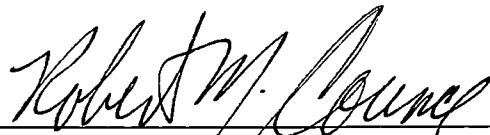


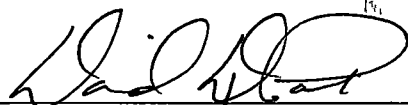
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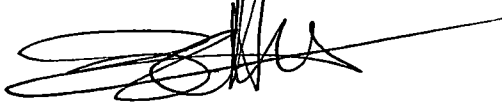


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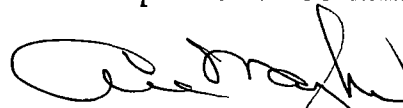


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Interim Vice Provost and
Dean of The Graduate School

The Effect of pH and Applied Electrical Potential on Oil Removal from a Solid Surface
in the Presence of Four Types of Surfactant Solutions

A Thesis

Presented for the

Master of Science

Degree

The University of Tennessee, Knoxville

Anthony Wayne Rowe

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ABSTRACT

Effective aqueous-based cleaning depends on the appropriate selection of surfactant(s), and pH conditions. Experiments involving the detachment of oil droplets from a metal surface in the presence of surfactant solutions are undertaken to observe the variation of droplet shape, particularly contact angle, and the time required for droplet removal. In parallel, tests of oil removal from the same metal surface in an industrial ultrasonic bath have been conducted under similar conditions. Similar trends are found for both types of tests, that is, conditions for which droplets detach more quickly also correspond to conditions of greater oil removal in an ultrasonic bath. Experiments of drop removal time and cleaning effectiveness in surfactant solutions of altered pH are conducted to better understand the role surfactants adsorbed at the surface play in the detachment process. Negatively charged oil/aqueous interfaces exhibit more efficient cleaning as well as drop removal kinetics at high surfactant solution pH, while positively charged oil/water interfaces exhibit faster detachment at low pH. Experiments are conducted, in parallel, in which the surface to be cleaned is connected directly to a low voltage power supply. A similar cleaning procedure is performed in which the dependent variable is applied electrical potential. Applied electrical potential ranges from 0 to ± 4 volts (current is limited to near zero) with respect to the surfactant solution. Trends indicate that surfactant solutions containing nonionic (Triton X-100) surfactants exhibit better cleaning and faster oil drop detachment as the applied electrical potential increases

in the positive direction. Cationic (CTAB) surfactant solutions perform better cleaning as voltage increases in the negative direction. Anionic (SDS) surfactant solutions perform better as voltage increases regardless of the polarity. Tests involving a zwitterionic (Chaps) surfactant support the three previous case trends. The pH and applied electrical potential is interpreted by a mechanistic model focusing on the adsorption of surfactant ions at the aqueous/solid interface and the electrostatic repulsion/attraction to the oil drop.

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NOMENCLATURE AND GLOSSARY OF TERMS

Symbol or Abbreviation	Meaning
γ	interfacial (surface) tension
O	organic liquid phase, oil in this case
S	solid phase, substrate
A	aqueous phase, cleaning solution
pH	measure of hydrogen ion concentration
θ	contact angle of the liquid with the solid
TCE	Trichloroethylene
VOC	volatile organic compound
AAC	aqueous alkaline cleaner
ORNL	Oak Ridge National Laboratory
CTAB	Cetyltrimethyl ammonium bromide
Triton X-100	Octophenol polyglycol ether
SDS	Sodium dodecyl sulfate
Chaps	3-[(3-cholamidotrophyl)- dimethylammonio]- 1- propane-sulfonate hydrate
cmc	critical micelle concentration
$S_{L/S}$	Spreading coefficient of liquid on a solid

hmc	hemimicelle concentration
M	molarity
mM	millimolar
°C	degrees Celcius
s	seconds
Triton X-100	Triton X-100
POE	polyoxyethylene
mV	millivolts
G	Gibbs free energy
W_a	work of adhesion
F_b	buoyancy force
F_k	kinetic force
F_s	interfacial tension force
F_D	drag force
g	acceleration due to gravity
ρ	density
V_{FS}	liquid volume attached to nozzle as necking starts
σ	interfacial tension
F	Harkins-Brown correction factor
U_F	velocity of the forming drop when

	necking starts
D_F	diameter of the detached drop
μ	viscosity
μl	microliter
T_C	critical temperature
T	temperature
W	weight of clean coupon
X	weight of contaminated coupon
Y	weight of coupon plus residue after cleaning
I	ionic strength
NaNO_3	Sodium nitrate
HCl	Hydrochloric acid
NaOH	Sodium hydroxide
De- I water	de-ionized water
POE	polyoxyethylene

PART I INTRODUCTION

The removal of oil from a solid surface in the presence of aqueous surfactant solutions is important in most cleaning and degreasing processes. Many solvents that were once used for cleaning and degreasing operations (chlorofluorocarbons) have now been phased out by the Clean Air Act Amendments of 1995 due to the detrimental health and environmental effects attributed to these solvents. Therefore, a search for new alternative cleaning agents to replace these solvents is needed. Aqueous based cleaning agents are at the forefront as viable alternatives to solvent cleaning methods as they have shown to compete with the organic solvents in their cleaning ability [1-3]

In spite of this, it is only recently that a real understanding of the factors involved in the cleaning process has started to emerge while a great deal about the subject remains obscure [4]. This is due to the complexity of the cleaning process. Several excellent reviews on the physical chemistry of detergency have been published in the past [5,6]. The technical literature contains a vast amount of information concerning fundamental properties such as adsorption, contact angles, and interfacial tension [7]. The cleaning literature primarily contains general information as to the types of chemical components used in aqueous cleaners. This study attempts to bridge the gap between the technical and cleaning literature while building from Starkweather's et al. [7,8] previous work.

Starkweather et al. [7,8] performed an in depth study to determine quantitatively the effect of surfactant solution pH on the displacement of an oil from a metal surface. They used Triton X-100 and SDS as the surfactants. The authors measured the interfacial

tension at the aqueous/oil interface as well as contact angle throughout the detachment process while varying the surfactant solution pH. Starkweather et al. [7,8] found as the pH of Triton X-100 increased, interfacial tension between the aqueous/oil interface decreased. This agreed well with trends observed by Basu et al. [9] for an interface of bitumen and water at different values. Liggieri et al. [10] showed that as the concentration of Triton X-100 increases, the interfacial tension of the aqueous solution with hexane decreases. The findings of Carroll [5] and Starkweather et al. [7,8] suggest that the removal of oil from a metal surface should be easier with solutions exhibiting a lower interfacial tension. Starkweather et al. [7,8] also found the contact angle of oil in the presence of Triton X-100 solutions to increase as pH increased. Carroll [5] found that if the contact angle of the oil on a solid surface was constant, the ease of removal was proportional to the interfacial tension between the oil and the surfactant solution. Therefore, knowing the contact angle and interfacial tension between the oil/aqueous interface has been shown to help predict the relative cleaning capabilities of surfactant solutions to aid in the displacement of oil from solid surfaces.

Aqueous-based cleaning involves the use of a surfactant to displace organic contaminants from surfaces of solid substrates. Several mechanisms (solubilization, roll-up, and emulsification) exist for oil removal from a solid surface. Solubilization utilizes the formation of micelles enabling oil to be incorporated to the core of a micelle. This occurs when the concentration of surfactant in the aqueous phase is greater than its cmc. McBain [11] proposed that solubilization was an important factor in detergent action,

however, Adamson [12] found no direct correlation between the concentration of micelles and detergent action. The roll-up mechanism of oil removal occurs as the contact angle that the oil makes with the solid surface is increased by adsorption of the surfactant from the cleaning bath. The surfactant solution preferentially wets the solid surface thereby replacing the solid/oil interfacial area with aqueous/solid interfacial area. This results in displacement of the entire drop if the contact angle reaches 180° [4].

Adamson and Stevenson [13] illustrate how lanolin films adhering to wood fibers are rolled up into easily detachable spheres when sodium cetyl sulfate is added to the aqueous phase. Emulsification is similar to the roll up mechanism with exception that the entire drop doesn't detach. Emulsification results in only a small droplet detaching from a larger drop. In this study, the removal of oil from the solid surface is achieved through an emulsification mechanism since only a portion of the drop detaches. In a typical drop detachment process various forces are involved in drop detachment [14]. The buoyancy force acts to detach the drop while the sum of the interfacial tension between the solid/oil interface acts to attract the oil to the surface thus hampering displacement. Only when the buoyancy forces overcome the interfacial tension force will the drop be detached from the surface. Van der Waals forces act to attract the oil drop to the solid surface.

Surfactants perform the major task of oil removal by adsorbing at the oil/aqueous and solid/aqueous interfaces. The result is to reduce the free energy thus decreasing interfacial tension of these phases. If the free energy per unit area of the aqueous/solid interface is less than that of the organic/solid, preferential wetting by the solution occurs

and the contaminant is released from the surface. The governing equation was developed in 1805 by Young and is known as Young's equation [12],

$$\gamma_{ow} \cos\theta = (\gamma_{ws} - \gamma_{os}), \quad (1)$$

where θ is the contact angle, γ_{ow} is the interfacial tension between the organic phase and the solid, γ_{ws} is the interfacial tension between the aqueous phase and the solid, and γ_{os} is the interfacial tension between the aqueous phase and the solid. According to equation 1, if the contact angle of the oil increases and the interfacial tension of the aqueous/oil interface decreases, the difference in the aqueous/solid and oil/solid interfaces must decrease. If the oil/solid interfacial tension remains constant, the aqueous/solid interface must decrease. Young's equations shows that adsorption of surfactants is equally important at the solid/aqueous interface as it is at the oil/aqueous interface which Starkweather et al. [7,8] studied. There is lack of technical literature concerning the orientation of surfactants at the surface and their effect on oil drop removal kinetics therefore it is necessary to understand the interactions the solid/aqueous interface in order to better formulate enhanced cleaning solutions. This study builds on that of Starkweather et al. [7,8] by further investigating drop removal kinetics and cleaning effectiveness in an ultrasonic bath for two other surfactant solutions; CTAB – cationic and Chaps – zwitterionic. The structure of the adsorbed surfactant layer at the solid/aqueous interface along with the principle of electrostatic repulsion/attraction will be used to model drop detachment trends.

Aqueous-based cleaning technology is a surprisingly complex process involving transient interactions among cleaning solutions, contaminants, and substrate surfaces. As an organic-contaminated substrate contacts a cleaning solution the interfacial tensions (free energies) among the contacted phase's change as a result of their interactions. An examination of Young's equation reveals that the wetting behavior of a liquid on a solid substrate, characterized by a contact angle, is critically affected by free energies in the liquid-vapor (or another liquid), liquid-solid, and the solid-vapor interfaces. If additional components are present in the liquid such as surfactants, interface adsorption can cause these energies to vary dramatically [15]. Concomitant effects on contact angle are then observed, which may lead to complete surface coverage or displacement of a liquid phase.

Nassauer and Kessler [16] reported that adsorption of surfactants onto metal surfaces could greatly be affected by surface potential. This potential was mainly influenced by the pH and oxidizing power of cleaning solutions. Hodgson and Berg [17] reported that a change in the surface charge by pH variation could affect ionic surfactant adsorption thus altering the aqueous-solid interface. Wahal and coworkers [15] performed experiments involving surfactant droplets resting in air on the surface of a parallel plate electrode. Results have shown contact angles always decrease regardless of the polarity of the applied electric field whereas magnitude of the change is sensitive to both polarity and strength of the field. Starkweather [7,8] has shown that pH adjustment of the cleaning solution medium affected the detachment of oil drops from a stainless

steel surface; either accelerating or decelerating the process of oil detachment. The observed phenomena was attributed to change in the interfacial tension at the oil/cleaning solution interface. Tsekov [18] studied the attachment of organic droplets and cells at a liquid-liquid interface in a system of a dropping mercury electrode in an aqueous cell suspension. The change in the water/mercury interfacial tension is attributed to the effects of applied voltage. Throughout the technical literature, there have been no reports of the effect of an applied potential on improving aqueous surfactant cleaning.

The purpose of this thesis is to provide a better fundamental understanding of the role electrostatic forces play in the process of oil drop detachment as well as cleaning effectiveness on a polished stainless surface. The effect of cleaning solution pH and directly applied surface potential on oil drop detachment is thoroughly studied. To date, there have been no reports of the effect of an applied potential on improving aqueous surfactant cleaning. This work builds on [7,8,19,20] previous work by directly introducing a small electrostatic potential across the metal substrate to alter surface charge instead of altering the cleaning solution pH. This work contrasts that of Starkweather's by focusing on the role electrostatic forces play at the solution/solid interface rather than the oil/solution interface. Since a shift in pH of the cleaning solution is known to render a charged surface based upon its isoelectric point [21], a similar effect of directly applying potential to the surface at the natural pH of the cleaning solution is thought to serve the same purpose. If indeed similar trends are noted, application of a small potential to the surface can provide the same enhanced cleaning results without the

increased amount of generated waste, expense, and corrosivity that acidic or basic media render. Four surfactants are used in this study each having a different charged hydrophilic group. They are SDS – anionic, CTAB – cationic, Triton X-100 – nonionic, and Chaps – zwitterionic. The charge of the surfactant along with alteration of the surface charge will allow for prediction of the wettability of the surfactant along the substrate thus providing valuable information on optimal cleaning conditions. Several parameters are studied including: the kinetics of detachment of an oil droplet from a stainless steel substrate, cleaning effectiveness in a bench-scale ultrasonic bath, and contact angle at various stages throughout the drop detachment processes. Zeta potential is used to measure the oil drop/aqueous phase interfacial charge as a result of pH alteration providing insight as to the actual charge of the oil drop in the presence of the cleaning solution. A mechanism based upon the orientation of surfactant molecules at the surface as well electrostatic attraction/repulsion forces is proposed to explain the resulting trends.

The experimental results from this study will be divided into three complete sections (Parts II, III, IV), each representing a stand alone publishable paper. In Part II, the pH of the cleaning solution is varied while monitoring the kinetics of an oil drop detaching from a solid surface. A model based electrostatic attraction/repulsion as well as the structure of the adsorbed surfactant layer at the surface/aqueous interface is proposed for explaining the observed trends. In Part II, oil drop detachment kinetics from a solid surface in the presence of four types of surfactant solutions is monitored as

function of directly applied electrostatic potential at the contaminated surface. A model based on electrostatic attraction/repulsion is proposed for explaining the observed trends. This is similar to Part II with the exception being the structure of the adsorbed surfactant layer. In Part III, the relationship between laboratory-scale oil drop detachment kinetics and industrial-scale ultrasonic bath cleaning effectiveness under similar conditions is shown. This provides a simple laboratory screening procedure that can be used in predicting the cleaning success of a particular cleaning solution in an industrial setting.

