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DISPLACEMENT OF A HYDROCARBON OIL FROM A METAL SURFACE USING A SURFACTANT SOLUTION

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ABSTRACT

Separation of oils from solid surfaces is important in cleaning and degreasing operations. Water and oils are immiscible requiring the use of an additive which is miscible with water yet has an affinity for oils. Surface active agents, known as surfactants, have this property, being miscible with water while having an affinity for hydrocarbons. In some cases, surfactant solutions displace oils from a solid surface (i.e., remove oil by replacing the oil/solid interfacial area with surfactant solution/solid interfacial area). The presence of alkalinity as well as surfactant concentration is known to affect the ability of a surfactant solution to wet the solid surface and displace the oil. Experiments have been performed to determine quantitatively the effects of surfactant concentration and pH on the displacement of an oil from a metal surface. The displacement is measured in terms of the contact angle formed by the oil on the solid

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surface in the presence of the surfactant solution, the amount of time needed for the surfactant solution to cause part of the oil to detach from the solid surface, and the volume of the detached oil. Measuring the contact angle of the oil as a function of time shows that surfactant concentration and pH affect the displacement of oil from a metal surface. Increasing the pH of a solution of Triton X-100, a non-ionic surfactant, enhances oil displacement. Increasing the surfactant concentration also enhances oil displacement. The volume of oil which detaches from the solid surface increases with increasing pH and increasing surfactant concentration.

INTRODUCTION

The displacement of oil from a metal surface with surfactant solutions is important in cleaning and degreasing operations. The Clean Air Act Amendments of 1995 ended the production of chlorofluorocarbons in the United States, thereby ending their use as cleaning agents as supplies are depleted. Chlorofluorocarbons are known to be ozone-depleting compounds (ODCs). Therefore, alternatives are needed to replace ODCs. Water-based cleaning agents have come to the forefront as viable alternatives to ODCs, as they have been shown to compete with ODCs in their ability to remove oils from metal surfaces (1-7).

Aqueous cleaning often involves three different types of energy: thermal, mechanical, and chemical. In the cleaning literature, more attention is usually given to the former two types rather than to chemical energy (8-10). Optimizing concentrations of chemical components in aqueous cleaners is needed to minimize the amount of mechanical and thermal energy required for cleaning purposes. A reduction in energy use translates into lower cleaning costs (11). Also, it is common for components of aqueous cleaners to be listed in general terms such as surfactants, pH builders, water softeners, etc. (12,13). Rarely are specific chemical components identified and discussed. For example, Seelig (11) states that pH and surfactant concentration influence cleaning, yet reports little information concerning the effect of these variables on a cleaning system. The technical literature contains a great deal of information concerning fundamental properties such as interfacial tension, contact angles, and adsorption, which are significant in determining how liquids wet solid surfaces. However, since the cleaning literature contains primarily general information about the types of chemical components used in aqueous cleaners, it is necessary to bridge the gap

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between the cleaning literature and the technical literature to render the information concerning fundamental parameters to the cleaning community.

The purpose of this work is to apply information from the technical literature to a cleaning system. Surfactant concentration and pH, which the cleaning literature states are important to cleaning (11), will be varied, while the fundamental variables that the technical literature states are important to wetting will be monitored. The surfactant, pH modifier, solid surface, and oil have been chosen upon communication with industry experts and are described later. The experimental procedure will be shown to have the potential to help optimize concentrations of chemical components in aqueous cleaners. The method described below will show that both the surfactant concentration and the pH of the cleaning solution are important variables to consider when building a surfactant cleaning solution just as the cleaning literature states. In addition, the data will show that individual cleaning solutions can be compared with one another with this experimental procedure. This last point is important, as most cleaners are compared by cleaning parts (1-7). That type of testing can be expensive because many metal parts are large, requiring large amounts of cleaning solution which must then be disposed of. The proposed method produces little waste compared with other procedures used presently.

