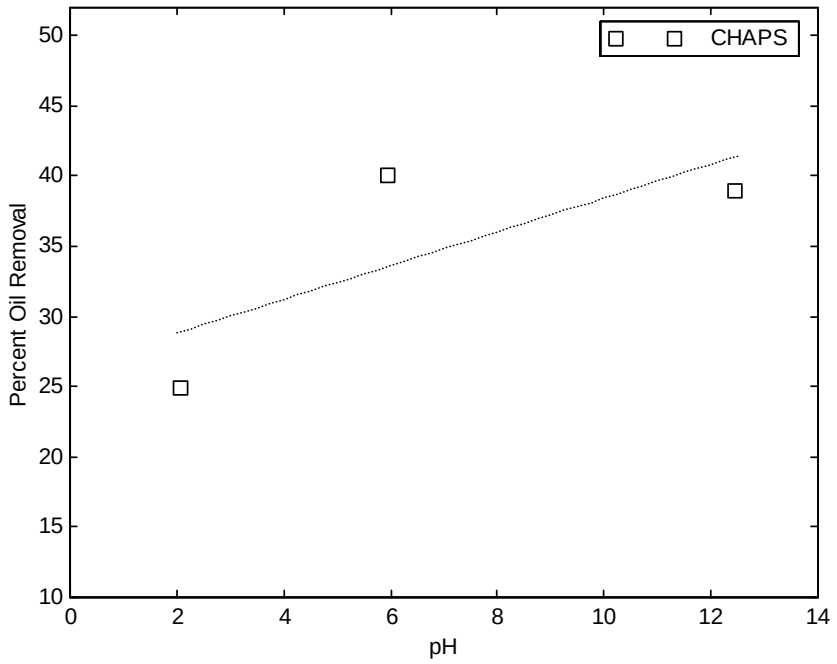

FIGURE 1-11 - Effect of pH on Cleaning in CHAPS Solutions

of Triton X-100, SDS, and CHAPS the cleaning effectiveness increased with increasing pH. For solutions of CTAB cleaning efficiency decreased with increasing pH. The percentage increase in cleaning efficiency was 13 percent for Triton X-100 solutions, 19 percent for SDS solutions, and 14 percent for CHAPS solutions. In CTAB solutions the cleaning effectiveness decreased by 15 percent over the studied pH range.

CONCLUSIONS

A mechanistic model was developed for the interpretation of the previously discussed experimental results. Figure 1-12 shows the

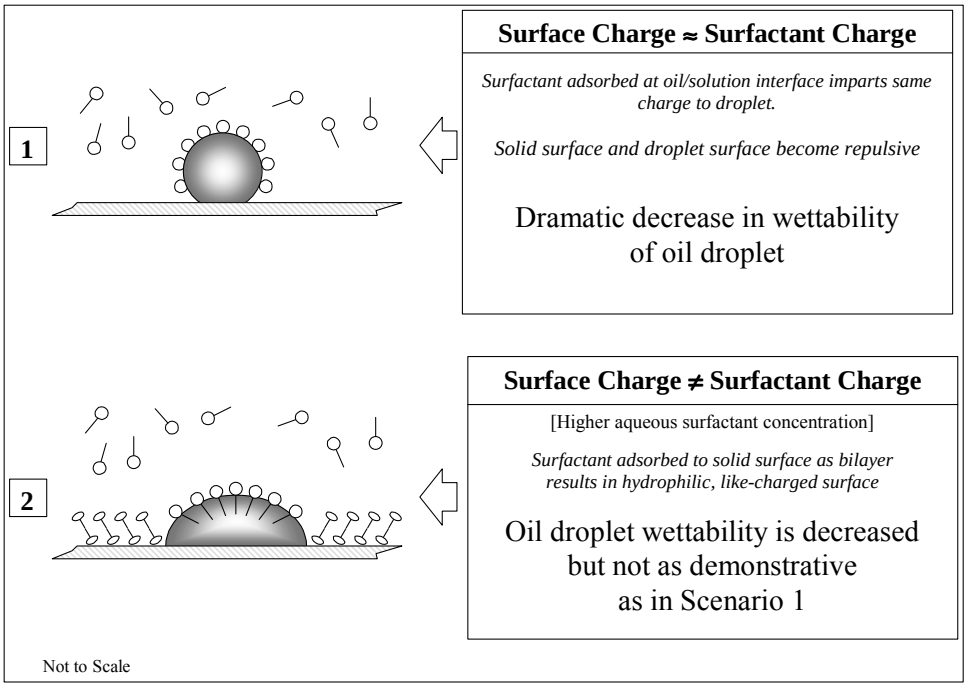

FIGURE 1-12 - Effect of pH on Oil Droplet Behavior

proposed surfactant adsorption model for the four surfactant types. Scenario 1 shows that for similar surface and surfactant charge there will only be adsorption at the oil/solution interface. Since the adsorption of surfactant has been seen to impart a surfactant like charge to the surface it is plausible that electrostatic repulsion between the droplet surface and solid surface when combined with buoyancy forces result in droplet detachment. Scenario 2 describes the system where the solid surface presents an opposite charge from the surfactant resulting in adsorption of surfactant at the solid/solution interface. For low

surfactant concentrations a monolayers can be expected to form. This presents a hydrophobic, oil-like surface to the oil droplet and could result in the droplet wetting the surface more. For higher concentrations the surfactant should form a bilayer. This would result in similar effects to that shown in Scenario 1, however they would not occur as quickly. If interfacial tension related detachment effects could be eliminated from consideration then the observed effect must be due to surfactant adsorption at the solid/solution interface.

Experiments involving the study of pH modifications on droplet behavior were undertaken in this phase of our experimental work. The results presented lead to the proposed mechanistic understanding of the resident phenomena. This work broadens the understanding of pH modified aqueous cleaning and could result in the improvement of industrial cleaning/degreasing processes. The methods and techniques used in this work could be utilized in an industrial setting to determine the optimum cleaning system parameters for a give cleaning process and the materials to be cleaned.

Effects of Applied Potential on Oil Detachment

BACKGROUND

Since it is known that pH alters the surface charge of the solid material it became obvious that other methods to manipulate surface charge could present interesting avenues to improve industrial cleaning/degreasing. The logical method for surface charge manipulate without altering the cleaning solution was in the application of a potential to the solid metal surface. It should be noted from the previous experimentation that the adsorption of surfactants at the oil/solution interface imparts a surfactant-like surface charge when the surfactant is of an ionic nature. Consequently the adsorption of a nonionic surfactant should present no variance from the surfactant free conditions. As a result the droplets should be repelled at positive potentials since they exhibit a naturally negative surface potential. Anionic surfactants would exhibit greater adsorption to the solid/solution interface in the presence of a positive solid surface charge. This adsorption would be halted or inhibited in the presence of negative solid surface potentials. Cationic surfactants would display the opposite behavior, adsorption increasing at negative potentials and decreasing for positive potentials. Zwitterionic surfactants can, depending on solution pH, have a positive or negative charge. As a result adsorption would be dependent on surface charge in a manner respective to the charge induced on the surfactant by the solution pH.