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PART II

Oil Detachment from Solid Surfaces in Surfactant Solutions of Various pH

ABSTRACT

Effective aqueous-based cleaning depends on the appropriate selection of surfactant(s) and pH conditions. In the experiments described in this paper, the detachment of oil droplets from a solid surface in surfactant solutions was studied and the variation of droplet shape, particularly contact angle, and time required for droplet removal were measured. In parallel, tests of oil weight removal from solid surfaces in an industrial ultrasonic bath have been conducted under conditions similar to drop detachment tests. Consistent trends were found in both types of tests; that is, conditions for which droplets detach more quickly correspond to conditions of greater oil removal in an ultrasonic bath. At high pH, faster drop detachment (and oil removal) kinetics were observed when the oil/water interface was negatively charged (per zeta potential measurements). In contrast, at low pH conditions, faster kinetics were observed when the interface was positively charged. The pH effect was interpreted well by a mechanistic model in which electrostatic interactions and solid-surface hydrophobicity changes due to surfactant adsorption onto solid surfaces under various pH conditions are considered. This study also demonstrates that single-drop-detachment tests and /or zeta potential

measurements could be useful as simple, time-saving screening methods for selecting promising conditions for specific cleaning applications

INTRODUCTION

The cleaning of solid surfaces is of considerable interest to industry. Solid surfaces must be cleaned as part of the manufacturing process to remove contaminants that could otherwise be deleterious to the subsequent process steps or for quality purposes. Contaminants can be grouped into categories of organic and inorganic as well as particulate and liquid. Organic liquid contaminants are of primary concern in the present study.

Traditionally, solvent cleaning methods such as solvent wiping and vapor degreasing have been employed for removal of organic contaminants due to their high cleaning efficiency, quick drying time, and low cost [1]. However, two of the most common halogenated solvents used in vapor degreaser systems as well as in other solvent cleaning processes, TCA (1,1,1 trichloroethane) and CFC – 113 (trichlorotrifluoroethane), have been found to cause serious ozone depletion as well as detrimental health hazards. For these reasons, the Clean Air Act Amendments of 1990 banned their production, effective in 1995. Other motivations for the replacement of halogenated solvents include [2]: (1) rising cost associated with compliance with increased environmental legislation; (2) health and safety concerns associated with solvent-based methods, (3) increased restriction on the use of halogenated solvents. A

transition to environmentally safe alternative cleaning technologies such as aqueous solution-based processes is prudent wherever possible. The advantages of aqueous cleaning agents over halogenated solvents include less environmental damage and less hazards to workers.

Aqueous-based cleaning involves the use of a surfactant to aid in the removal of contaminants from surfaces of solid substrates. A surfactant molecule has both a hydrophobic tail group and a hydrophilic head region and is soluble in water as well as in organic oils. The primary component of an aqueous-based cleaner is water which has a high surface tension (72 dynes/cm at 20°C). The presence of surfactants significantly lowers the interfacial tension of the cleaning solution/contaminant interface, an important factor in the interaction of contaminants, surfaces, and solution. Other components, such as pH modifiers are commonly added to water to enhance cleaning efficiency [3]. Several mechanisms of oil removal from a solid surface have been identified [4, 5], including emulsification, roll-up, and solubilization. The roll-up mechanism involves the removal of an entire oil drop from a contaminated surface, while the emulsification mechanism involves the detachment of only a portion of the oil drop from the surface. The mechanism of solubilization utilizes the formation of micelles enabling oil to be incorporated into the core of a micelle. This occurs only when the concentration of surfactant is greater than the critical micelle concentration. McBain [6] proposed that solubilization was an important factor in detergent action (effectiveness of removing

contaminants) while Adamson [7] found no direct correlation between micelle concentration and detergent action.

The technical literature contains a vast amount of information concerning fundamental properties such as surfactant adsorption, contact angles, and interfacial tension [8]. In addition, the cleaning literature contains general information as to the types of chemical components used in aqueous cleaners for various purposes. This study attempts to bridge the gap between the technical and trade literature by building upon previous work by Starkweather et al. [8-10]. This study focuses on building a model of oil detachment from metal surfaces based on the adsorption/absorption of surfactants and electrostatic interactions (attraction/repulsion) of the oil and the metal surface; the metal surface may be modified by interaction with the solution. This paper does not seek to dispute other modeling approaches on these phenomena, but to contribute a particular viewpoint to the developing body of knowledge.

BACKGROUND

The particular system of interest in this study is the removal of a sessile oil drop from a solid surface in an aqueous surfactant solution. For a static oil drop, the angle between the solid surface and the oil-aqueous interface at the contact line between the three phases is given by Young's equation

$$\gamma_{O,AQ} \cos \theta = \gamma_{S,AQ} - \gamma_{S,O} \quad (1)$$

where $\gamma_{O,AQ}$ is the interfacial tension between the oil and aqueous phases, $\gamma_{S,AQ}$ is the interfacial tension between the solid and aqueous phases, $\gamma_{O,AQ}$ is the interfacial tension between the solid and oil phases, and θ is the contact angle of the drop at the surface. Therefore, for a static drop, a greater contact angle corresponds to a smaller interfacial tension of the oil/aqueous interface, assuming the oil/solid and solid/aqueous interfacial tensions remain constant. In a typical drop detachment process multiple forces are involved [11]. The buoyancy force acts to detach the drop while the interfacial tension of the oil/aqueous interface acts to maintain the droplet surface. Van der Waals forces are responsible for adhering the oil drop to the surface. Only when the buoyancy forces overcome the interfacial tension and Van der Waals forces will the drop detach from the surface.

Among many parameters, pH has been shown to significantly affect the removal of oil from solid surfaces in the presence of surfactant solutions. It is known that increased cleaning solution pH affects oil removal from model surfaces by lowering the interfacial tension at the solution/oil interface [8-10], [12]. Starkweather et al. [8-10] quantitatively determined the effect of surfactant solution pH on the displacement of oil from a metal surface. Two surfactants, Triton X-100 (nonionic) and sodium dodecyl sulfate (SDS; anionic) were used. The authors measured the interfacial tension at the aqueous/oil interface as well as contact angle evolution throughout the detachment process while varying solution pH. The authors found as the pH of Triton X-100 solution increased, the interfacial tension between the aqueous/oil interface decreased. This

agreed well with trends observed by Basu et al. [12] for an interface of bitumen and water. Liggieri et al. [13] showed that as the concentration of Triton X-100 increases, the interfacial tension of the aqueous/oil interface decreases. The findings of Carroll [14] and Starkweather et al. [8-10] suggest that the removal of oil drops from a metal surface should be more rapid under conditions that result in a lower aqueous/oil interfacial tension. Starkweather et al. [8-10] also found the contact angle of oil in the presence of Triton X-100 solutions to increase as pH increased. Carroll [14] found if the contact angle of the oil phase on a solid surface was constant, the ease of removal was proportional to the interfacial tension between the oil and surfactant solution.

Most authors have focused on studying the oil/aqueous interface rather than the aqueous/solid interface. This study focuses attention to the aqueous/solid interface as well. It is widely known that pH variation of cleaning solutions affects the adsorption and orientation of surfactant molecules at the solid surfaces. Hodgson and Berg [15] have shown that the nature of the surface charge on a Kevlar fiber affects the adsorption of ionic surfactants on the surface. They concluded that at low pH, the fibers become protonated, acquiring a net positive charge, while at high pH, the fibers are expected to take on a net negative charge. The two surfactants used were cetyl trimethylammoniumbromide (CTAB, a cationic surfactant) and SDS. In their studies of wetting of Kevlar fibers in SDS solutions, the contact angle decreased with increasing pH, with surface being completely wet at a pH of 12. In the studies of wetting of CTAB solutions, the contact angle increased with increasing pH. The data is rationalized by the

orientation of surfactant molecules at the solid surface. For SDS solution at high pH, the surfactant molecules adsorb with their tails oriented to the solid surface while exposing the head groups to the solution. At low pH, SDS molecules orient themselves with the head group bonded at the surface and the tail group extended into the solution. If the surface and surfactant molecules are attractive, the hydrophobic tails of the surfactant are directed outward from the solid surface, changing the solid surface characteristics from hydrophilic to hydrophobic and favoring oil to wet this region. Fuerstenau and Wakamatsu [16] and Hankins et. al [17] show the effect of pH on adsorption of SDS at the alumina-water interface. Adsorption by electrostatic attraction of surfactant anions onto positively charged surfaces was found to occur significantly only below pH 9, the point of zero charge of alumina. Bohmer et al. [18] found that nonionic surfactants do not readily adsorb to make a hydrophilic surface hydrophobic as other ionic surfactants do. However, Rosen [19] reports the oxygen of POE (polyoxyethylene) chains interact electrostatically with protonated surfaces at low pH. Other researchers have also shown that anionic surfactants adsorb to hydrophilic surfaces by their head-groups [17]. One possible explanation is that under typical conditions (near neutral pH), most surfaces are negatively charged, resulting in attractive forces between the surface and head-groups of cationic surfactants. A repulsive force exists between anionic surfactant head-groups and the negative surface resulting in tail-down orientation to the surface. Goloub [20] found that adsorption of cationic surfactants onto a silica surface increases as pH increases because the silica surface is more negatively charged. Since a silica surface is

hydrophilic, similar adsorption patterns can be expected on stainless steel surfaces. Gao et al. [21] report similar adsorption of cationic surfactants onto silica gel. They found four distinct regions in the adsorption isotherm: (1) adsorption due to electrostatic interactions, (2) adsorption resulting from both the electrostatic attraction and the specific interaction between the surface-active cations and the silica surface, (3) second-layer of adsorption begins to be significant, and (4) second-layer adsorption is substantial. A surfactant with a like-charged head-group as that of the surface will result in orientation of the surfactant in a tail-down fashion to the surface, whereas the case of an oppositely charged head-group from that of the surface will result in a head-down fashion to the surface.

Selection of the appropriate surfactant(s) and pH for a specific cleaning task is the first important step in the cleaning process. This paper, for the first time, correlates the simple single-droplet detachment experimental data with prototypic industrial cleaning tests of oil removal from solid substrates. Four types of surfactants (anionic, cationic, zwitterionic, and nonionic) are included in the study to better understand the interactions among the oil, surfactant solution, and the solid surface under various pH conditions. A mechanistic model is proposed to interpret the observed oil detachment/ removal kinetics.

PROPOSED MODEL

There are several forces that exist on an oil droplet at the solid/aqueous interface, including buoyancy force, downward surface tension, and electrostatic

repulsive/attractive forces. In the model presented here, pH and surfactant type may only affect interfacial tension and two electrostatic interactions. The theory used in building the mechanistic model for drop detachment arises by utilization of a mechanism proposed by Hodgson and Berg [15] as well as Rosen [19]. Those authors report that the hydrophilic head groups of ionic surfactants are attracted to an oppositely charged solid surface, resulting in a monolayer of surfactant molecules on the surface. Since the hydrophobic tails are directed outward, oil and other hydrophobic materials are able to wet this monolayer-covered solid surface. It is widely known that as the surface characteristics change from hydrophilic to hydrophobic the interfacial tension of the aqueous/solid interface increases. This interpretation has been supported via an increase in contact angle measurements of water on the resulting hydrophobic surface as the packing density of the monolayer increases [15].

Surfactants may be charged (due to ionization, dipole moments, head group protonation/deprotonation) which gives rise to attractive or repulsive forces between surfactant molecules adsorbed at the oil/solution interface and those adsorbed at the solid/solution interface. Zeta potential measurements of oil droplets allow for determination of oil surface charge while exposed to a solution containing a particular surfactant. Petermann et.al. [22] have measured the zeta potential of stainless steel as a function of pH and found that at high pH the surface is negatively charged while at low pH the surface acquires a positive charge. The point of zero charge is found to be near a pH of 4. It is therefore reasoned that at low pH anionic surfactant molecules would be

attracted to the surface resulting in a monolayer of surfactants adsorbed to the surface with the tail regions directed into the solution, while cationic surfactant head groups are attracted to negatively charged surfaces (high pH conditions). Characterization of the oil drop surface charge is deduced experimentally from zeta potential measurements. The overall charge imposed on the oil drop is deduced by the measured zeta potential of the oil droplets emulsified in the desired cleaning solution. A negative zeta potential corresponds to a negatively charged oil drop surface while a positive zeta potential corresponds to a positively charged drop surface. The actual charge of surfactant molecules is qualitatively deduced by comparison of the zeta potential of an oil/water emulsion to that of the oil/surfactant solution emulsion at a given pH.

When charged surfactant molecules contact an oppositely charged solid surface, the result is head-group adsorption to the surface with hydrophobic chains of surfactant directed into the solution. This provides a hydrophobic surface for enhanced attachment of oil to the surface. It is hypothesized that when a solution containing an anionic surfactant contacts a negatively charged surface, a repulsive force exists between the negatively charged oil drop surface and the head groups of anionic surfactant molecules protruding into the solution from the solid surface, thereby favorably detaching the drop. It is hypothesized that when a solution containing an anionic surfactant contacts a like-charged surface, two factors combine favorably towards drop detachment – hydrophilicity of the charged surface and electrostatic repulsive forces between the negatively charged oil-drop surface and the head groups of anionic surfactant molecules

protruding into the solution from the solid surface. Figure 1 shows the proposed mechanistic model for oil detachment in four types of surfactants.



Figure 1. Proposed mechanistic model for oil drop detachment as a function of solution pH

When the surfactant molecules and solid surface are unlike charged, as shown on the left-hand side of Figure 1, the result is adsorption of surfactant to the surface by their head groups thus allowing the hydrophobic tail groups to protrude into the aqueous phase. This alters the surface characteristics from hydrophilic to hydrophobic thus allowing the oil to wet the surface more favorably. On the other hand, if the surfactant molecules and surface are like charged, as shown on the right-hand side of Figure 1, the result is adsorption of surfactant to the surface by their tail groups allowing the hydrophilic head groups to protrude into the aqueous phase. This results in electrostatic interaction between the drop surface and the surfactant head groups depending on the charge of the drop surface.

MATERIALS AND EXPERIMENTAL METHODS

Experiments are conducted with aqueous solutions of each of four different surfactants. In all cases the oil contaminant was Mar-Temp 355, a quenching oil manufactured by Houghton International, that consists mostly of mineral oil. A polished coupon of 455 stainless steel was used as the surface for cleaning. Starkweather [8-10] measured the roughness to be 1975 Angstroms. All experiments are conducted at room temperature and atmospheric pressure. The surfactant solutions were prepared fresh daily to ensure consistent data. The surfactants, along with their respective concentrations used in the study, are shown in Table 1 [23].