As mentioned above, the technical literature contains information which can help provide an understanding of how fundamental variables provide insight into a cleaning solution's ability to displace an oil from a metal surface. The particular system of interest here is a sessile drop of oil on a stainless steel surface. Miller and Raney (14) discuss two mechanisms of detergency relating to the displacement of oil from a metal surface. The emulsification mechanism removes only part of the oil from a solid surface at one time, whereas the roll-up mechanism removes all of the oil at one time. The emulsification mechanism relates to the work presented here. Basu *et al.* (15) showed that the interfacial tension between an oil and an aqueous solution decreases as the pH of the aqueous solution increases. They also showed that the equilibrium contact angle of bitumen on a glass surface increases as the pH increases. Carroll (16) concluded that, given a constant contact angle, the ease with which an oil can be removed from a solid surface increases as the interfacial tension between the oil and the aqueous solution decreases. Martin-Rodriguez *et al.* (17) found that the pH of a solution of Triton X-100,

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a nonionic surfactant used in this study, affects the adsorption of the surfactant onto different latex surfaces. Liggieri *et al.* (18) showed that as the concentration of Triton X-100 increases, the interfacial tension of the aqueous solution with hexane, an organic liquid, decreases. Thus the literature provides insight into how surfactants, pH modifiers, and surfaces interact. However, more work needs to be completed in this area. Very few data are available measuring the changes in the contact angle of an oil on and the detachment of oil from a metal surface. Therefore, the work will incorporate the study of a metal surface, stainless steel.

The change in the contact angle of the oil on the metal surface is measured as a function of time. Measurement ceases when part of the oil detaches from the metal surface. Figure 1 indicates that the physical mechanism used by the Triton X-100 solution to cause the oil to detach from the metal surface is the emulsification mechanism discussed by Miller and Raney (14). This mechanism causes only part of the oil to detach from the surface at one time, as shown in Figure 1. Thus, the mechanism must repeat itself in order to remove the remainder of the oil from the metal surface. The change in the contact angle corresponds to the displacement of the oil from the metal surface as the surfactant emulsifies the oil. Then contact-angle results presented below are discussed in terms of oil displacement.

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EXPERIMENTAL METHODS

All experiments described below were conducted at room temperature of 22 ± 1°C and at atmospheric pressure. The experiments were performed on a vibration isolation table from Newport.

Contact-Angle Measurements

Experiments were conducted using Triton X-100, sodium hydroxide (NaOH), a stainless steel surface, and Mar-Temp 355 quench oil. The quench oil was supplied by the E. F. Houghton Company, while the NaOH and Triton X-100 were supplied by the Fisher Chemical Company. The roughness of the stainless steel surface was measured

Figure 1. Displacement of oil by Triton X-100 via the emulsification mechanism.

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using profilometry (Dektak 8000) and was determined to be 1975 Å. The roughness of the surface is known to affect the determination of contact angles in the form of hysteresis (19, 20). Therefore, in reporting the results, we used a contact angle normalized with respect to the initial one to stress the change in the angle. A typical initial contact angle in this study was found to be approximately 5°.

Figure 2 is a diagram of the experimental apparatus. The stainless steel surface was washed repeatedly with 95% ethanol and distilled water between experiments to ensure consistent spreading of the oil prior to submersion in the surfactant solution. Schrader (21) showed that the cleanliness of the surface was important to ensure consistent wetting properties. The surface was then allowed to sit in air for 2 minutes. A 2-μL drop of the oil was then placed onto the metal surface and allowed to spread for 5 minutes. After the 5-minute time period, the metal surface was submerged into the surfactant solution and monitored with a Kodak EktaPro High Grain Imager. Experiments were videotaped with an Omnivision S-VHS Video Cassette Recorder Model PV-54990 manufactured by Panasonic. Pictures were printed for analysis using a Mitsubishi Video Copy Processor Model P63NM. The monitor was a Sony Trinitron Color Imager Monitor Model PVM-1341.