In addition to affecting surfactant adsorption the application of a potential to the solid surface has also been shown to affect the wetting of the organic droplet. Determination of the natural surface charge of the droplet would indicate which potential would be most effective in removing it. Since the oil of choice in these studies exhibits a negative surface potential a negative solid surface potential would result in droplet repulsion. This information should be considered in the analysis of the experimental results from any study of applying potentials to solid surfaces. Correlations between wetting of organic droplets, detachment of droplets, and cleaning efficacy will be shown in these experiments and mechanistic model will be formulated to aid in the interpretation of the experimental results.

EXPERIMENTAL

Information regarding the materials used in these experiments is presented in the paper titled “Oil Droplet Detachment from Metal

Surfaces as Affected by and Applied Potential" which is included in the Appendix. Experiments were undertaken to evaluate the effect of solid surface applied potentials on single drop detachment and prototypic surface cleaning using ultrasonication. The pH of the solution was maintained as a constant value using hydrochloric acid and sodium hydroxide. The electric potential was applied to the stainless steel surface using a Hewlet-Packard low-voltage DC power supply.

Droplet detachment studies were undertaken in a dedicated apparatus designed to monitor the evolution of droplet shape, contact angle, and detachment time when the stainless steel surface was submerged in aqueous surfactant solutions. This apparatus can be seen in Figure 2-1.

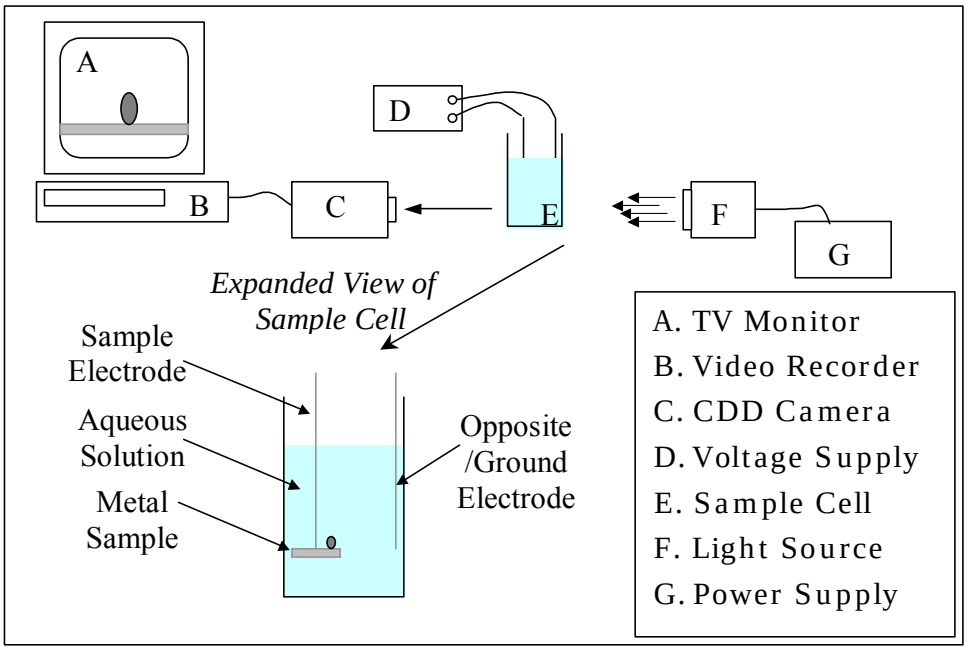

FIGURE 2-1 – Droplet Analysis Apparatus

The stainless steel coupon was clean in the method described previously. The procedures developed concerning placement of the droplet and the submersion of the coupon were also identical and maintained constant in order to insure consistency throughout the experimentation. Droplet images were again extracted from the imaging system and analyzed as detailed previously.

Tests for cleaning efficiency were undertaken in the manner described in the studies of pH effects. Procedures, measurements, and the analysis also follow the previous pH studies.

The experimental methods and conditions, droplet sizes, and surfactant specific concentrations were maintained unchanged for each surfactant type studied. This insures the consistency of the results and reinforced that the phenomena were due to the application of solid surface potentials.

RESULTS

Since the solid surface potential is known to have an effect on the dynamics of oil detachment from solid surfaces the purpose of this investigation was to compare the trends over a range of applied surface potentials for the four different surfactant types. The effects of applied surface potential on droplet detachment time for solutions of each of the four surfactants can be seen in Figures 2-2 through 2-6. It is evident that applied potential has significant