Table 1. Surfactants used in this study

<u>Surfactant</u>	<u>Abbrev.</u>	<u>Type</u>	<u>CMC</u>	<u>Supplier</u>
Octophenol polyglycol ether	Triton X-100	Nonionic	0.0003 M	Fisher Biotech
Cetyltrimethyl ammonium bromide	CTAB	Cationic	0.007 M	Aldrich
Sodium dodecyl sulfate	SDS	Anionic	0.008 M	Fisher Biotech
3-[(3-cholamidotrophyl)- dimethylammonio]- 1-propane-sulfonate hydrate	Chaps	Zwitterionic	Unknown 0.009M	Aldrich

Single Drop Detachment Experiment

The experiments are carried out by using a dedicated apparatus capable of monitoring the dynamic evolution of droplet shape, contact angle, and droplet detachment from metal surface in an aqueous surfactant solution (Figure 2). The purpose of this experiment is to determine the kinetics of oil droplet removal as a function of pH. HCl and NaOH (both at chemical grade) were used for pH adjustments. The monitoring apparatus included a high quality image camera connected to a video recorder and television monitor. A video copy processor was used to print an image of the oil droplet at several stages during the detachment process. These images were used to measure the contact angle and geometry of the droplet near detachment.

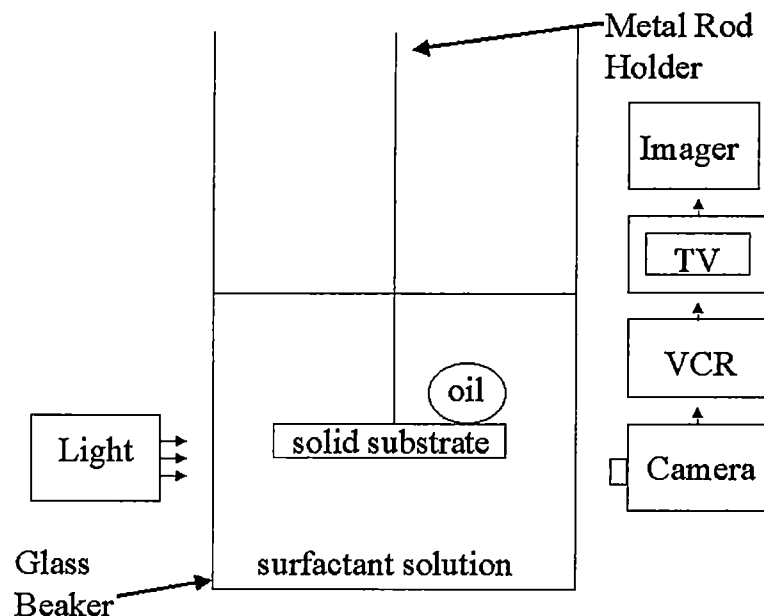


Figure 2. Schematic of the drop detachment experiment

Typically, a 200-ml aliquot of the prepared surfactant solution was added to a 250-ml square-shaped glass beaker in which the metal coupon was submerged. The polished stainless steel coupon was cleaned after each experiment with a solution of 2% Micro detergent and de-ionized water mixture and rinsed with de-ionized water. The metal surface was allowed to air dry for 5 minutes, then a 2-microliters droplet of Mar-Temp 355 oil was placed on the surface by use of a pipeter. The oil droplet was allowed to contact the metal surface for 5 minutes before the coupon was submerged in the beaker

of surfactant solution. The drying time of the metal surface after pre-washing, time allowed for the oil droplet to contact the surface, room temperature (22 °C), drop size (2 microliter), surfactant concentration, and monitoring methods were maintained unchanged throughout the study.

Bench-Top Ultrasonic Bath Cleaning Experiment

Tests of oil removal under similar conditions were conducted using a bench-top ultrasonicated cleaning bath (Crest Ultrasonic Bath from Ultrasonics Corporation) to illustrate a direct correlation between these cleaning results and those of single drop detachment experiments. The same four surfactants were used in this cleaning study. In this experiment a stainless steel coupon was first cleaned in a 2% solution of Micro® detergent and rinsed well with de-ionized water. The coupon was then dried in an oven for 5 minutes at 120 °C. The coupon was cooled to room temperature and the mass of the clean coupon, W , was recorded. The coupon was submerged in Mar Temp-355 oil for 5 minutes then hoisted by an attached wire to drain excess oil for 3 hours. The contaminated coupon with mass X was placed inside a 2000-mL glass beaker containing the desired surfactant solution. The beaker was suspended in the ultrasonic bath, and the bath was tuned to 108 watts of output. The ultrasonic energy at the point where the coupon was suspended was measured at 11 watts per square inch by an ultrasonic meter (Ultrasonic Energy Meter II from ppb Inc.) Upon removal from the bath, compressed air was blown along the surface of the cleaned metal for 1 minute to remove excess solution

for. The mass of the cleaned coupon, Y , was recorded. Percent oil removal was calculated by the equation:

$$\text{Percent oil removal} = [(X-Y)/(X-W)]*100 \quad (2)$$

Contact Angle Analysis

Contact angle measurements were made by first recording the drop detachment process onto VHS tapes using the video cassette recorder. A series of droplet images at different times from each experiment were printed using a video copy processor. On these pictures, lines were drawn tangent to the oil droplet at the point of contact between the three phases (oil/metal, oil/surfactant, surfactant/metal). The contact angles at left and right sides of the drop were measured and averaged using the printed enlarged images. A protractor was used to determine the angles.

Zeta potential measurements

Zeta potentials of oil droplets suspended in aqueous surfactant solutions of various pH were measured using a Lazer Zee Meter Model 501 (Pen Kem, Inc.) to qualitatively deduce the charge of the individual surfactant molecule as well as the oil drop surface in the cleaning solution. In these studies only single-surfactant solutions were used and only the pH of the solutions were altered. A 1% (by volume) mixture of Mar-Temp 355 oil and de-ionized water was homogenized for 10 minutes. Droplet-size distributions measured using a light-scattering instrument (Coulter LS-130 indicated that

the agitation caused 80% (by volume) of the droplets to be smaller than 1 micron in diameter. A 5-mL aliquot of the oil/water emulsion was first dispersed into 40 mL of de-ionized water adjusted to a selected pH. The resulting emulsion was introduced into the zetameter cell for analysis.

RESULTS

The pH of a surfactant cleaning solution affects the kinetics and performance of oil removal from a solid surface. The purpose of this study is to compare trends of experimental oil removal in four types of surfactant solutions over a range of pH. The data presented below will help elucidate the mechanisms by which oil is removed from the surface.

Effect of pH on Drop Detachment Time

This experiment shows quantitatively the time needed for the first droplet to detach by an emulsification mechanism from the remainder of the 2-microliter oil drop on a polished stainless steel surface submerged in a pH-controlled surfactant solution.

Figure 3 shows that oil drop detachment time depends on the pH and type of surfactant.

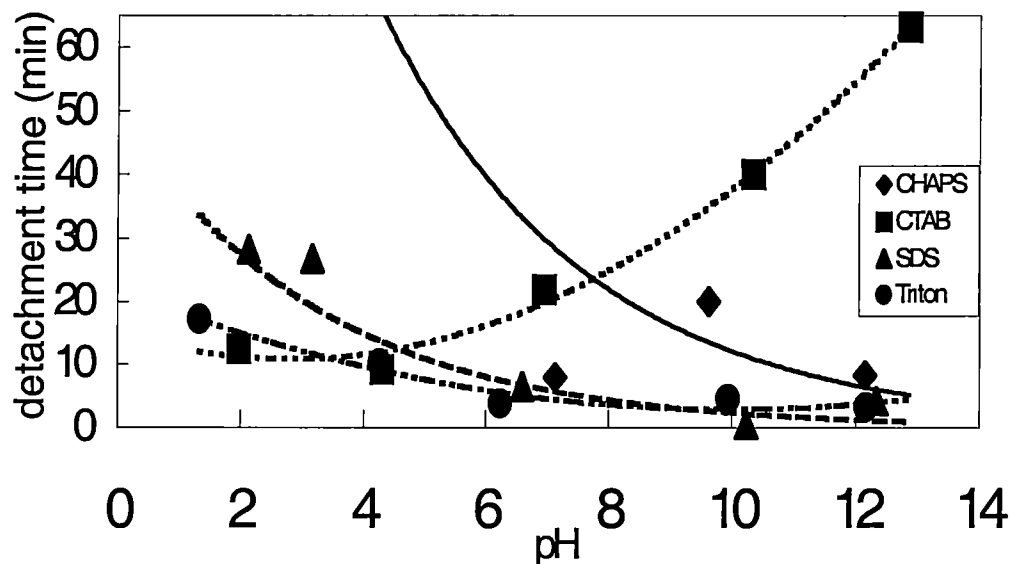


Figure 3. Effect of pH on oil drop detachment time in four types of surfactant solutions

Drop detachment time in solutions of Triton X-100, SDS, and CHAPS decrease with increasing pH, while solutions of CTAB demonstrate the opposite trend in which single drop detachment time increases with increasing pH. For solutions of Triton X-100, an increase in pH from 1.3 to 12.2 resulted in a decrease in detachment time of 81%. For SDS solutions, an increase in pH from 2.1 to 12.3 resulted in a decrease in drop detachment by 85%. For solutions of CTAB, a decrease in pH from 12.9 to 2.0 resulted in a decrease of detachment time by 80%. For Chaps solutions, there was no detachment within 120 minutes at low pH, while at high pH detachment occurred within 9 minutes. For SDS and Triton X-100 solutions, detachment time decreases rapidly with increased pH initially then flattens past a pH of 7. The detachment time for Chaps solutions show a

similar trend, decreasing with increasing pH, although the effect of pH on removal could not be determined below pH 7 since no detachment was observed. With solutions of CTAB, drop detachment time increases nearly exponentially with increasing pH, signifying a pH dependence over the range of 2.0 to 12.9. At high pH conditions (such as pH=10), effectiveness of surfactant type on drop detachment kinetics follow the order: SDS > Triton X-100 > Chaps > CTAB.

Effect of pH on Cleaning Effectiveness in an Ultrasonic Bath

The effect of pH on cleaning effectiveness in an ultrasonic bath is shown in

Figure 4

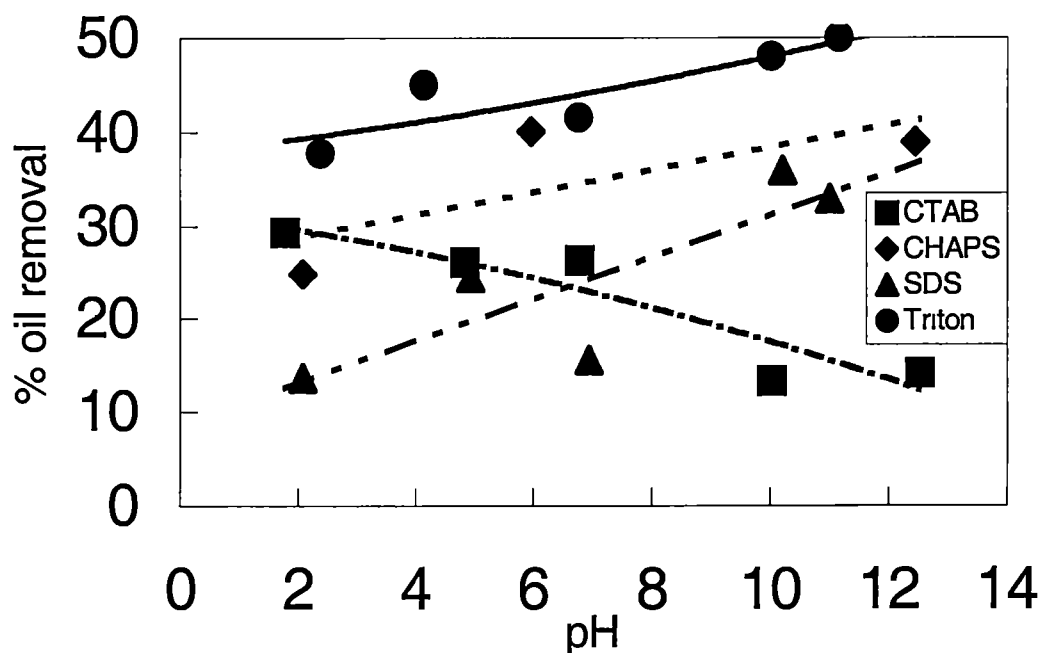


Figure 4. Effect of pH on cleaning effectiveness in four types of surfactant solutions

In solutions containing SDS, CHAPS, and Triton X-100, cleaning effectiveness increases as pH is increased from 1.5 to 12.5. In contrast, in solutions with CTAB cleaning effectiveness increases as pH decreases. For Triton X-100 solutions, an increase in pH from 2.4 to 11.2 resulted in an increase of percentage oil removal (POR) by 13%. For solutions of SDS, an increase in pH from 2.1 to 12.5 resulted in an increase of POR by 19%. For solutions of Chaps, an increase in pH from 2.1 to 11.0 resulted in an increase of POR by 14%. For CTAB solutions, an increase in pH from 1.8 to 12.5 resulted in a decrease of POR by 15%. At unmodified solution pH (the pH of the surfactant in de-ionized water with no pH modifiers), the order of surfactants in terms of cleaning effectiveness (strong to weak) is: Triton X-100 > Chaps > CTAB > SDS. At high pH, cleaning effectiveness (strong to weak) is: Triton X-100 > SDS > Chaps > CTAB. At low pH the trend is: CTAB > Triton X-100 > SDS > Chaps.

Effect of pH on Contact-Angle Evolution

The effect of pH on contact angle is shown in figure 5. In this figure, the measured contact angles are plotted as a function of normalized time, which is defined here as the ratio of the time the oil droplet was in contact with the aqueous solution divided by the time needed for a droplet to detach from the surface.

Figure 5 shows that an increase in pH of solutions of the nonionic Triton X-100, anionic SDS, and zwitterionic Chaps results in an increase in contact angle. Solutions of the cationic CTAB yielded a decrease in contact angle with increased pH.