The oil receded symmetrically along the metal surface, as can be seen in Figure 1. Therefore, each photograph shows two nearly identical contact angles, one on the left side of the drop and one on the right side of the drop. Both angles were measured and

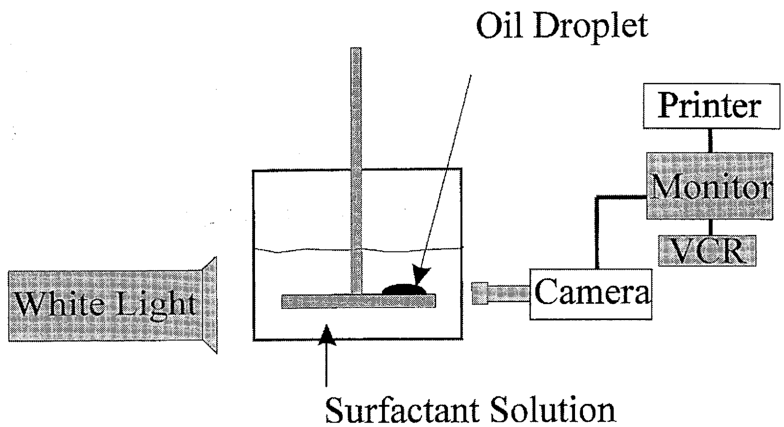

Figure 2. Apparatus used for measuring the changes in the contact angle.

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averaged to yield a contact measurement. Figure 3 shows how the angles were drawn tangent to the oil/surfactant solution interface at the surface of the solid.

An error analysis of this method was performed by measuring the contact angle of a solid spherical object on a solid surface and comparing the measurement to the known contact angle of 180°. The error was determined to be ±3.5%. Uncertainty in the determination of the contact angle results also from the scale of magnification (22). As the region near the contact line is highly curved, the uncertainty due to the magnification increases. Therefore, the same scale of magnification was used for each experiment to eliminate some of the bias associated with the location of the tangent line as depicted in Figure 3. This uncertainty is less important in this study since the focus is the change in the contact angle under different conditions and not the angle itself.

Interfacial Tension Measurements

The interfacial tension of solutions of Triton X-100 with the oil were measured as a function of both pH and surfactant concentration. The procedure used was the

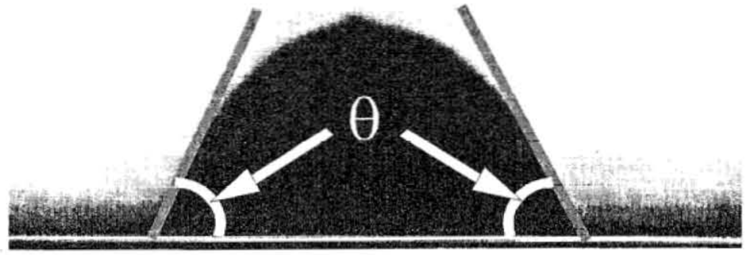

Figure 3. Illustration of a contact-angle measurement.

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pendant drop method and is described in detail by Adamson (23). Therefore, no detailed discussion of the method will be presented here. The equipment used is the same as that mentioned in the previous section except for using a U-shaped tube on which a pendant oil drop was formed. The tube is made of stainless steel and has a flat, smooth surface for the oil to wet completely and form an interface with the surfactant solution. The dimensions which are measured using this procedure are described by Adamson (23) and were measured directly with the Kodak imager mentioned above.

Volume of the Detached Droplet

A second measure of the ability of a surfactant solution to displace oil from a solid surface is the volume of the first droplet oil which detaches from the solid surface as a result of the emulsification mechanism mentioned earlier. The volume is measured in terms of a ratio. The ratio is the diameter of the detaching droplet divided by the diameter of the oil at the oil/metal interface. Both diameters are measured at the point the oil is about to detach from the surface, as is illustrated in Figure 4. The equipment used is exactly the same as that used for measuring the changes in the contact angle as a function of time. The typical diameters of the detaching droplet and the oil at the oil/metal surface measure more than 50 pixels with the magnification of the image system. The uncertainty in determining the drop edge is within ±1 pixel, which may result in an error up to 2%.