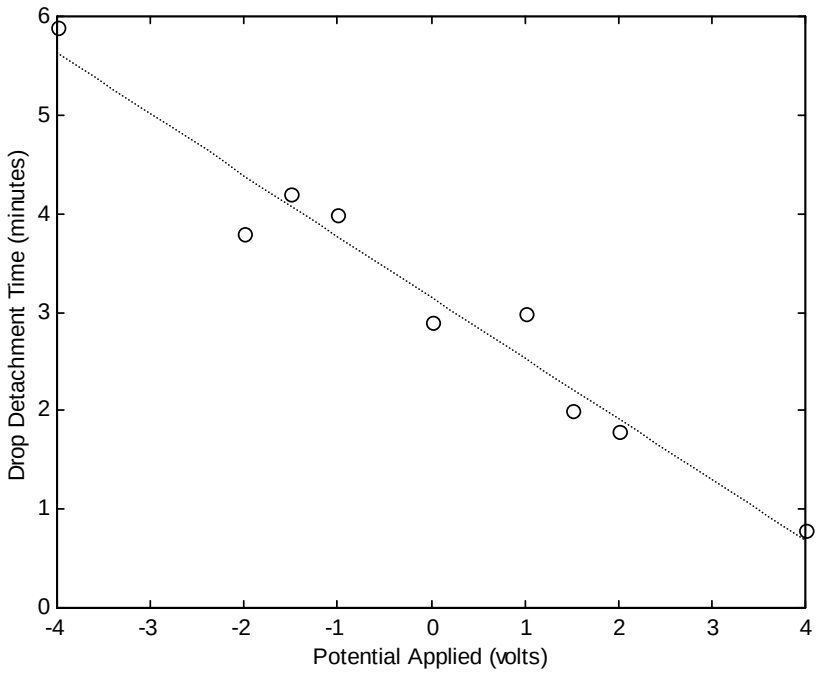

FIGURE 2-2 - Effect of Potential on Detachment in Triton X-100 Solutions

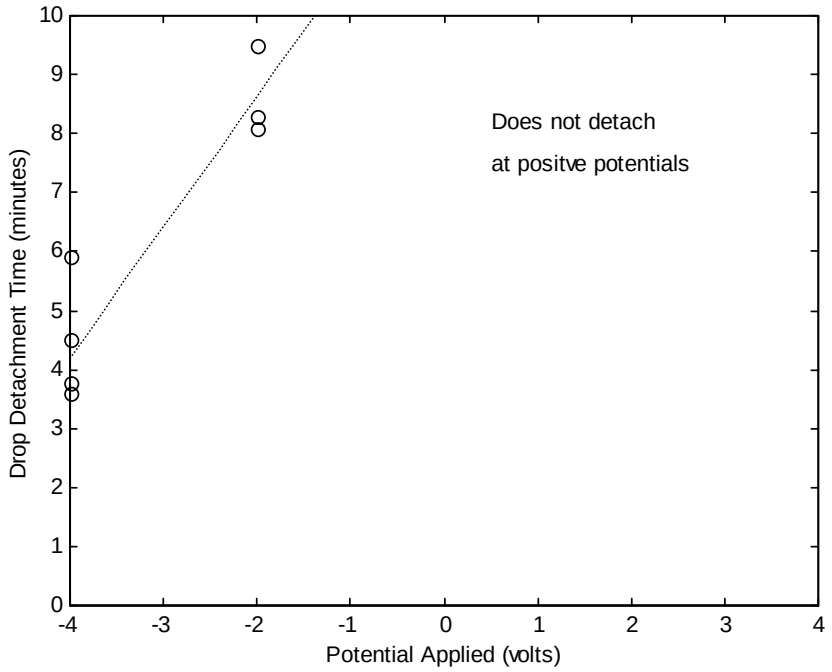

FIGURE 2-3 - Effect of Potential on Detachment in CTAB Solutions

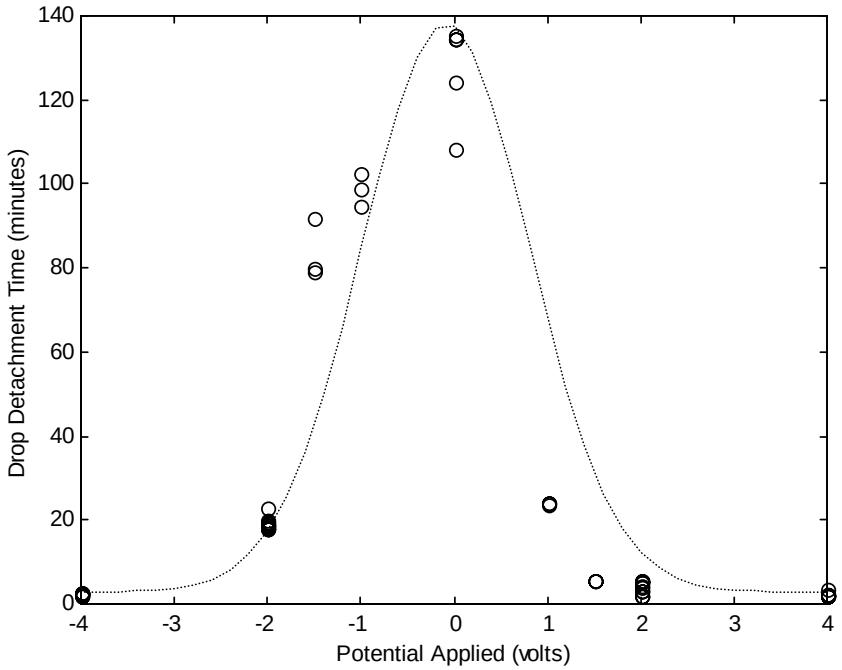

FIGURE 2-4 - Effect of Potential on Detachment in SDS Solutions

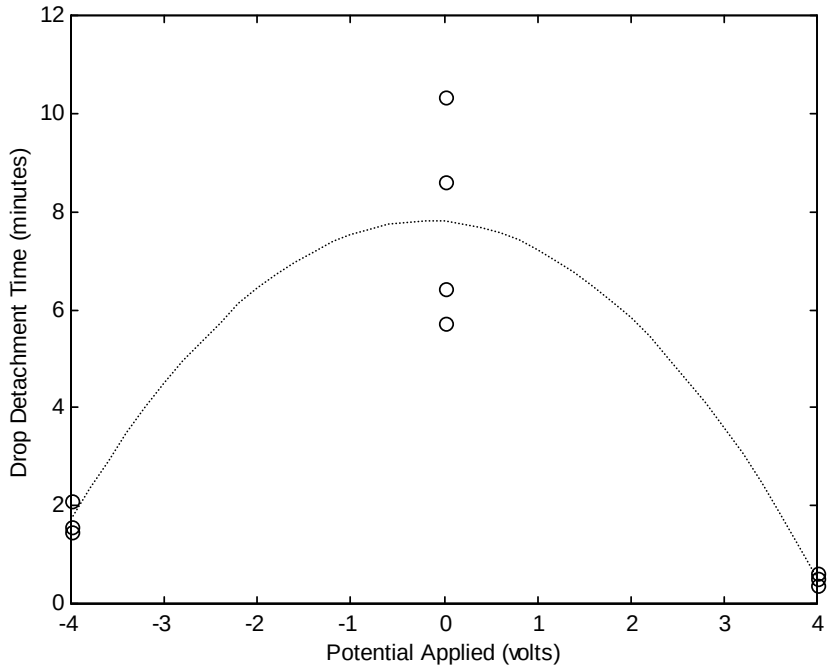

FIGURE 2-5 - Effect of Potential on Detachment in CHAPS Solutions of pH = 12.15

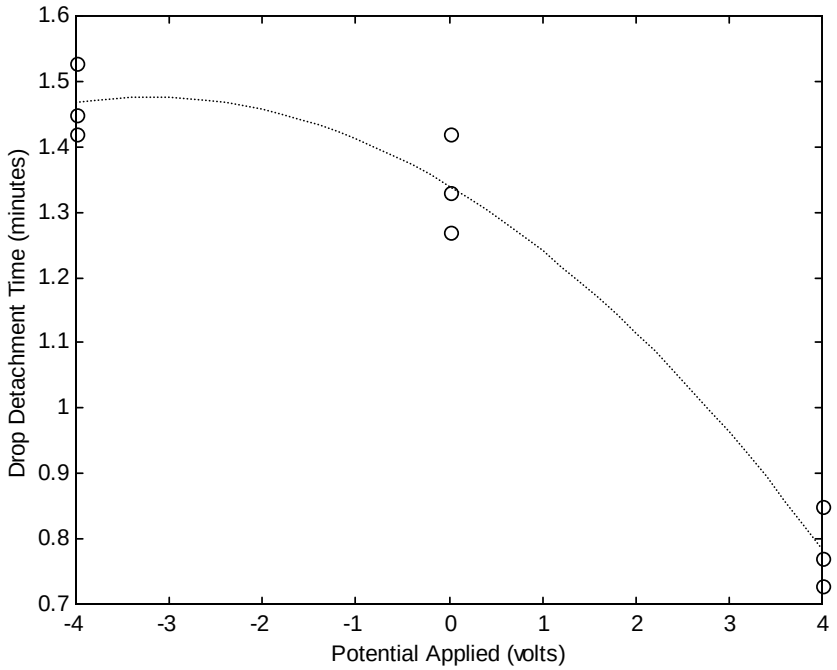

FIGURE 2-6 - Effect of Potential on Detachment in CHAPS Solutions of pH = 5.95

effects relative to the surfactant type. Oil droplets on the metal surface exhibits a monotonic decrease in detachment time as the applied potential increases from negative to positive values. It is evident that droplet detachment time is least for positive potentials. For solutions of CTAB, the cationic surfactant, only negative applied potentials exhibit an effect on droplet detachment. For these potentials the detachment times were seen to decrease. SDS, an anionic surfactant, exhibited detachment time decreases for both negative and positive applied potentials when compared to no applied potential. The results for CHAPS where taken at pH values of 2, 6, and 12. The trends observed show that CHAPS appears to act as a cationic surfactant at low pH values, a nonionic surfactant at neutral pH, and an anionic surfactant at high pH.