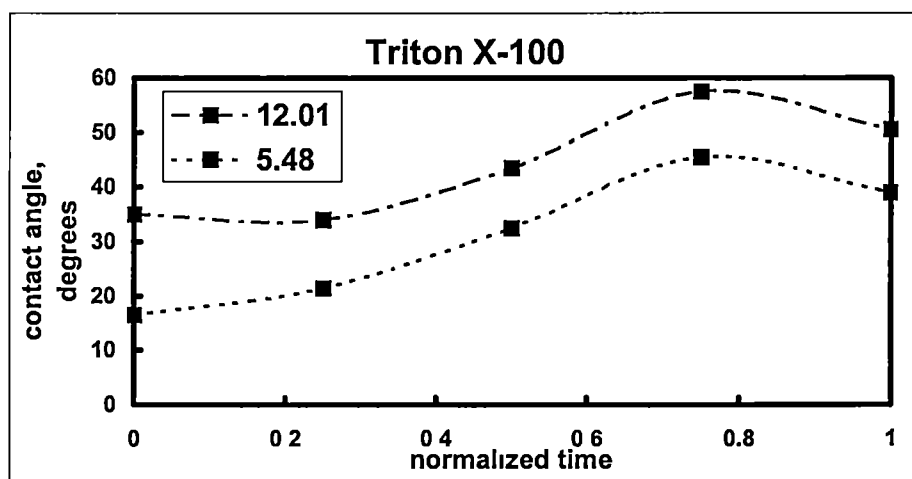


Figure 5. Effect of pH on contact angle evolution

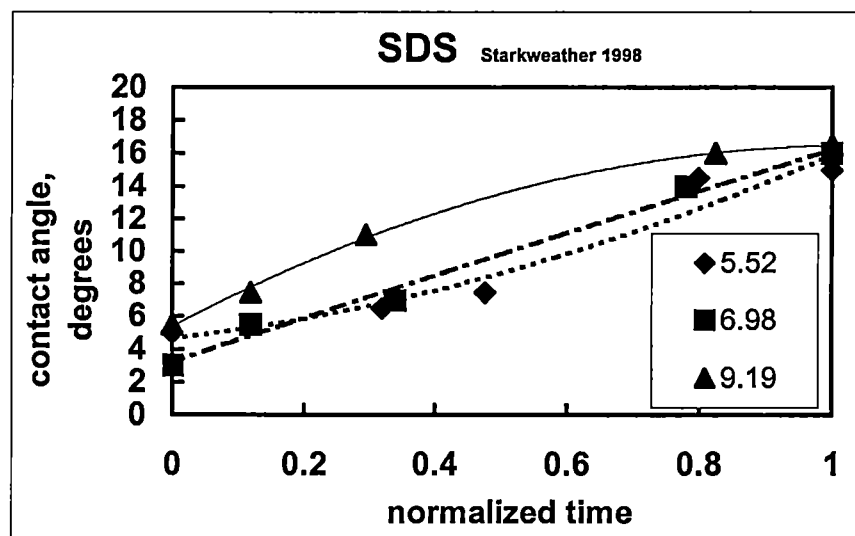
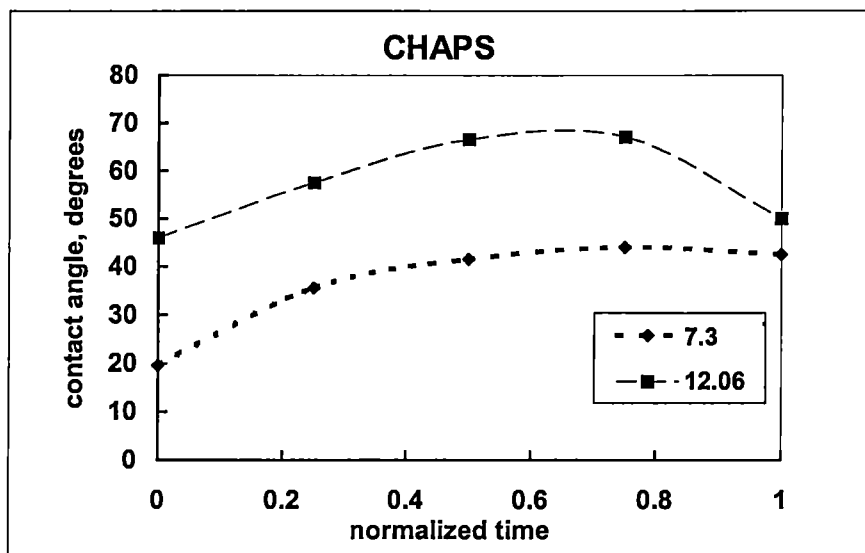


Figure 5. Effect of pH on contact angle evolution (continued)

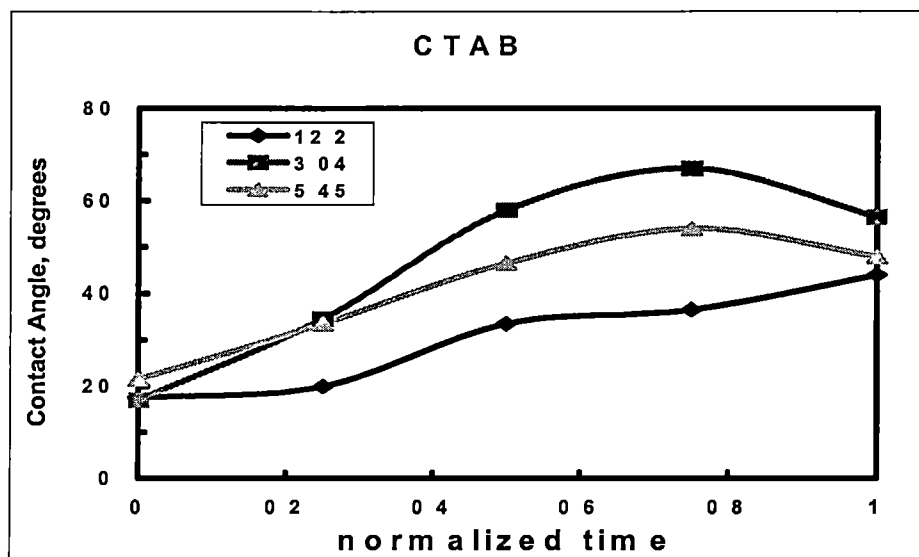


Figure 5. Effect of pH on contact angle evolution (continued)

The factors contributing to variation of contact angle can be explored through a consideration of Young's equation. To the author's knowledge only two of the four terms ($\gamma_{O,A}$ and θ) in Young's equation can be conveniently measured directly.; however, this equation still provides valuable insight of the dependence of contact angle on the solid/solution interface. An increase in contact angle must correspond to a decrease in interfacial tension between the aqueous/oil interface assuming the solid/oil and the

aqueous/solid interfacial tension remains constant. With increasing pH, the interfacial tension at the oil/aqueous interface, $\gamma_{O,A}$ decreases for nonionic and anionic surfactants [8-10] resulting in a larger contact angle. This allows removal of oil with less work. Alternatively, a decrease in $\gamma_{S,A}$ and/or an increase in $\gamma_{S,O}$ can also result in an increased contact angle.

Effect of pH on Zeta Potential of Oil-Droplet Surfaces

Zeta potential measurements for the surfactant/oil/water emulsions over a pH range of 2 to 13 are shown in Figure 6

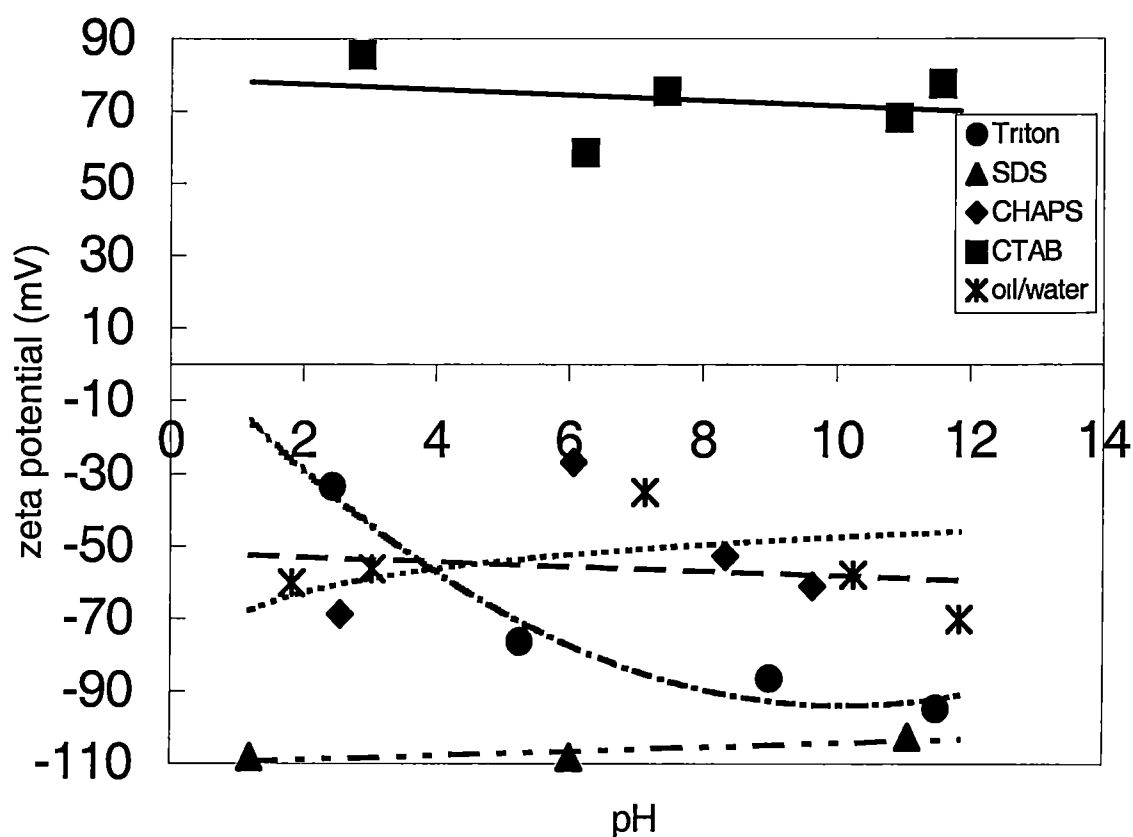


Figure 6. Effect of pH on the zeta potential of sub-micron oil drops in four surfactants

An oil/water emulsion with no surfactant is measured as a control; in that case, the zeta potential varied from -30 mV to -65 mV over the pH range. Sub-micron oil drops in solutions of Triton X-100, SDS, and Chaps exhibited a negative zeta potential, indicating the oil surface in contact with the aqueous phase is negatively charged over the range of the studied pH. In contrast, oil drops in CTAB solutions exhibited a positive zeta potential, indicating a positively charged oil surface. Oil droplets in solutions of SDS were found to have a nearly constant zeta potential independent of pH, while solutions

containing Triton X-100 and CTAB show a decrease in zeta potential as pH is increased. The zeta potential of the Chaps solution emulsion remains relatively similar to that of the control (oil/water emulsion). The charge of the surfactants may be deduced by comparison of the measured zeta potentials with that of the control. From the values presented in Figure 6, Triton X-100 appears to be negatively charged at high pH and positively charged at low pH, even though Triton X-100 is considered a nonionic surfactant.

DISCUSSION

The observed trends for drop detachment as a function of pH and surfactant type support the proposed surfactant monolayer adsorption mechanism presented in Figure 1. This allows for development of a mechanistic model for oil removal in each type of surfactant shown in Figure 7. The left-hand side of the figure corresponds to low pH conditions while the right-hand side corresponds to high pH conditions. The order from top to bottom of surfactants is as follows: CTAB, SDS, Triton X-100, and Chaps.

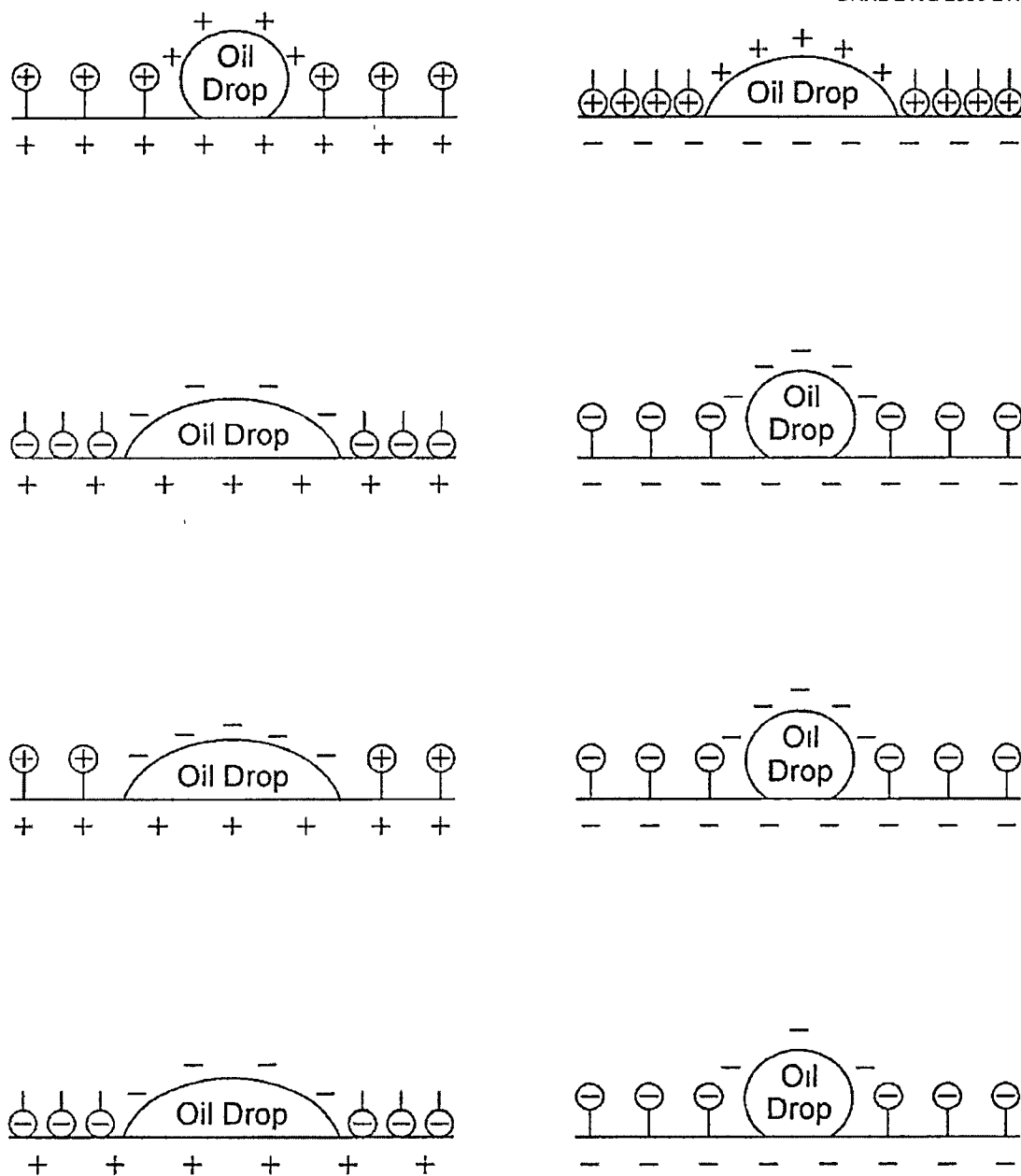


Figure 7. Mechanistic model of oil detachment as a function of pH

Oil droplets were found to detach more quickly in basic solutions of Triton X-100 as opposed to acidic solutions, as shown in Figure 3. Although this trend was explained by Starkweather et al. [reference] as the result of a variation of oil/aqueous interfacial tension alone, it is consistent with a model that also considers the effect of surfactant adsorption at the solid surface. By zeta potential measurements shown in Figure 6, it was determined that Triton X-100 molecules become slightly protonated at low pH and acquire a negative charge at high pH, while the oil surfaces exposed to Triton X-100 solutions are negatively charged over the pH range tested. At low pH, because both the solid surface and the surfactant molecules are positively charged, a tail-down orientation of surfactant (tail groups attached to the solid surface, with head groups directed into the solution) can be expected at the solid/solution interface. In this case, the oil drop has a greater affinity to the solid surface due to attractive forces between the negatively charged drop surface and the positively charged surfactant head-groups. At high pH, both the solid surface and the surfactant molecules are negatively charged, again resulting in a tail-down orientation of surfactant at the solid/solution interface. However, at high pH the oil drops detach more quickly from the solid surface due to repulsive forces between the negatively charged drop surface and the negatively charged surfactant head-groups.