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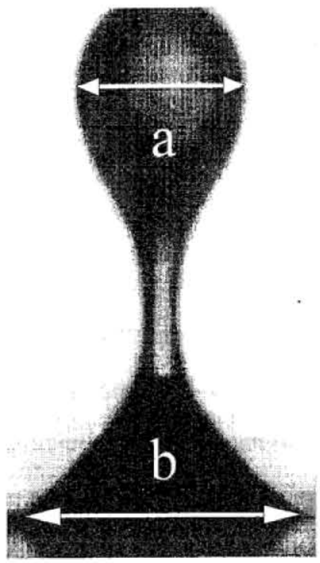

Figure 4. Illustration of *a/b* for comparing the volumes of the detached droplets.

RESULTS AND DISCUSSION

Interfacial Tension

The interfacial tension between the oil and solutions of Triton X-100 was measured as a function of both concentration and pH. Figure 5 is a plot of the interfacial tension, γ, as a function of the concentration of Triton X-100. Figure 6 is a plot of the interfacial tension, γ, as a function of pH at two different concentrations of Triton X-100. Figure 5 shows that the interfacial tension of the oil/Triton X-100 solution interface decreases as the concentration of Triton X-100 increases. This is in agreement with the trend observed by Liggieri *et al.* (18) for a Triton X-100 solution/hexane interface. The interfacial tension of a surfactant solution will decrease until the critical micelle concentration (CMC) is reached. Martin-Rodríguez *et al.* (17) report the CMC point for Triton X-100 is $9.2 \pm 0.3 \times 10^{-4}$ *M*, which is near 0.05% by volume. Figure 5 shows that at Triton X-100 concentrations above the CMC point, the interfacial tension does not

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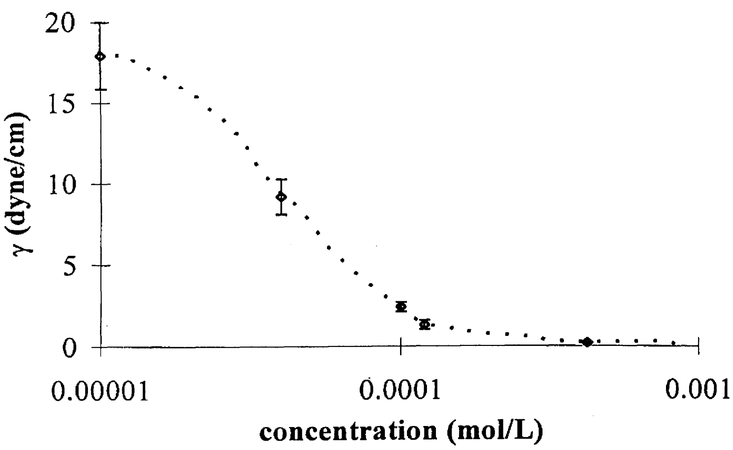

Figure 5. Oil/surfactant solution interfacial tension as a function of Triton X-100 concentration.

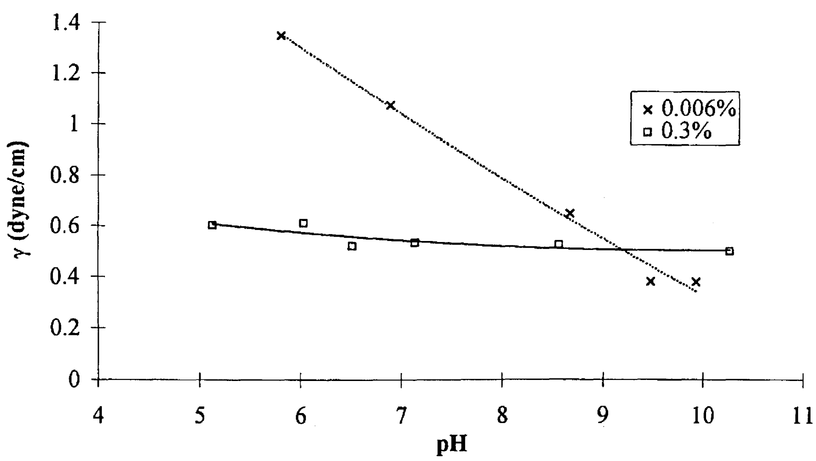

Figure 6. Oil/surfactant solution interfacial tension as a function of pH.