Cleaning effectiveness for three of the four surfactants (Triton X-100, CTAB, and SDS) as affected by applied potentials can be seen in Figure 2-7 through 2-9. As would be expected from the droplet

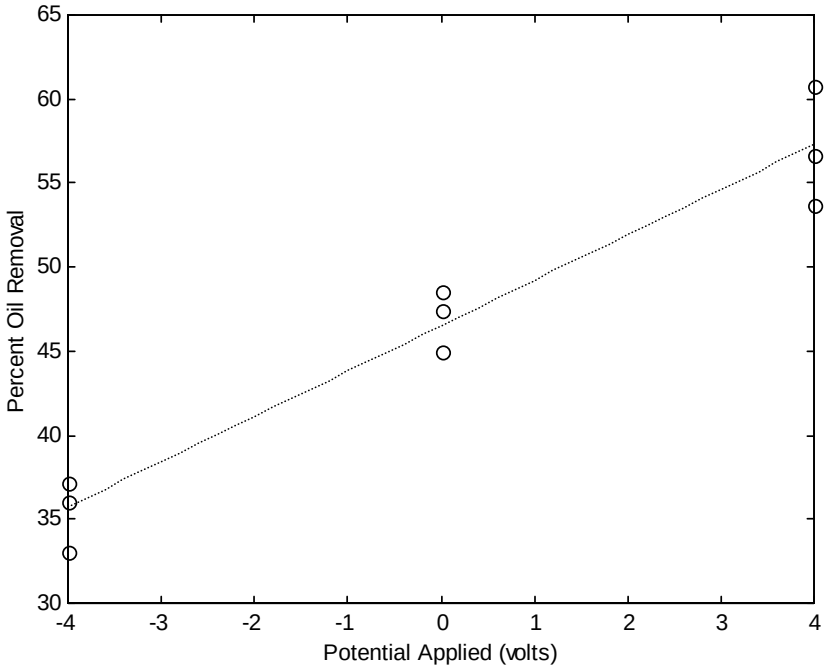

FIGURE 2-7 - Cleaning Effectiveness for Triton X-100 Solutions

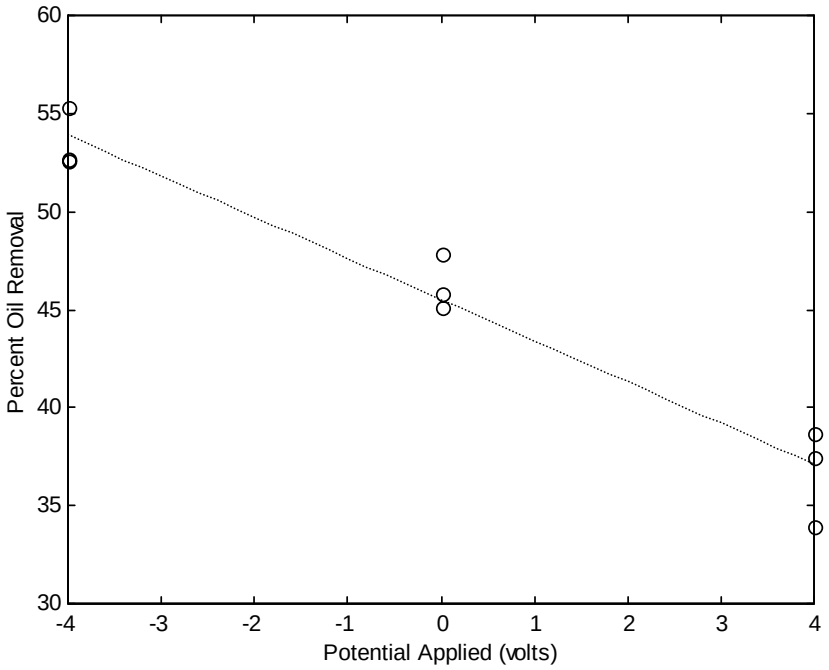

FIGURE 2-8 - Cleaning Effectiveness for CTAB Solutions

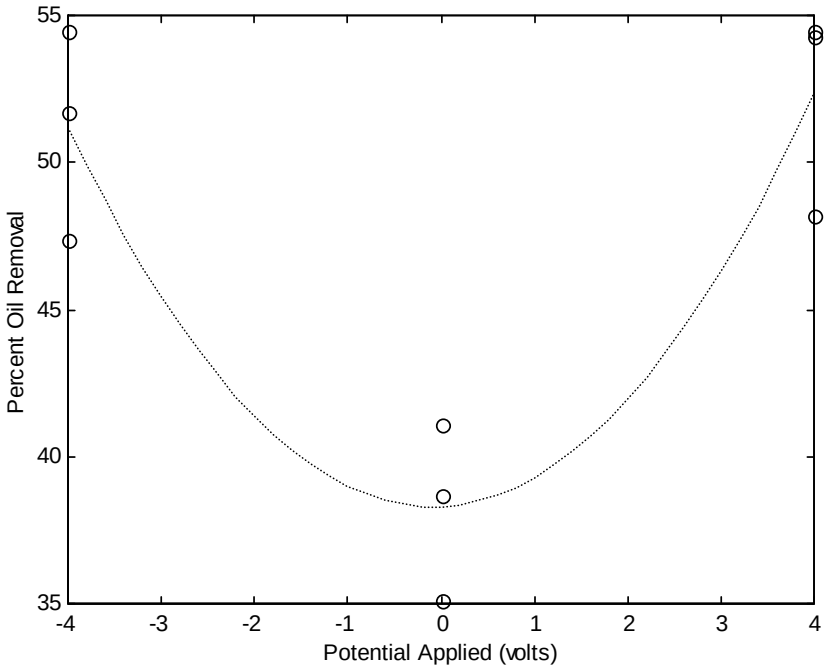

FIGURE 2-9 - Cleaning Effectiveness for SDS Solutions

detachment results the cleaning effectiveness of surfactant solutions were affected by applied potential as follows. The effectiveness of Triton X-100 solutions was increased by 10 percent for positive applied potentials. Negative applied potentials reduced the cleaning effectiveness. For solutions of CTAB the application of positive potentials improved by a maximum of 7 percent for negative potentials. Conversely application of a positive potential decreased cleaning effect. As would be expected for solutions of SDS the cleaning efficiency was seen to exhibit a maximum of 15 percent for both negative and positive potentials. As a result of these experiments it is evident that droplet detachment time can be used to qualitatively predict the performance of an ultrasonic cleaning bath.