Oil drops are shown to detach more quickly in basic solutions of SDS as opposed to acidic solutions, as shown in Figure 3. By zeta potential measurements shown in Figure 6, SDS molecules carry a relatively high negative charge independent of pH, and

the oil drop surfaces exposed to SDS solutions were shown to be negative over the pH range tested. At low pH, the solid surface becomes positively charged whereas the surfactant molecules are negatively charged, resulting in an attraction of the surfactant head-group to the surface with the tail-group of the surfactants directed toward the cleaning solution. As this occurs, the stainless steel surface becomes more hydrophobic resulting in a greater affinity of the oil drop for the surface. In this case the oil drop tends to remain adhered to the solid surface due to interactions between the surfactant tail-groups and the oil drop. At high pH, both the solid surface and the surfactant molecules are negatively charged, resulting in a tail-down orientation of surfactant at the solid/solution interface. In this case, the oil drops are quickly detached from the solid surface due to the hydrophilicity of the solid surface and to repulsive electrostatic forces between the negatively charged drop surface and surfactant head groups.

Oil drops were found to detach more quickly in acidic solutions of CTAB compared to basic solutions, as shown in Figure 3. The zeta potential measurements shown in Figure 6 indicated that both the CTAB molecules and the oil-drop surfaces exposed to CTAB solutions are positively charged over the pH range tested. At low pH, since both the solid surface and the surfactant molecules are positively charged, a tail-down orientation of surfactant at the solid/solution interface could be expected. Hydrophilicity of the solid surface and repulsive forces between the positively charged surfactant head-groups and the drop surface increases the rate at which the oil drop is detached from the surface. At high pH, the solid surface is negatively charged and the

surfactant molecules are positively charged resulting in a head-down orientation of surfactant at the solid/solution interface. The oil drops are detached from the solid surface at a slower rate due to the increased hydrophobicity of the tail-groups of the surfactant molecules at the solid surface.

Oil drops were found to detach more quickly in basic solutions of Chaps as opposed to acidic solutions, as shown in Figure 3. Through zeta potential measurements, Chaps molecules were found to become slightly protonated at low pH and acquire a negative charge at high pH. However, the oil drop surfaces exposed to Chaps solutions are negatively charged over the pH range tested, as shown in Figure 6. Therefore, at low pH, both the solid surface and the surfactant molecules are positively charged, resulting in a tail-down orientation of surfactant at the solid/solution interface. In this case, the oil drop remains adhered to the solid surface due to attractive forces between the negatively charged drop surface and the positively charged surfactant head-groups. At high pH, both the solid surface and the surfactant molecules are negatively charged, again resulting in a tail-down orientation of surfactant at the solid/solution interface. In this case, the oil drops detach more quickly due to repulsive forces between the negatively charged drop surface and surfactant molecules oriented in the tail-down fashion at the solid surface.

SUMMARY

Experiments involving the detachment of oil drops from a metal surface in aqueous solutions containing surfactants were conducted to explore the effect of the pH

and surfactant type of the aqueous solutions on oil removal. At high pH, faster drop detachment was observed when the oil/water interface was negatively charged. In contrast, at low pH conditions, faster kinetics were observed when the interface was positively charged. A mechanistic model that includes electrostatic interactions and solid surface hydrophobicity modified by surfactant adsorption as well as the effect of surfactants in reducing the oil/water interfacial tension was developed to interpret these observed trends.

This paper has practical implications for the improvement of aqueous cleaning approaches. Simple bench-scale experiments of drop detachment correlate with a prototypic industrial ultrasonic cleaning bath. Single-drop detachment testing could thus be used as a quick, simple, and economic method for screening surfactants and optimizing cleaning. In addition, zeta potential measurements may also provide valuable information in determining the optimum solution pH for maximum cleaning performance.

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PART III
LABORATORY-SCALE DROP DETACHMENT TESTS CAN GUIDE
CLEANING APPROACHES

INTRODUCTION

Historically, the metal-working industry has relied upon halogenated solvents for surface cleaning. These solvents were employed because of high cleaning efficiency, quick drying time, and low cost. Cleaning methods included solvent wiping and vapor degreasing, efficient methods of removing organic contaminants from surfaces containing small crevices and for cleaning oil-impregnated parts such as bearings. However, two of the most common solvents used in solvent cleaning processes, TCA (1,1,1 trichloroethane) and CFC – 113 (trichlorotrifluoroethane) have been found to cause ozone depletion as well as serious health hazards. For these reasons the Clean Air Act Amendments of 1990 banned their production in 1995.

Current emphasis is on switching from traditionally used volatile solvents to new aqueous-based cleaning technologies. Primary reasons for the replacement of halogenated solvents include^{1,2}: (1) rising costs associated with compliance with increased environmental legislation, (2) health and safety concerns associated with solvent-based methods, (3) increased restriction on the use of other halogenated solvents. Properly utilized aqueous cleaners can be as effective as vapor cleaners, and can provide a reduction of generated hazardous waste³.

Aqueous cleaning, as the name suggests, utilizes water as the main ingredient of the cleaning process. Lorincz⁴ reports cleaning capability to be controlled by the following: type of contaminant, intricacy of parts, material of construction, and cleanliness level required. Agitation of the part to be cleaned is also very important. Scislowski⁵ reports agitation to speed up removal of oils, soils, and greases from the surface for the simple reason that it brings fresh solution in contact with the contaminants, and the physical action itself helps to dislodge the materials clinging to the surface. Temple⁶ reports impingement to be a key factor in aqueous cleaning. According to the author, 80% of the cleaning is affected by mechanical action while only 20% by chemical action. Thompson and Eichholtz⁷ compared the cleaning efficiency of oils from a stainless steel surface by vapor degreasing of several chlorinated solvents and ultrasonic cleaning by aqueous surfactants. The authors conclude ultrasonic cleaning yielded the cleanest surfaces and was found to be especially effective in removal of oils from small pores and crevices in the surface.

Due to the high surface tension of water (72 dynes/cm), surfactants are added to reduce the surface tension, allowing the cleaning solution to displace the contaminant of interest. Surfactants are known to enhance the cleaning power of water by a combination of effects, involving adsorption at interfaces, alteration of interfacial tensions, solubilization, and emulsification of contaminants⁸. Since the type of surfactant formulated used in the cleaning bath is specific for a particular contaminant and substrate,

there arises a need for quick, simple, economical screening methods for predicting the type of surfactant formulation needed for efficient removal of a particular contaminant.

To the authors' knowledge, selection of aqueous-based cleaners is based almost entirely upon "trial and error" methods and knowledge gained through practical experience. Evaluation of a cleaner's success is measured by a technique of weight gain based on American Society for Testing and Materials (ASTM) standards. Tam¹ has demonstrated that weight gain can be used objectively to evaluate the efficiency of a cleaner under various conditions.

Previously, Ng and Brand⁹ presented a way to logically and experimentally screen cleaning formula candidates for effective contaminant removal. The method is performed by comparing the contact angle of a water droplet on a clean surface with that on a contaminated surface after cleaning with a candidate cleaning solution. If the cleaning solution fails to adequately remove the contaminant, the contact angle of the water drop on the treated surface is much higher than the control, while effective cleaning of contaminated surfaces yields a contact angle similar in magnitude to that of the control surface. Ng and Brand⁹ illustrated the approach using stainless steel surfaces and tetradecane as the model contaminant. While effective, that approach requires equipment to measure contact angle and requires high accuracy measurements.

Starkweather et al.¹⁰ monitored detachment time of oil drops from stainless steel surfaces while varying surfactant concentration and pH of cleaning solutions. It was shown that alteration of the cleaning solution pH could dramatically reduce the time

required for drop detachment. The authors indicated that drop detachment time could be quantitatively predicted by measuring interfacial tension under various solution conditions. Starkweather et al.¹¹ also performed cleaning tests with oil-contaminated ball bearings in surfactant solutions of different pH. It was found that pH had a similar effect on drop detachment kinetics. These findings suggest that oil-drop detachment tests could be used to predict cleaning solution effectiveness.

THE EXPERIMENTS

This work aims to show that simple laboratory-scale, drop-detachment tests can be used to guide the selection of cleaning solutions for industrial cleaning approaches. The experiment section will be divided into two parts: 1) single-drop detachment experiment 2) ultrasonic cleaning bath effectiveness experiment. In these experiments three cleaning solutions, each containing a single surfactant and pH and ionic-strength modifiers, were employed. For each cleaning solution, tests were conducted with variation of two parameters including pH and ionic strength.

Single Drop Detachment Experiment

These experiments are carried out by using a dedicated apparatus capable of monitoring the evolution of oil droplet detachment from a polished stainless steel surface in the desired aqueous surfactant solution. The purpose of this experiment is to determine the kinetics of oil droplet removal from the surface while modifying the cleaning

solution. The monitoring apparatus included a high quality image camera connected to a video camera recorder and television monitor. A schematic of the experiment is shown in Figure 1.

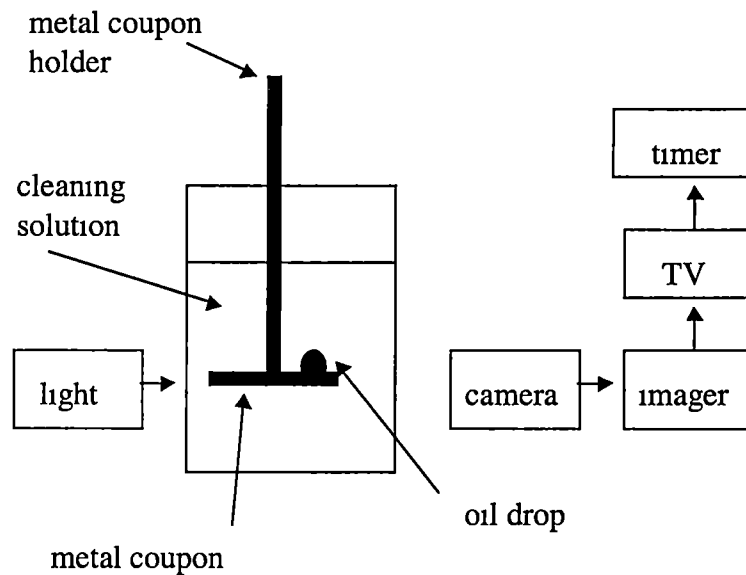


Figure 1. Schematic of drop detachment experiment

Typically, a 200-ml aliquot of the prepared surfactant solution was added to a 250-ml square-shaped glass beaker in which the metal coupon will be submerged. The polished stainless steel coupon used was rinsed and cleaned after each experiment with a solution of 2% Micro detergent/de-ionized water mixture and water. The metal surface was allowed to air dry for 5 minutes, then 2 microliters of Mar-Temp 355 oil (the contaminant chosen in the study) was added as in a spherical drop by use of a pipeter.

The oil was allowed to contact the metal surface for 5 minutes before the metal coupon was submerged in a square beaker of surfactant solution. The drying time of the metal surface after pre-washing, time allowed for the oil droplet to contact the surface, room temperature, drop size, surfactant concentration, and monitoring methods were maintained unchanged throughout the study