significantly decrease. Figure 6 shows that the interfacial tension decreases as the pH of the Triton X-100 solution increases. However, the higher concentration of Triton X-100, which is 0.3% by volume, does not exhibit much of a decrease due to increasing the pH. This concentration is significantly above the CMC point which, as previously mentioned, is near 0.05%. Therefore, at concentrations above the CMC point, neither increasing the concentration nor increasing the pH of a Triton X-100 solution will significantly decrease the interfacial tension. The trend shown in Figure 6 is in agreement with that observed by Basu *et al.* (15) for an interface of bitumen and water at different pH values.

Since increasing the pH and increasing the surfactant concentration both result in lowering γ between the oil and the surfactant solution, the data presented below show that the contact angle and volume of the detached oil drop change as a function of pH and surfactant concentration. This finding demonstrates quantitatively Carroll's (16) conclusion that the removal of oil from a metal surface should be easier with solutions exhibiting a lower interfacial tension (i.e., containing a high concentration of Triton X-100 and/or a high pH). Moreover, as a result of surfactant transport, the surface tension of a Triton X-100 solution changes with time during droplet deformation as shown by Zhang *et al.* (24). This dynamic surface tension of a Triton X-100 solution plays a certain role in the displacement of an oil drop in terms of evolution of the contact angle.

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Changes in the Contact Angle

Figure 7 is a plot showing the typical change in the contact angle as a function of time with a Triton X-100 concentration of 0.006% by volume and a pH of 9.46. Combined with pictures, Figure 7 shows how the shape of the drop changes with time. The trend is that the contact angle continues to increase until attaining a maximum and the buoyancy force causes part of the oil to detach from the solid surface. During the drop detachment the remaining oil relaxes back onto the metal surface. Thus, the contact angle decreases. The trend shown in Figure 7 is the same regardless of pH and Triton X-100 concentration. What differs are the amount of change in the contact angle, the time until detachment, and the volume of the detaching droplet.

The changes in the contact angle of the oil on the metal surface were measured as functions of both pH and surfactant concentration. Figure 8 shows the effect of pH on

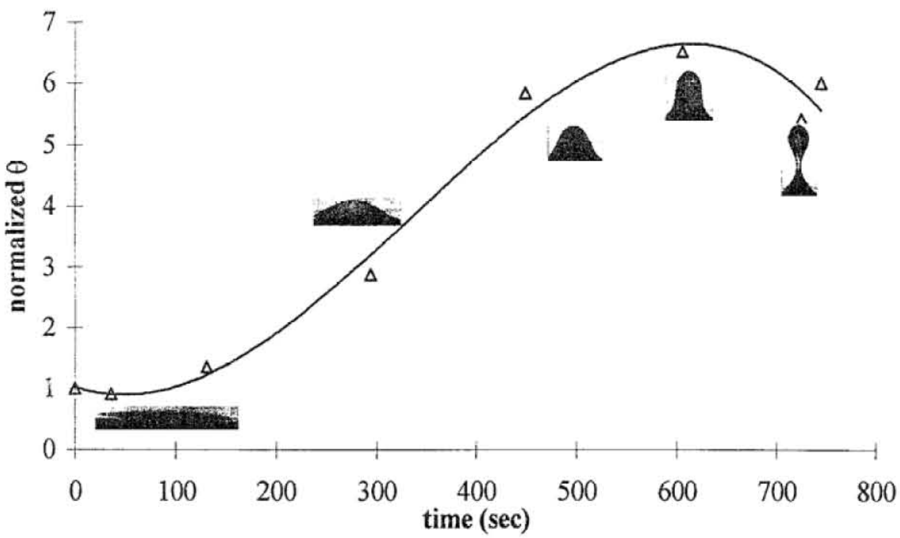

Figure 7. Change in the contact angle using 0.006% Triton X-100 and pH 9.46 as a function of time.