CONCLUSIONS

The mechanistic model shown in the previous experimental study of pH must be modified to interpret the effects of applied potentials on cleaning. The previous model relies on short range electrostatic attraction/repulsion effects while the new model must account for the dramatic effect of applied potentials more dominant long range electrostatic attractive/repulsive effects. The old model states that at high pH the surface is negatively charge while at low pH the surface is positively charge. As a result the adsorption of surfactant monomers would be improved for conditions of opposite charge. Figure 2-10 details the new mechanistic model for applied

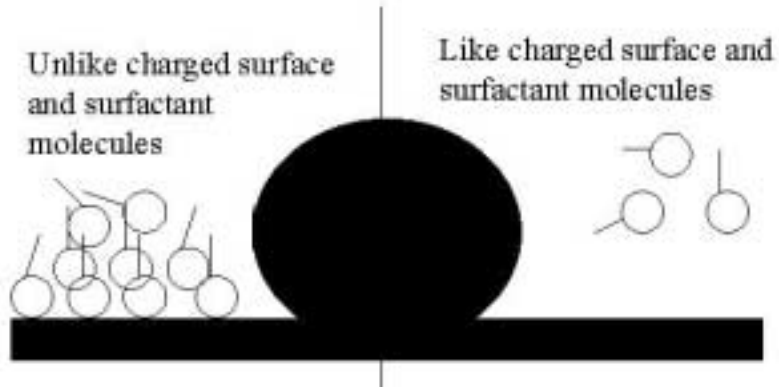

FIGURE 2-10 - Mechanistic Model for Generic Case

potentials in general, while Figure 2-11 details the specific affects on surface adsorption for the surfactants studied. When the

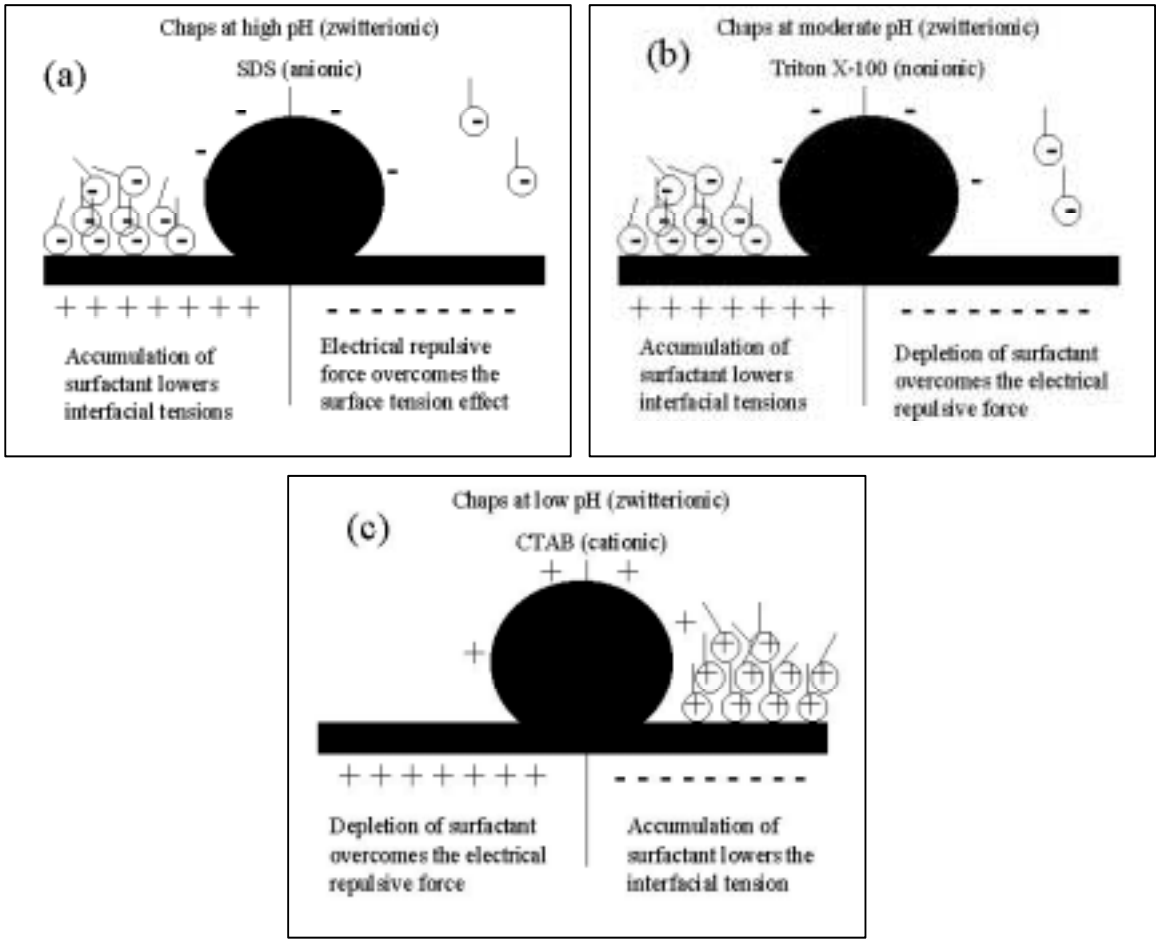

FIGURE 2-11 - Mechanistic Model for Specific Cases

surfactant head groups and the charge on the metal surface are similar adsorption will be diminished to the metal surface and in some cases the oil droplet will be repulsed. This is the foundation for the mechanistic model presented and can be utilized for various surfactants and surface potentials as detailed in the above figure. A through discussion of this model is presented in the indicated paper included in the Appendix.

Experiments involving the study of applied potentials on droplet behavior were undertaken in this phase of our experimental work. The results presented lead to the proposed mechanistic understanding of the phenomena observed. As with the pH studies the methods and techniques utilized in this experimental work could be used to improve industrial cleaning/degreasing processes.

Effects of Ionic Strength on Oil Detachment

BACKGROUND

In the previous two phases of our work we have studied phenomena that manipulate the behavior of surfactants at in various solution interfaces. In this phase of our experimental study we are investigating the effect of changing solution ionic strength on the contact angles of an organic species on a metal surface. The expectation of this work is not to prove that the effect exists. This has been proven many times over in the literature regarding micellular formation and adsorption at the air/solution interface. Our goal is to show that minimal changes in solution ionic strength, as modified by sodium chloride, can have a significant positive effect on droplet behavior and subsequently on industrial cleaning and degreasing.