Ultrasonic Cleaning Bath Experiment

To verify that small-scale cleaning experiments are relevant to actual cleaning processes, tests of oil removal under similar cleaning solution conditions were conducted using a bench-top ultrasonicated cleaning bath (Crest Ultrasonics). The ultrasonic bath used in this study is shown in Figure 2. The objective was to illustrate a direct correlation between these cleaning results and those of single drop detachment. The same surfactants were used in this cleaning study. In this experiment a stainless steel coupon was first cleaned in a solution of Micro detergent and rinsed well with de-ionized water. The coupon was then dried in an oven for 5 minutes at 120 °C. The coupon was cooled to room temperature and the mass of the clean coupon W was recorded. The coupon was submerged in Mar Temp-355 oil for 5 minutes then hoisted by an attached wire to drain excess oil for 3 hours. The contaminated coupon with mass of X was placed inside a 2000-mL glass beaker containing the desired surfactant solution. The beaker was placed inside the Crest Ultrasonic bath while the bath was tuned to 108 watts of output. Upon removal from the bath, compressed air was blown along the surface of the cleaned metal

for 1 minute to remove excess solution for. The mass of the cleaned coupon *Y* was recorded. Percent oil removal was calculated by the equation:

$$\text{Percent oil removal} = [(X-Y)/(X-W)]*100$$

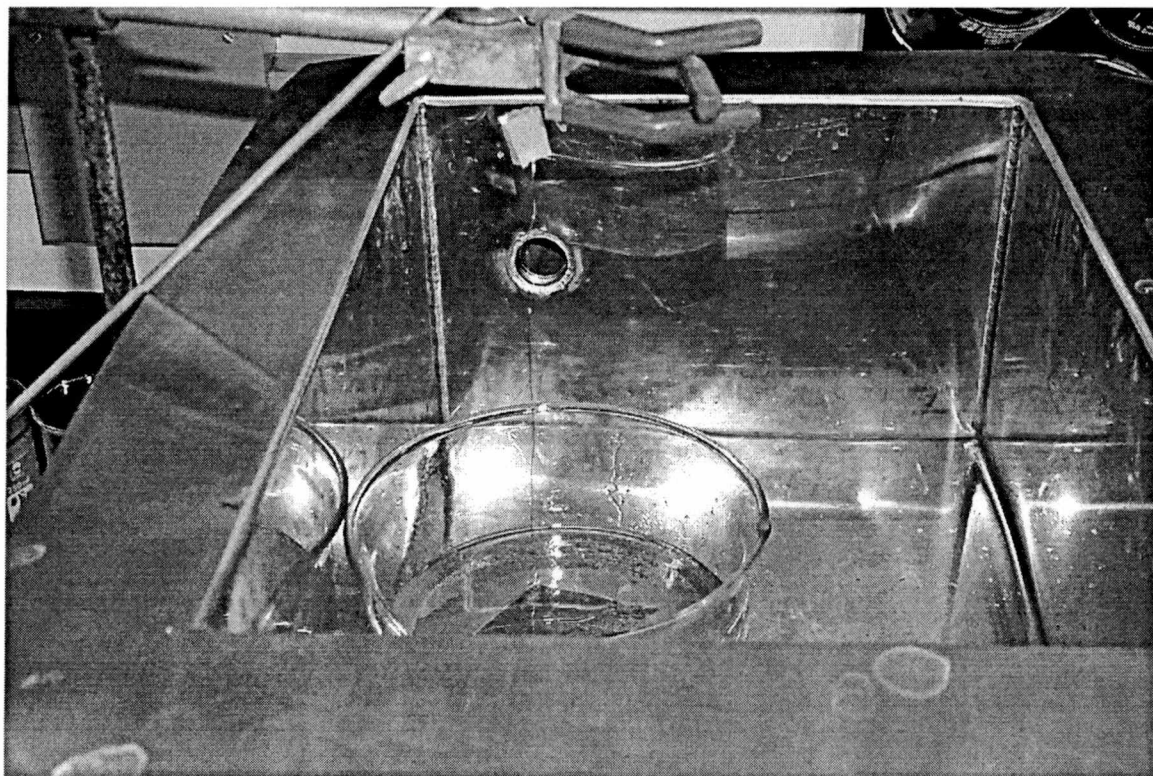


Figure 2. Ultrasonic bath used in this study

RESULTS AND DISCUSSION

The relationship between oil-drop detachment and cleaning effectiveness is best investigated by plotting data for cleaning effectiveness directly against drop detachment time for tests conducted at matching conditions. For a direct relationship, such a plot will have a negative slope, since conditions of greater oil removal in cleaning tests would correspond to lesser detachment times. Results are shown below for three different cleaning solutions with variation of two different parameters.

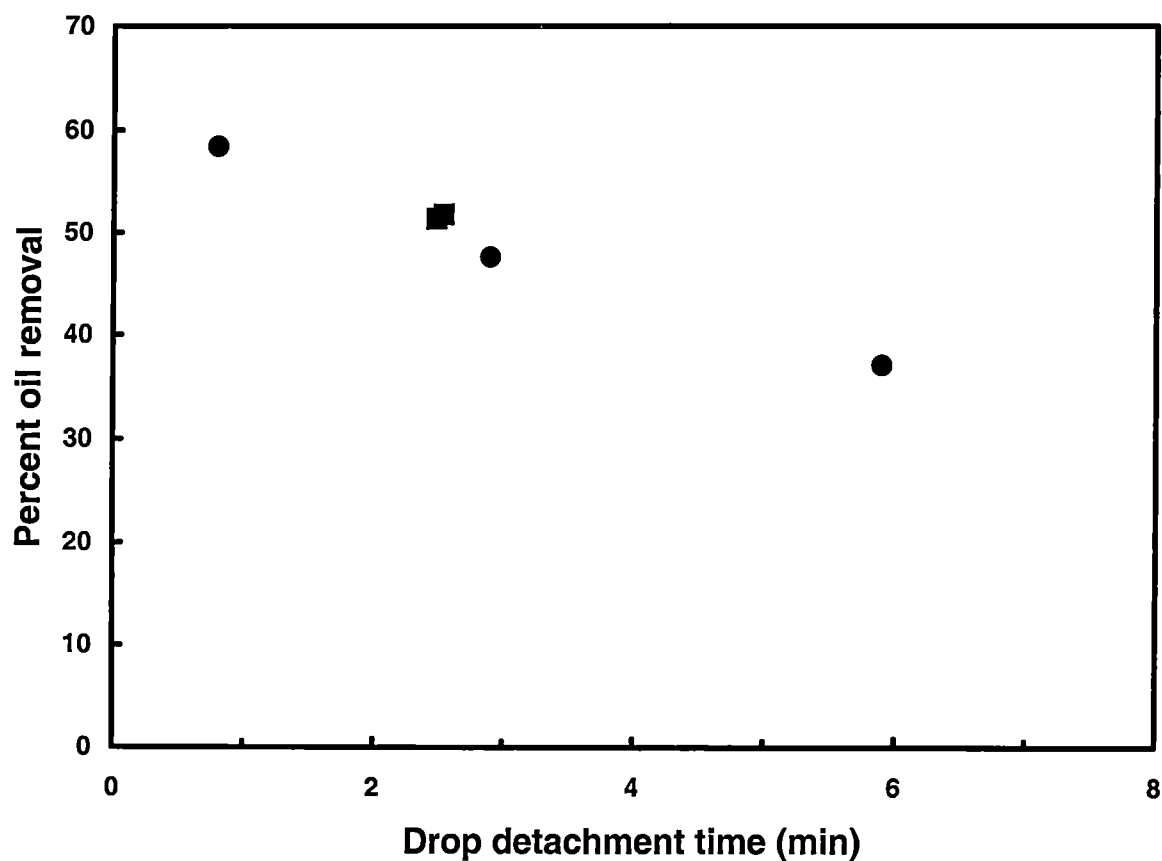


Figure 3. Correlation between drop detachment time to effectiveness of ultrasonic cleaning for a cleaning solution containing an anionic surfactant with variation of two parameters – pH (circles) and a proprietary property (squares) An additional point lies at a detachment time of 127 minutes and 38.6% removal.

Figure 3 shows a comparison of the measured detachment times of oil drops from stainless steel surfaces and the measured cleaning effectiveness in an industrial ultrasonic cleaning bath for the same surfaces using a cleaning solution containing an anionic surfactant. As shown in Figure 3, as both parameters (pH and proprietary parameter) are varied, cleaning effectiveness decreases monotonically as single-drop detachment time

increases. As pH is increased from 6.1 to 10.1, drop detachment time decreases from 5.9 minutes to 0.8 minutes, and cleaning effectiveness increases from 37.1% to 58.4%.

Likewise, as the proprietary parameter is varied in the proper direction, drop detachment time decreases from 127 minutes to 2.5 minutes, and cleaning effectiveness in the ultrasonic bath increases from 38.6% to 51.8%. Results for this cleaning solution indicate that a decrease in drop detachment time adequately predicts an increase in the contaminant removal effectiveness in the ultrasonic bath.

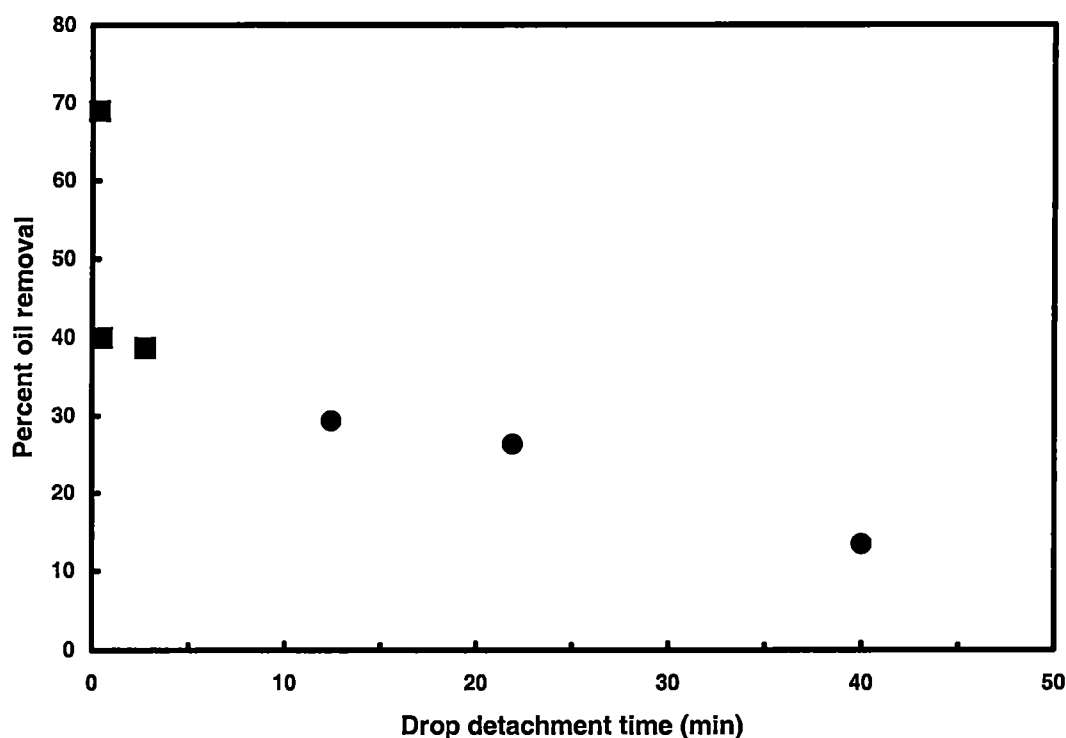


Figure 4. Correlation between laboratory-scale oil drop detachment time to effectiveness of ultrasonic cleaning for a cleaning solution containing a cationic surfactant with variation of two parameters – pH (circles) and ionic strength (squares).

Figure 4 shows a similar correlation between detachment times and cleaning effectiveness for a cleaning solution containing a cationic surfactant with variation of pH and ionic strength. As shown in Figure 4, as both parameters are varied, cleaning effectiveness decreases monotonically as single-drop detachment time increases. As pH is increased from 2.0 to 10.1, drop detachment time decreases from 40 minutes to 12.5 minutes, and cleaning effectiveness increases from 13.4% to 29.3%. Likewise, as the ionic strength is increased from 0.001 to 0.05 *M*, drop detachment time decreases from

2.8 minutes to 0.35 minutes, and cleaning effectiveness in the ultrasonic bath increases from 38.7% to 69%. As with the previous example, the data for this cleaning solution indicate that a decrease in drop detachment time adequately predicts an increase in the cleaning effectiveness with variation of two parameters. The sharp slope observed at low values of detachment time indicates the sensitivity of cleaning effectiveness to detachment time. That is, if the drops detach very quickly, the solution is more likely to be effective in cleaning.

Figure 5 shows similar data collected for solutions containing a nonionic surfactant, with variation of two parameters, pH and a proprietary parameter. Showing a similar trend to the anionic surfactant, as pH is increased from 1.7 to 12.0 drop detachment time decreases from 28.3 to 0.45 minutes, and cleaning effectiveness increases from 13.7% to 35.9%. The relationship between drop detachment time and cleaning effectiveness also has a negative slope with variation of the other parameter; however, the curves do not coincide. With variation of the second parameter, conditions resulting in a drop detachment time of 17 minutes correspond to a cleaning effectiveness of 37.8%, while a drop detachment time of 3.25 minutes corresponds to a cleaning effectiveness of 50%. This large difference in the magnitude of cleaning effectiveness for similar drop detachment times may be due to different mechanisms of oil removal under different cleaning conditions.

This final example indicates that the results of drop detachment should be interpreted with care. The tests appear to be quite valuable for quickly identifying

cleaning trends when varying a single parameter; however, the tests could give misleading results under certain conditions if multiple parameters are varied. Certainly, the selection of a candidate cleaning solution should be verified by pilot cleaning tests under realistic conditions.

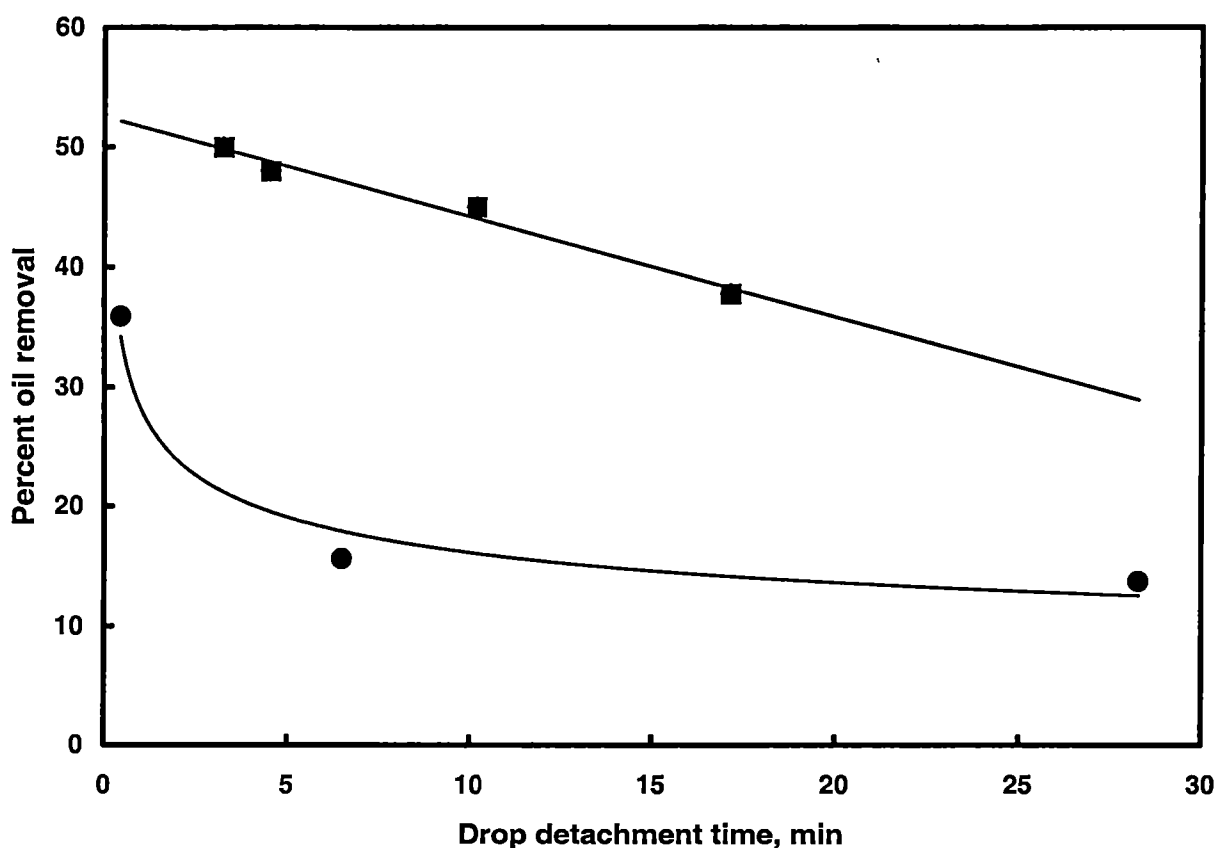


Figure 5. Correlation between laboratory-scale oil drop detachment time to Effectiveness of ultrasonic cleaning for a cleaning solution containing a nonionic surfactant with variation of two parameters – pH (circles) and a proprietary property (squares).