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the evolution of the contact angle. The Triton X-100 concentration is fixed to be 0.3% by volume. Figure 8 indicates that the time required for the surfactant solution to cause part of the oil to detach from the surface decreases as the pH of the surfactant solution increases. Also, the change in the contact angle increases as the pH of the surfactant solution increases. Figure 9 shows the effect of surfactant concentration on the change in the contact angle of the oil on the metal surface while maintaining a constant pH. The time required for the surfactant solution to cause part of the oil to detach from the surface decreases as the concentration of Triton X-100 increases. Thus, Figures 8 and 9 indicate that increasing the surfactant concentration and pH of the cleaning solution enhances the displacement of oil from the metal surface. The data shown in Figures 8 and 9 are therefore in agreement with Carroll (16), as increasing the pH and the surfactant concentration eases the removal of oil from the metal surface.

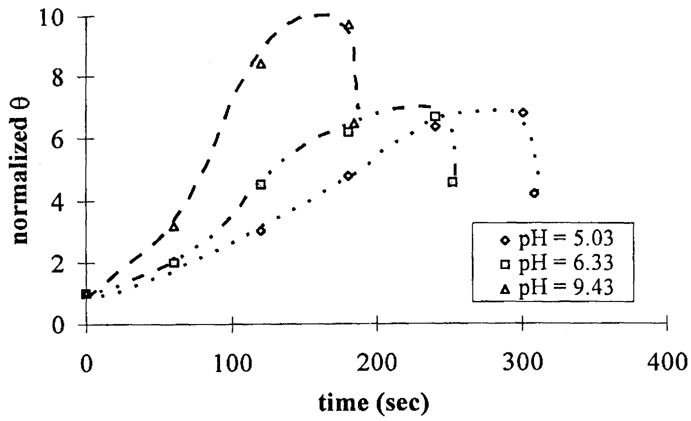

Figure 8. Effect of pH on the contact angle using 0.3% Triton X-100.

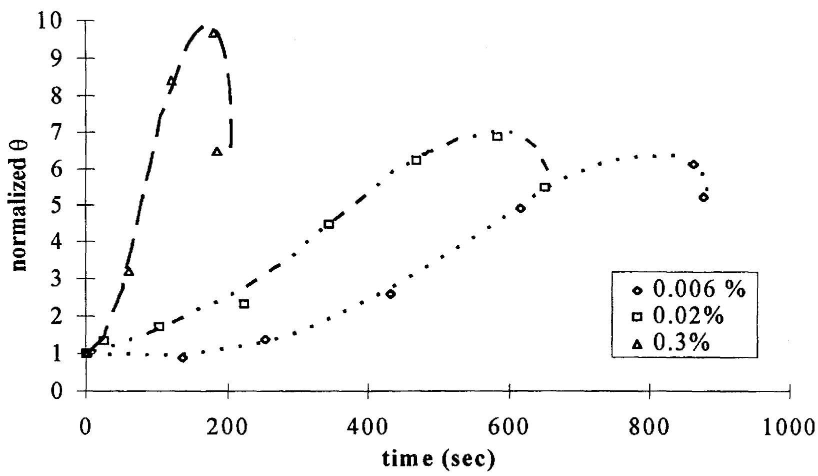

Figure 9. Effect of Triton X-100 concentration on the change in the contact angle at pH 10.0.