EXPERIMENTAL

The experimental set-up for this phase of our work can be seen in Figure 3-1. Unlike the previous two studies it was decided to use

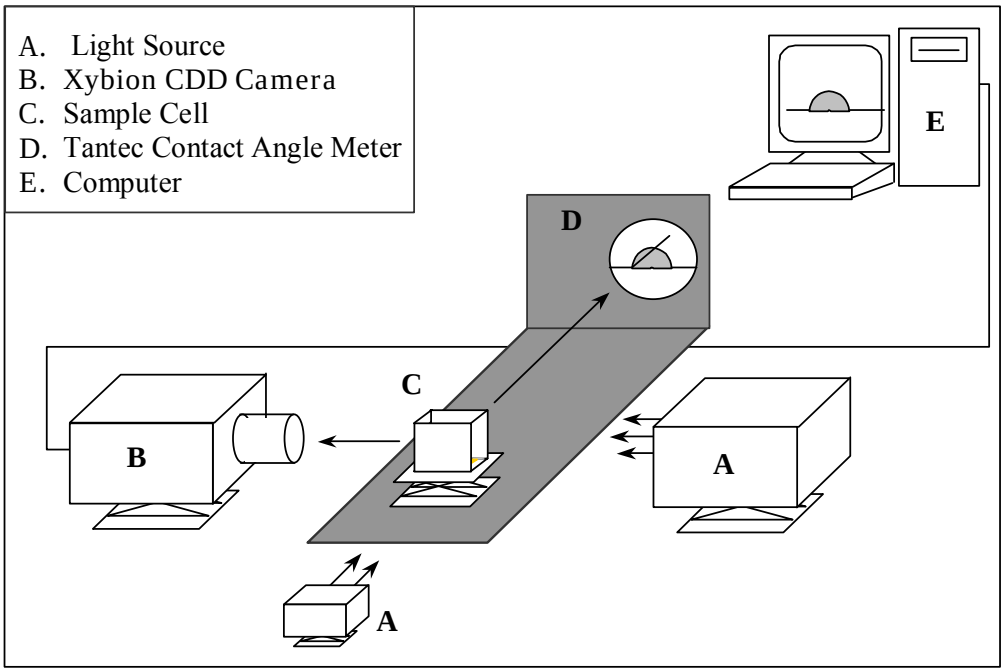

FIGURE 3-1 – Droplet Analysis Apparatus

hexadecane as the organic phase and a gold-coated microscope slide for the metal surface. This decision was done mainly due to

the large amount of literature regarding hexadecane and gold surfaces. The hexadecane is laboratory grade purchased from Fisher Scientific and the gold slides where manufactured by Asylum Research. Other deviations from the previous experimental set-up are the use of a Tantec Contact Angle Meter and that a new optical glass walled sample cell was purchased from SpectroCell Inc. to replace the square-shaped beaker. The metal surfaces used in this phase of study were repeatedly cleaned using hexane, acetone, isopropanol, and deionized water.

The experiments in this phase of study will cover the following:

- Effect of surfactant concentration on hexadecane contact angles on gold in ionic surfactant solutions.
- Effect of ionic strength on hexadecane contact angles on gold in ionic surfactant solutions.
- Correlate response of hexadecane and Mar-Temp 355 contact angles on polished steel to that observed on gold.
- Measurement of interfacial tensions at the air/solution interface and at the oil/solution interface to determine the effects of ionic strength changes on interfacial tension.
- Effect of ionic strength on cleaning effectiveness.

Currently the first two bulleted items have been competed and work is proceeding on the remaining three.

RESULTS

As indicated above work has completed on two of the five research targets for this phase of experimentation. Preliminary results can be seen in Figures 3-2 through 3-5. Since this raw data is in the early stages of analysis no conclusions have been drawn regarding a mechanistic model for the effect of ionic strength. It is however very interesting that the ionic strengths studied in the second portion of these experiments is about $1/1000^{th}$ the ionic strength of seawater. For these trials an approximate change in the contact angles for hexadecane on gold of +20 percent is observed. From earlier work we have learned that an increase in contact angle normally corresponds to an increase in cleaning effectiveness. Further experimentation and the development of a mechanistic model should illuminate and verify this correlation for ionic strength modifications.

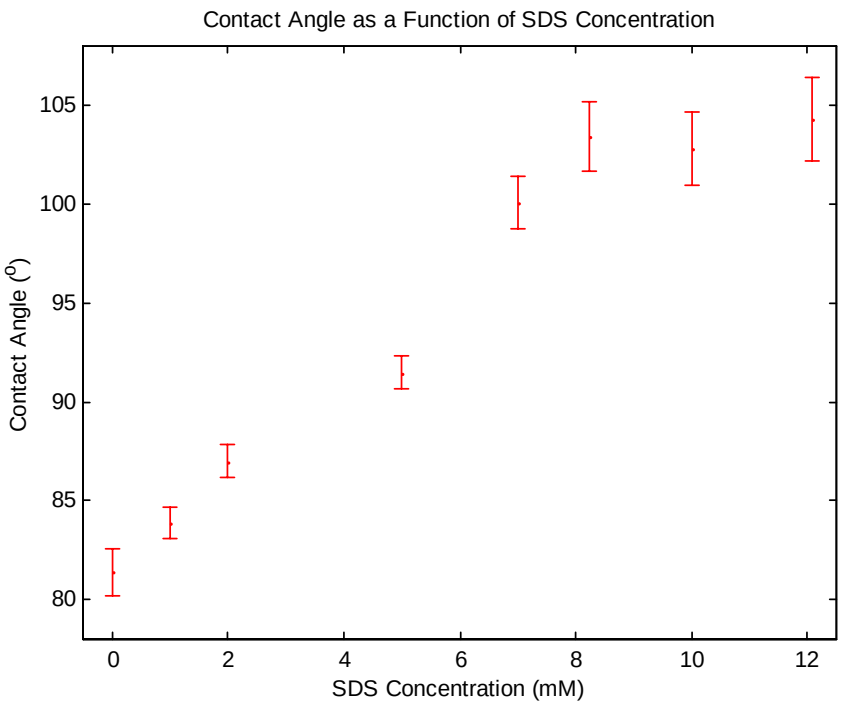

FIGURE 3-2 – Effect of Surfactant Concentration on Contact Angles in SDS Solutions