SUMMARY

The idea of a simple laboratory drop detachment experiment at predicting the cleaning effectiveness in an industrial ultrasonic bath is supported by data collected in Figures 3,4,and 5 for three different types of cleaners (based upon the type of surfactants) This promises to be very useful in the cleaning industry which is based largely upon a trial and error method of testing one formula after another until finding the most effective formulation for the application intended. Instead of testing each formulation at the industrial-scale level, a simple technique of monitoring the desired oily contaminant detachment time from the surface of interest can provide the same results without generating large amounts of waste, lengthy time, and large expenditures. For each case, cleaning solution conditions that favor rapid oil displacement also favor a higher cleaning effectiveness inside the ultrasonic bath, whereas cleaning solution conditions that impede oil removal drastically reduce the cleaning effectiveness in the ultrasonic bath. With this in mind, it is simple, economical, and quick to predict the cleaning effectiveness from a simple laboratory experiment requiring only a small aliquot of cleaning solution, glass beaker, a sample of the surface of interest, the desired contaminant to be removed, and a stopwatch.

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PART IV

Effect of Electrical Potential on Oil Detachment from Solid Surfaces in Aqueous Surfactant Solutions

ABSTRACT

Oil drop detachment from a solid surfaces submerged in an aqueous surfactant solution involves surfactant molecule adsorption at the oil/aqueous and solid/aqueous interfaces. Previous studies have investigated the effect of surfactant adsorption at the oil/aqueous interface on the reduction of interfacial tension, which is responsible for enhancing the oil detachment from solid surfaces. However, we believe that surfactant adsorption at the solid/aqueous interface also plays a significant role in the oil detachment process. In this paper, an electrical potential was applied on a solid substrate (metal) and the effects of electrical potential on oil drop detachment and oil-layer removal from solid surfaces were studied. Experiments were conducted with four types of surfactants (cationic - CTAB, anionic - SDS, nonionic - Triton X-100, and zwitterionic - Chaps) to observe the time required for detachment under various surface electrical potentials. It was discovered that the surface electrical potential (0 to ± 4 volts) significantly affects the kinetics of oil detachment and removal as well as cleanliness of solid surfaces. A mechanistic model based on the surfactant accumulation/depletion near the solid/aqueous interface and electrostatic repulsion was developed to explain the surface potential effect. The accumulation of surfactant molecules near the solid and oil

surfaces reduces the solid/aqueous and the oil/aqueous interfacial tension and, thus, enhancing the oil detachment. On the other hand, if the applied surface potential and the surfactant head groups are like charged, a depletion of surfactants at the surface may slow the drop detachment process. Depending on the charge of the surfactant molecule, electrostatic repulsive forces between the solid surface and the surfactant molecules adsorbed at the oil/aqueous interface may be strong enough to displace the oil drop regardless of surfactant depletion. In addition, it was found that drop-detachment time measurements provide a direct means to predict oil-removal in an ultrasonic bath.

INTRODUCTION

Oil contaminant removal from a solid surface represents a significant process for industrial cleaning and surface decontamination applications. Chlorinated solvents have long been used by industry for cleaning processes. However, they have been identified as causes of environmental and health concerns [2]. For this reason traditional solvents need to be replaced with aqueous-based solutions. Aqueous-based cleaning technology is a surprisingly complex process involving transient interactions among cleaning solutions, contaminants, and substrate surfaces. Surfactant adsorption is an important phenomenon involved in aqueous cleaning processes. In fact, the adsorption of surfactants on solid surfaces is important in many areas such as enhanced oil recovery, surfactant-enhanced soil remediation, formation of organic thin films, ore flotation, wetting, adhesion, detergency, and dispersion stability [1]

In an aqueous surfactant cleaning process, the interfacial tensions (free energies) among the contacted phase (aqueous/oil – AO, aqueous/solid – AS) change as a result of surfactant molecule interactions with the interfaces. An examination of Young's equation (1) reveals that the wetting behavior of a liquid on a solid substrate, characterized by a contact angle, is critically affected by free energies in the AO, AS, and the oil/solid (OS) interfaces.

$$\gamma_{AO} \cos\theta = (\gamma_{AS} - \gamma_{OS}), \quad (1)$$

where θ is the contact angle, γ_{AO} is the interfacial tension between the organic phase and the aqueous phase, γ_{AS} is the interfacial tension between the aqueous phase and the solid, and γ_{OS} is the interfacial tension between the organic phase and the solid. Surfactant adsorption at AO and AS interfaces can cause these free energies or interfacial tensions to reduce dramatically [3]. Concomitant effects on contact angle and contact line are then observed, which may lead to complete surface coverage or displacement of an oil phase. If the free energy per unit area of the aqueous/solid interface is less than that of the oil/solid, preferential wetting by the solution occurs and the contaminant is released from the surface. Therefore, surfactants have been used to perform the major task of oil removal for surface cleaning and decontamination. Previous studies have investigated the effect of surfactant adsorption at the oil/aqueous interface on the reduction of interfacial tension, which is responsible for enhancing the oil detachment from solid surfaces. However, we believe that surfactant adsorption at the solid/aqueous interface also plays a significant role in the oil detachment process.

Surfactant Adsorption

The adsorption of surfactants onto charged surfaces have been widely studied. Surfactants are known to adsorb onto hydrophilic surfaces based upon the charge imposed on the surface. Our earlier work has shown that variation of the solution pH dramatically alters the charge of the oil drop surface, charge of the solid surfaces, as well as the charge of surfactant molecule (per zeta potential measurements) [16]. Petermann et al. [17] measured the zeta potential of several passive metals finding that with low pH solutions, the metal surface is positively charged whereas high pH solutions deprotonate the surface leading to a negatively charged surface. The isoelectric point of stainless steel surface was determined to be near a pH of 4.

Ralston and Kitchener [19] studied the adsorption of CTAB on amosite asbestos and concluded that at low concentrations of 10^{-5} M there is a layer with an area of nearly $100 \text{ \AA}^2/\text{molecule}$ while above 10^{-4} M the area drops to $26 \text{ \AA}^2/\text{molecule}$. A lowering of the contact angle at higher concentrations is attributed to formation of a bilayer with polar heads next to the aqueous phase. Cases and Mutaftschiev [20] have reported adsorption isotherms for CTAC (the analogous chloride) on biotite and conclude that a bilayer structure is obtained at concentrations near cmc. Rennie et al. [21] used the technique of specular reflection of neutrons to study the structure of a layer of CTAB adsorbed onto an amorphous silica surface. The authors report bilayer coverage at high concentrations. Even at concentrations well below cmc the adsorbed layer is substantially thicker than that expected for a simple monolayer.

The major driving force for formation of surfactant aggregates is to achieve the minimum contact area between the hydrophobic ends of the surfactant molecule and the surrounding water molecules [22]. The major opposing force is the decrease in the conformational entropy of the polar head group and the accompanying counterion. Wangerund and Jonsson [22] report that at low surfactant concentrations these two contributions to the gain in free energy for formation of a bilayer will not be large enough to overcome the loss in entropy due to gathering of surfactant monomers needed to form the bilayer. This entropy loss decreases with increasing surfactant concentration, and at a certain concentration the formation of a bilayer is possible. The exact concentration of the bilayer formation has been greatly debated however most researchers agree that the critical bilayer formation concentration $> \text{cmc}$.

Nassauer and Kessler [23] reported that adsorption of surfactants onto metal surfaces could greatly be affected by surface electrostatic potential, influenced by the pH and oxidizing power of cleaning solutions. Hodgson and Berg [18] reported that a change in the surface charge by pH variation could affect ionic surfactant adsorption thus altering the hydrophobicity of the solid surface. Wahal and coworkers [3] performed experiments involving aqueous droplets containing surfactants resting in air on the surface of a parallel plate electrode. Their results indicated that contact angles always decrease, regardless of the polarity of the applied electric field, while the magnitude of the change is sensitive to both polarity and strength of the field.

Oil Detachment From A Solid Surface

Single oil droplet detachment kinetics have been studied to help understand the physics of the oil removal process. Scheele and Meister [4] discussed the various forces involved drop detachment process. The buoyancy force acts in an upward force to detach the drop while the interfacial tension between the solid/oil interface acts to attract the oil to the surface thus hampering displacement. Only when the buoyancy forces overcome the net interfacial tension force will the drop be detached from the surface.

There is a considerable amount of technical literature covering the subject of oil removal from model surfaces by adsorption of surfactants at the aqueous/oil interfaces [5-12]. Thompson [2] reports three major mechanisms for the removal of oil drops from a substrate including emulsification, roll-up, and solubilization. The first two are the most important to our study since the concentrations used are at cmc (critical micelle concentration). For solubilization to take place the concentration of surfactant used must be greater than or equal to cmc [5]. Partial drop detachment, or emulsification, occurs when the surface tension forces holding the drop together are exceeded by gravitational and hydrodynamic forces pulling it apart. Thompson [2] lists oil/water interfacial tension, contact angle, and drop size as factors in determining the ease in which the drop ruptures and the proportion of the drop that detaches. The continued importance of the contact angle demonstrates that roll-up is, however, an integral part of the emulsification process.

It has previously been shown that oil drop detachment kinetics depend on the surfactant solution properties including concentration and pH. Starkweather et al. [10] has shown that an increase in surfactant solution concentration up to the cmc results in a decrease in the time needed for oil drops to detachment from a solid surface. The authors also studied the effect of solution pH on drop detachment kinetics. They found, for a nonionic surfactant, as solution pH increases, oil drop detachment time due to the decrease of aqueous/oil interfacial tension. This agreed well with trends observed by Basu et al [13] for an interface of bitumen and water. Liggieri et al. [15] showed that as the concentration of Triton X-100 (nonionic) increases, the interfacial tension of the aqueous/oil interface decreases. The findings of Carroll [7] and Starkweather et al. [10-11] suggest that the removal of oil drops from a metal surface should be more rapid with solutions exhibiting a lower aqueous/oil interfacial tension. Tsekov [14] studied the attachment of organic droplets at a liquid/mercury interface and the liquid mercury was used as an electrode. The decrease in the water/mercury interfacial tension was attributed to the effects of applied voltage.

In summary, earlier work by us [16] and others has shown that solution pH indirectly alters the electrostatic charges at the solid surface which, in turn, has a significant effect on adsorption of surfactant molecular monolayers. In this work, we have demonstrated that interfacial tension variation at the aqueous/solid interface due to the accumulation/depletion of surfactant molecules plays a significant role in the oil detachment process, although the aqueous/oil interfacial tension and electrostatic

repulsion are also important parameters. Experiments of oil detachment/removal from solid surfaces were conducted with various constant solid surface electrical potentials, which are believed to affect the surfactant accumulation/depletion (thus, the interfacial tensions) behavior near the aqueous/oil and aqueous/solid interfaces. A mechanistic model of surface electrical potential effect was proposed and explained our experimental data for oil drop detachment and oil removal in all types of surfactant solutions. It was also found that drop-detachment time measurements provide a direct means to predict oil-removal in an ultrasonic bath.

PROPOSED MECHANISTIC MODEL

In the presence of an electrical potential on the solid surface the earlier proposed electrostatic surfactant adsorption model [16] for interpretation of surfactant effect on oil detachment from a solid surface have to be modified. The major difference in these two situations is the nature of the surface potential (electrical potential versus electrostatic potential). The applied electrical potential is maintained constant (not affected by the solution conditions) and the electrical field effect is long-ranged. In contrast, the surface potential due to electrostatic charges is short-ranged and can be varied/neutralized by changing solution conditions such as variation of pH, ionic strength, etc

It is widely known that at low surface electrostatic charge densities a monolayer of surfactants adsorbs at the solid surface [22]. Adsorption occurs due to electrostatic attraction and the monolayer is able to neutralize the charge imposed on the solid

surface. In the presence of applied voltage (electrical potential) on a solid surface, a monolayer of surfactants adsorbing to the surface is no longer able to neutralize the surface charge. The electrical field due to constant electrical potential near the solid surface can continue to attract unlike-charged surfactant molecules or repulse the like-charged molecules, resulting in the accumulation or depletion of surfactant molecules near the solid surface. The adsorption process is known to be a function of surfactant concentration, surface charge density, and the nature of the surface electrostatic potential. Since the same surfactant concentrations are used throughout the study (their respective cmc concentration), the only variable is the magnitude and polarity of electrical potential applied on the solid surface.

As the electrical potential across the metal surface increases, so does the long-ranged attractive/repulsive electrical forces between the surface and individual surfactant ions. At extremum cleaning solution pH, Kessler [23] measured the surface electrostatic charge to only be 1000 mV which is insufficient for surfactant aggregate formation to take place resulting in only a monolayer adsorbed to the surface [22]. At high surface electrostatic charge densities a strong repulsive force is thought to exist when surfactant ions are like-charged as the solid surface charge, thus depleting the surrounding solution of surfactant ions. The strength of the repulsive force is dependent upon the charge of the surfactant head group. By Coulomb's Law if a highly charged anionic surfactant (per zeta potential measurements) contacts a highly negatively charged surface, the repulsion is expected to be greater than that between the same highly charged negatively surface and

a weakly charged anionic surfactant. When a weakly charged anionic surfactant is used in combination with a negatively charged solid surface; this is expected to result in a local depletion of the surfactant molecules adsorbed at the solid/aqueous interface. If the surfactant head groups and the solid surface are highly similar charged, it is believed the long-ranged electrical repulsive force between the drop surface and the solid surface is high enough in magnitude to repel a portion of the oil drop even though surfactants may be depleted near the aqueous/solid interface. This mechanistic model based on the accumulation/depletion phenomena and long-ranged electrostatic repulsion between solid surface and the oil surface can be applied to various situations with different surfactants and solid surface electrical potential. Figure 1 illustrates the proposed mechanistic model.