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Volume of the Detached Droplet

The volume of the detached droplet was measured as both functions of pH and concentration of Triton X-100. The variable used to measure the volume of the detaching droplet is the ratio a/b which was defined in Figure 4. The variable a represents the diameter of the detaching droplet, and the variable b represents the diameter of the oil/metal interface. Increasing the pH and surfactant concentration was found to cause a to increase and b to decrease. Therefore, the ratio a/b increases and thus the volume of the detached oil is observed to increase as the pH and surfactant concentration are increased. Figure 10 indicates that both pH and surfactant concentration affect the volume of oil which detaches from the surface. Figure 10 shows that the volume of the detached oil droplet increases as both the surfactant concentration and pH increase, a result of the increasing effect of the buoyancy force relative to the surface tension force. However, changing either of these two variables has a more noticeable effect at lower surfactant concentrations and pH values than at higher surfactant concentrations and pH values. This can be explained by earlier statements regarding the interfacial tension not changing as much when increasing the pH and surfactant concentration of a solution whose pH and surfactant concentration are already relatively high. The results in Figure 10 can be explained by the better wetting properties of a Triton X-100 solution with a lower surface tension. The surfactant solution with a lower surface tension wets the solid surface better than a solution with a higher surface tension. Thus, the contact angle of the oil on the surface increases and more of the oil is displaced. Therefore b decreases as less oil is in contact with the metal surface. More oil is therefore in contact with the surfactant solution. The buoyancy force therefore increases relative to the interfacial tension force and, as a result, more oil detaches from the metal surface.

CONCLUSIONS

The method described above has been shown to illustrate how surfaces, surfactants, and oils interact with one another. The pH and the concentration of the surfactant can both be studied to determine their effect upon the removal of an oil from a

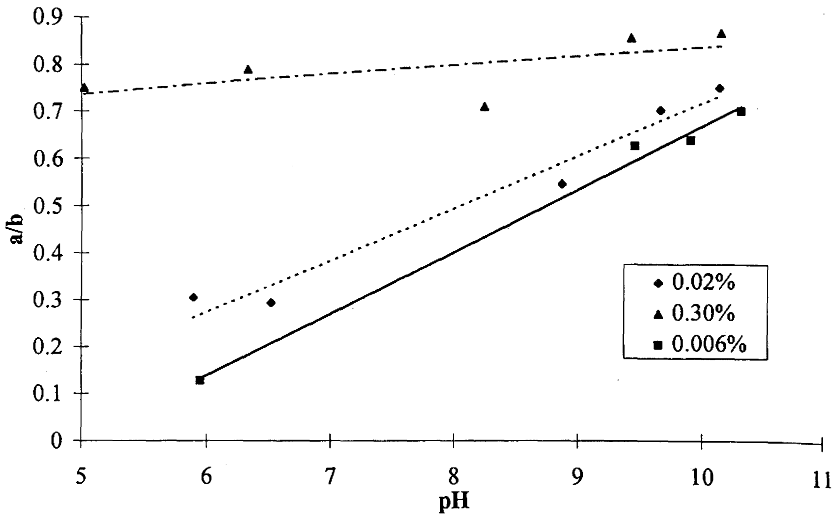

Figure 10. Effect of pH and surfactant concentration on the volume of oil which detached from the surface.

metal surface. Thus, these variables, when used in conjunction with one another, can provide insight into how effectively a particular cleaning solution will perform relative to other cleaning solutions.

The interfacial tension between the oil and the surfactant solution, the time required for part of the oil to detach, the volume of the detached droplet, and the change in the contact angle have all been measured and shown to affect the displacement of the oil from a stainless steel surface. The main conclusions are as follows:

- Increasing the pH and concentration of Triton X-100 enhances the change in the contact angle of the oil on the metal surface.
- Increasing the pH and concentration of Triton X-100 increases the volume of the oil droplet which detaches from the metal surface.

Presently, studies are under way to apply the results of this work to actual cleaning processes and to determine whether the method presented in this paper

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accurately predicts the results of actual cleaning experiments under the same conditions. Also, more comprehensive experimental and theoretical studies are in progress incorporating additional variables.

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