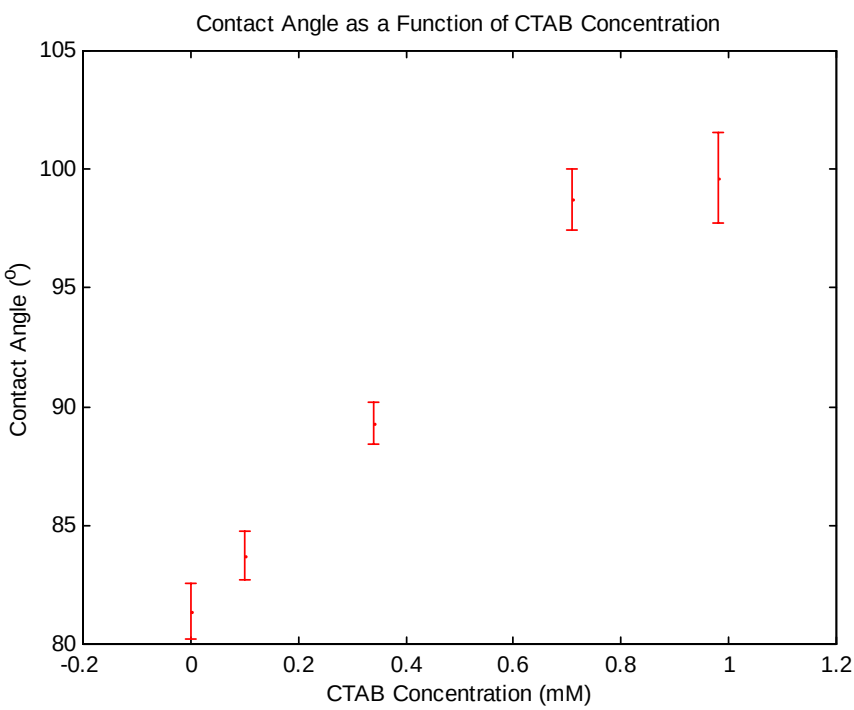

FIGURE 3-3 – Effect of Surfactant Concentration on Contact Angles in CTAB Solutions

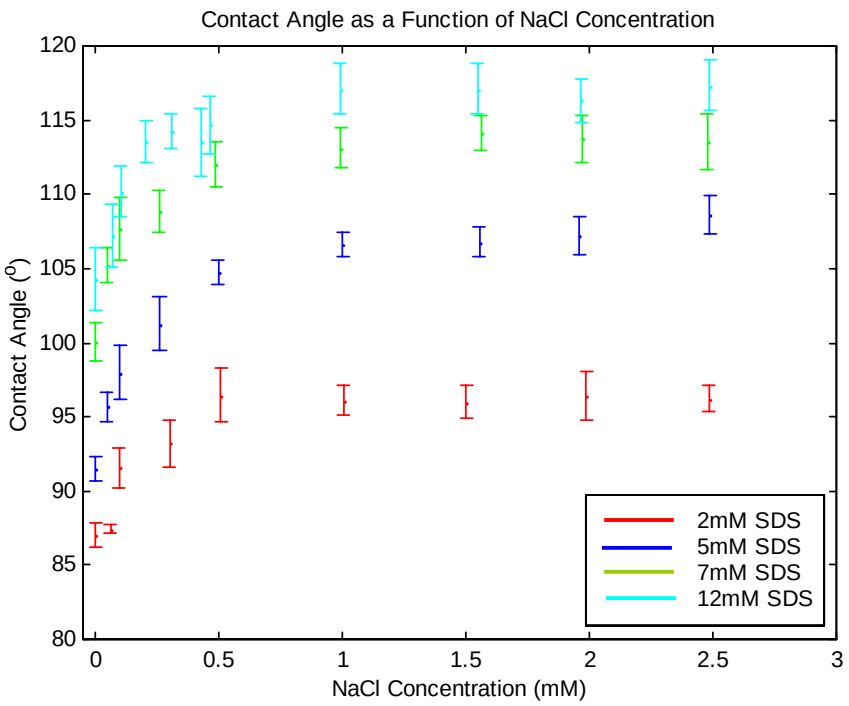

FIGURE 3-4 – Effect of Ionic Strength on Contact Angles in SDS Solutions

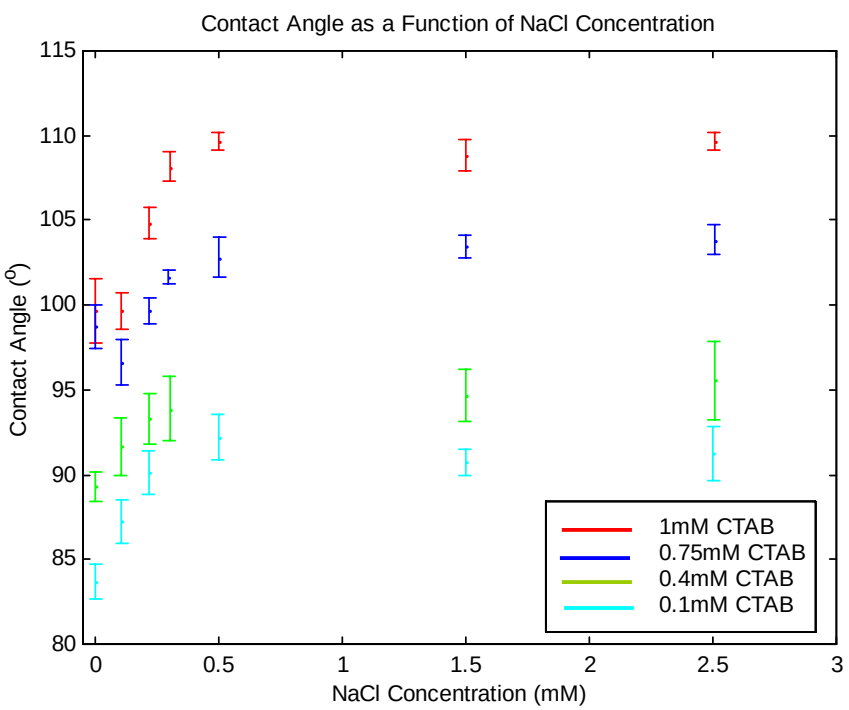

FIGURE 3-5 – Effect of Ionic Strength on Contact Angles in CTAB Solutions

CONCLUSIONS

At this point in the analysis of the data no conclusions have been drawn further than that ionic strength has an effect on the contact angles of hexadecane droplets on gold. It is expected that this will hold true for hexadecane on steel and Mar-Temp 355 on steel. When this study is completed, as in the previous cases, the methods and techniques could be used to improve industrial cleaning/degreasing processes.

Thermodynamic Modeling of Oil Detachment

BACKGROUND

A parallel investigation into the development of a classical thermodynamic model for predicting cleaning performance has been underway during the completion of the physical experimentation presented previously. Such a model is being developed to predict the effect on droplet contact angle and potential detachment due to the modification of cleaning system physical parameters. The model is comprised of a system of mass transfer actions that describe the movement of water, oil, and surfactant in the observed system. Figure 4-1 illustrates the

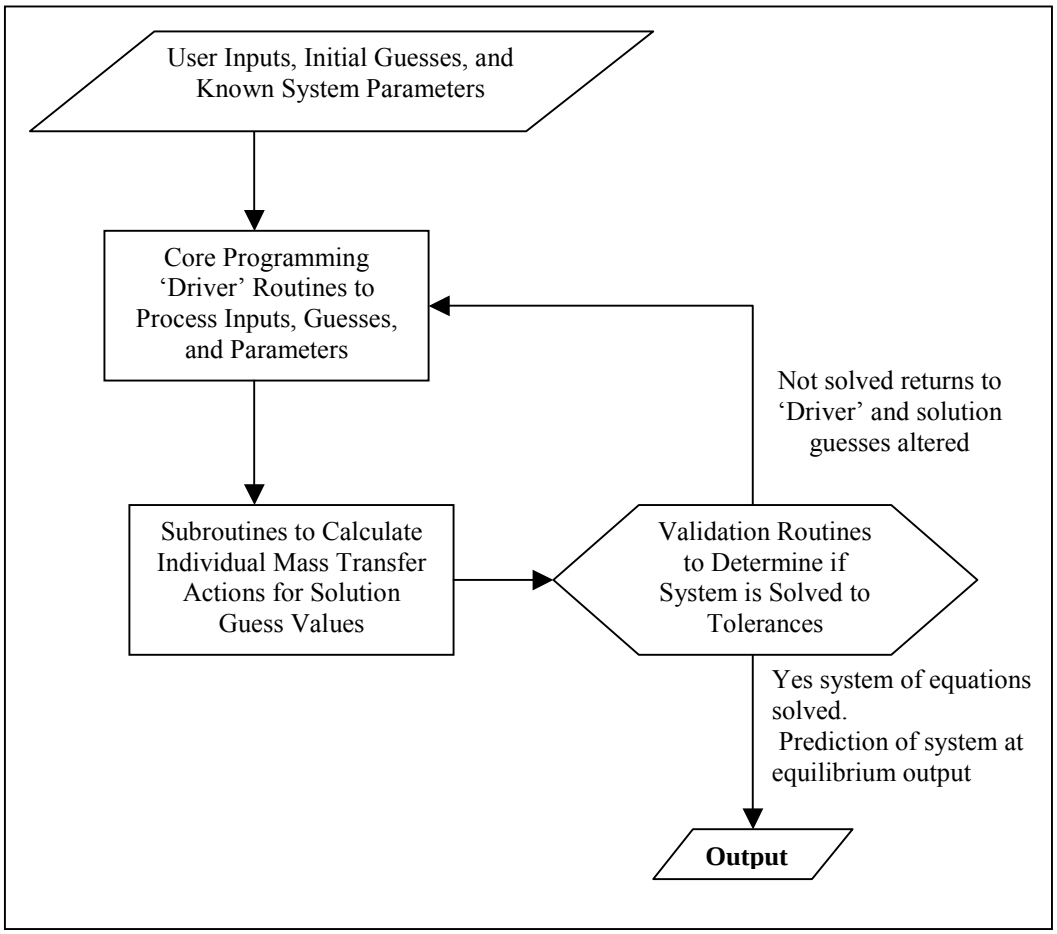

FIGURE 4-1 – Computational Approach to Modeling of Organic Contact Angles on Solid Surfaces

approach to modeling such activities using classical thermodynamics and basic numerical methods. The five mass transfer actions are as follows:

- Surfactant *(solution)* ↔ Surfactant *(micelle)*
- Surfactant *(solution)* ↔ Surfactant *(solid/solution absorbed)*
- Surfactant *(solution)* ↔ Surfactant *(oil/solution absorbed)*
- Oil *(liquid)* ↔ Oil *(solid/oil absorbed)*
- Water *(solution)* ↔ Water *(solid/solution absorbed)*

where the term in parenthesis indicates the location of the respective component. These five mass transfer actions describe the movement of water to and from the solid/solution interface, the movement of organic to and from the oil/solid interface, the formation of surfactant micelles in solution, the aggregation of surfactant monomers at the solid/solution interface, and the adsorption of surfactant at the oil/solution interface. Other mass transfer actions could be postulated but these five were selected for the initial modeling effort. The model takes the approach that equilibrium constants for each action can be determined by solving for the state of minimum Gibbs free energy for a given set of cleaning system parameters. These parameters include but are not limited to surfactant type, oil type, solid type, temperature, ionic strength, solution pH, and solution surfactant concentration. The computational model is designed such that each mass transfer action is a separate subroutine and can be removed and replaced should a better approach be determined. This allows the model to adjust dynamically to changes in current theory and provides for flexibility in correlation to experimental results. A through and detailed discussion of the modeling work can be seen in the paper titled “Thermodynamic Model for the Prediction of Contact Angles of Oil Droplets on Solid Surfaces in SDS Solutions” which is included in the Appendix.

EXPERIMENTAL

The experimental procedures are identical to those presented in the work on ionic strength effects. All data and results produced

during the ionic strength work will be utilized for comparison and improvement of the modeling work.

RESULTS & CONCLUSIONS

Preliminary results presented in the aforementioned article can be seen in Figure 4-2. From this plot is can be seen that the modeling

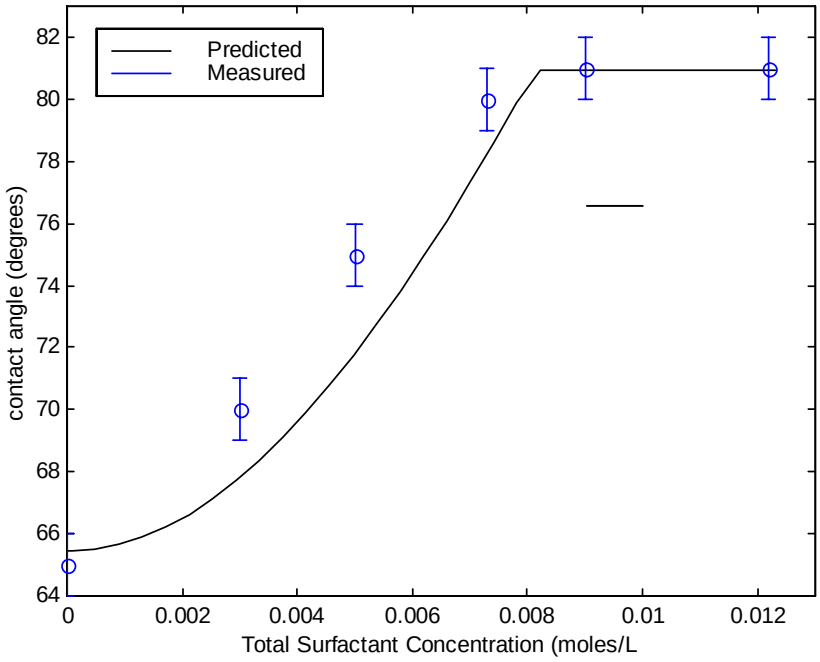

FIGURE 4-2 – Comparison of Experimental to Predicted Hexadecane on Gold Contact Angles

approach provides an excellent qualitative trend prediction and provides an average error not greater that 1.5 percent. As with the investigations into ionic strength this work is an on going process and subsequent improvements are being prepared for a second publication to be submitted in the near future.