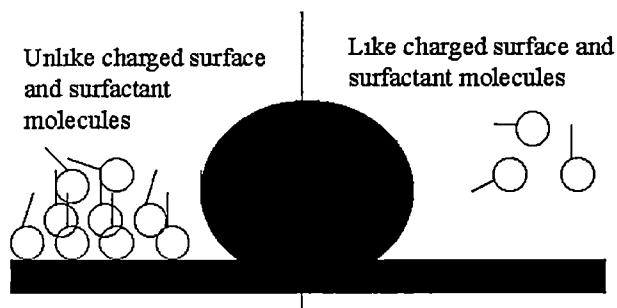


Figure 1. Proposed mechanistic model depicting the effect of applied electrical potential on accumulation of surfactant molecules (Left) or depletion (Right).

EXPERIMENTAL METHODS

Experiments were conducted with aqueous solutions of each of four different surfactants. In all cases the oil contaminant was Mar-Temp 355 quenching oil (Houghton International), consisting mostly of mineral oil. A polished stainless steel coupon was

used as the surface for cleaning. Starkweather et al. [10] measured the roughness to be 1975 Angstroms. All experiments are conducted at room temperature and atmospheric pressure. The surfactant solutions were prepared fresh daily to ensure consistent data. The surfactants along with their respective concentration used in the study are shown in Table 1 [24]

Table 1. Surfactants used in this study

<u>Surfactant</u>	<u>Abbrev.</u>	<u>Type</u>	<u>CMC</u>	<u>Supplier</u>
Octophenol polyglycol ether	Triton X-100	Nonionic	0.0003 M	Fisher Biotech
Cetyltrimethyl ammonium bromide	CTAB	Cationic	0.007 M	Aldrich
Sodium dodecyl sulfate	SDS	Anionic	0.008 M	Fisher Biotech
3-[(3-cholamidotriphenyl)- dimethylammonio]-	Chaps	Zwitterionic	Unknown 0.009M	Aldrich

Single Drop Detachment Experiment

The experiments were carried out using an apparatus capable of monitoring the dynamic evolution of droplet shape and droplet detachment from a metal surface in an

aqueous surfactant solution. A stainless steel rod was used as the counter electrode. The purpose of this experiment is to determine the kinetics of oil droplet removal as a function of applied surface potential. HCl and NaOH (both at chemical grade) were used for pH adjustments. The monitoring apparatus included a high quality image camera connected to a video camera recorder and television monitor. A schematic of the experiment set up is shown in Figure 2.

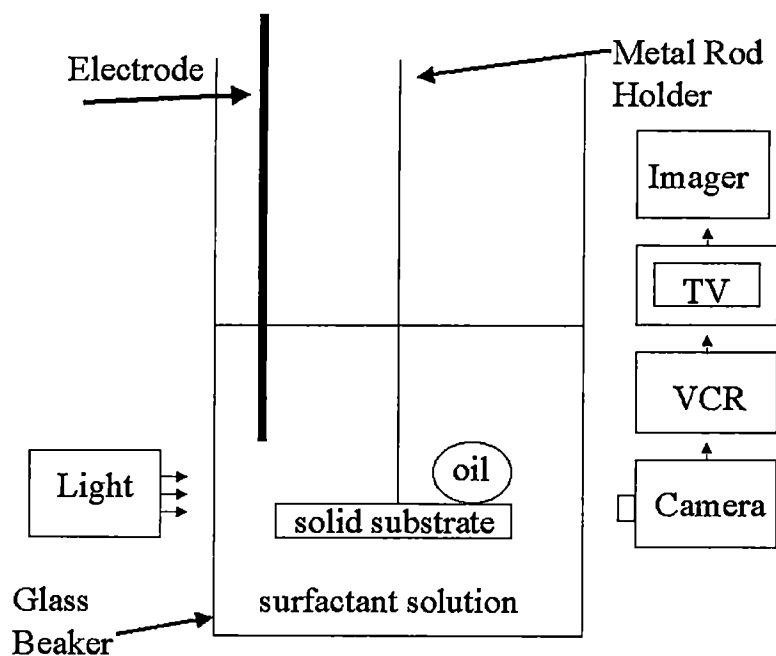


Figure 2. Schematic of drop detachment experiment

A transformer was used to control the brightness of the light source. A video copy processor was used to print a copy of the oil droplet at several stages during the

detachment process. These high quality images were used to monitor the geometry of the droplet near detachment.

Typically, a 200-ml aliquot of the prepared surfactant solution was added to a 250-ml square-shaped glass beaker in which the metal coupon was submerged. The polished stainless steel coupon used was rinsed and cleaned after each experiment with a solution of 2% Micro detergent/de-ionized water mixture and water. The metal surface was allowed to air dry for 5 minutes, then a 2 microliter droplet of Mar-Temp 355 oil (the contaminant chosen in the study) was placed on the metal surface using a pipeter. The oil droplet was allowed to contact the metal surface for 5 minutes before the metal coupon was submerged in a square beaker of surfactant solution. The experimental parameters, including drying time of the metal surface after pre-washing, time allowed for the oil droplet to contact the surface (5 minutes), room temperature (22°C), drop size (2 microliters), surfactant concentration (cmc), and monitoring methods were held constant throughout the study.

Application of Electrical Potential to the Surface

A low-voltage power direct current power supply was used to apply an electrical potential to the coupon during the experiments. When applying electrical potential to the coupon to obtain a positively charged surface, the positive lead of the power supply was connected directly to the stainless steel substrate while the grounded negative lead was connected to a stainless steel counter electrode placed in solution. For a negatively

charged surface, the positive terminal of the power supply was grounded and connected to the counter electrode. Current was also monitored throughout the study; for all experiments, the current was less than 5 mA indicating that minimal electrolysis occurred, and underscoring the low conductivity of the solutions. A schematic of the application of positive surface potential is shown below in Figure 3.

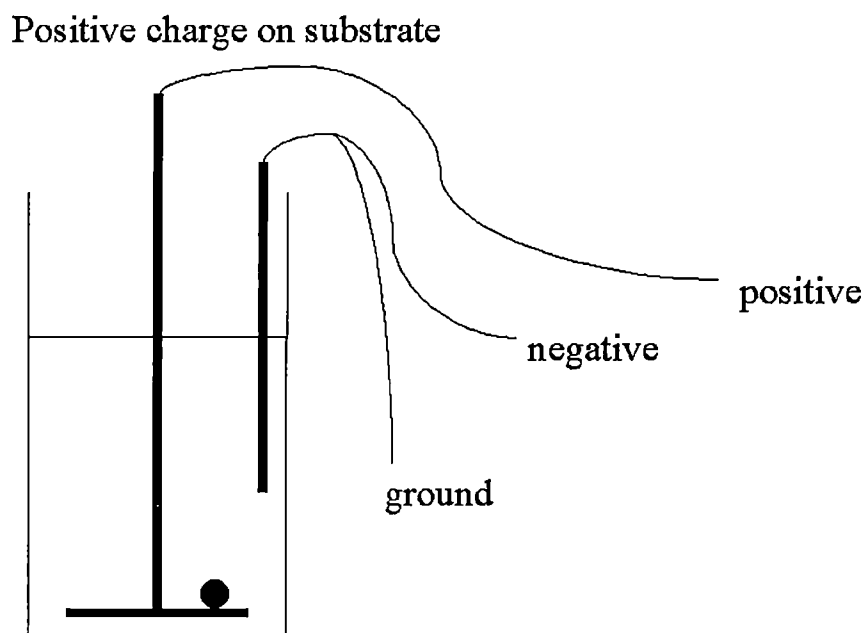


Figure 3. Schematic illustrating how positive potential is applied to the surface.

Bench Top Ultrasonic Bath Cleaning Experiment

Tests of oil removal under similar conditions were conducted using a bench-top ultrasonicated cleaning bath (Crest) to illustrate a direct correlation between these cleaning results and those of single drop detachment experiments. The same four surfactants were used in this cleaning study. In this experiment a stainless steel coupon was first cleaned in a solution of Micro® detergent and rinsed well with de-ionized water. The coupon was then dried in an oven for 5 minutes at 120 °C. The coupon was cooled to room temperature and the mass of the clean coupon W was recorded. The coupon was submerged in Mar Temp-355 oil for 5 minutes then hoisted by an attached wire to drain excess oil for 3 hours. The contaminated coupon with mass of X was placed inside a 2000-mL glass beaker containing the desired surfactant solution. The beaker was placed inside the Crest Ultrasonic bath while the bath was tuned to 108 watts of output. Upon removal from the bath, compressed air was blown along the surface of the cleaned metal for 1 minute to remove excess solution. The mass of the cleaned coupon Y was recorded. Percent oil removal was calculated by the equation:

$$\text{Percent oil removal} = [(X-Y)/(X-W)]*100 \quad (1)$$

RESULTS

The application of electrical potential to a stainless steel surface is shown to affect the effectiveness and kinetics of oil removal in the presence of surfactant solutions. The purpose of this study is to compare trends of oil removal in four types of surfactant

solutions as the magnitude and polarity of an electrical potential delivered to the surface is modified. The data presented will help elucidate the mechanism by which oil is removed from the surface.

Single Drop Detachment Experiment

In this experiment the detachment time of an oil drop from the surface is monitored as a function of applied electrical potential. This experiment quantitatively shows the time needed for the first droplet (two-microliter) to detach from the surface submerged in a desired surfactant solution while modifying the surface potential. In this paper, drop detachment time refers to the time needed for the first emulsified droplet to detach from the sessile oil drop on the surface. These experimental data are shown in Figures 4-9. In each of these experiments no pH modification was made to the cleaning solution except that of Chaps which is zwitterionic.

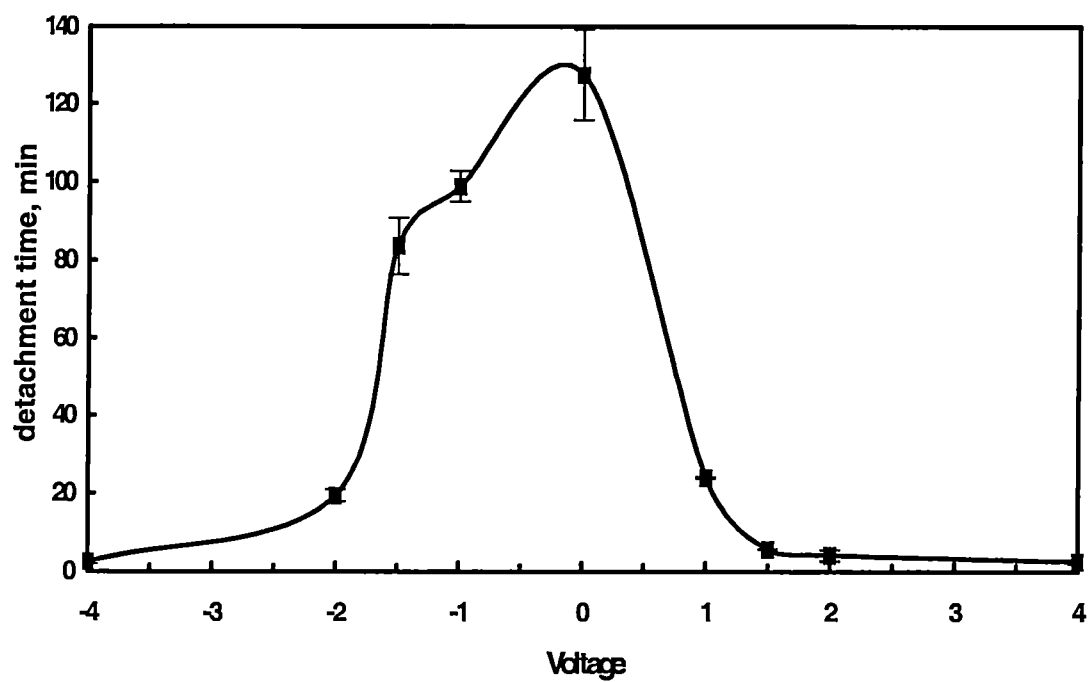


Figure 4. Effect of electrical potential on drop detachment in solutions of SDS

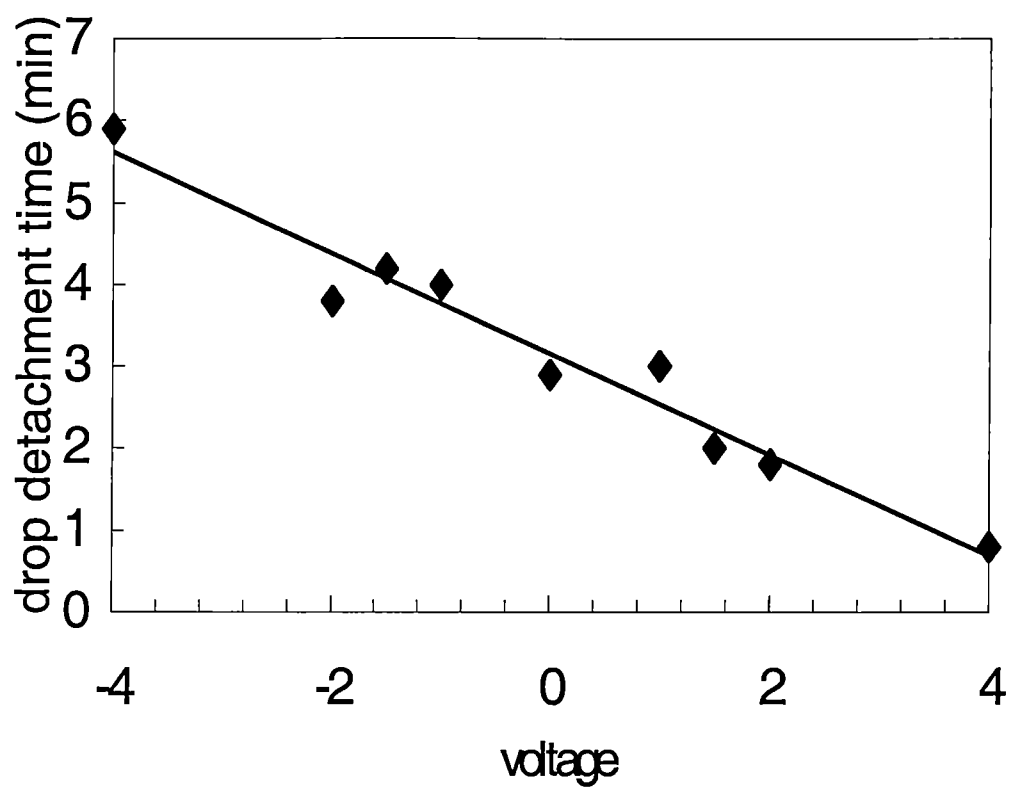


Figure 5. Effect of electrical potential on drop detachment in solutions of Triton X-100

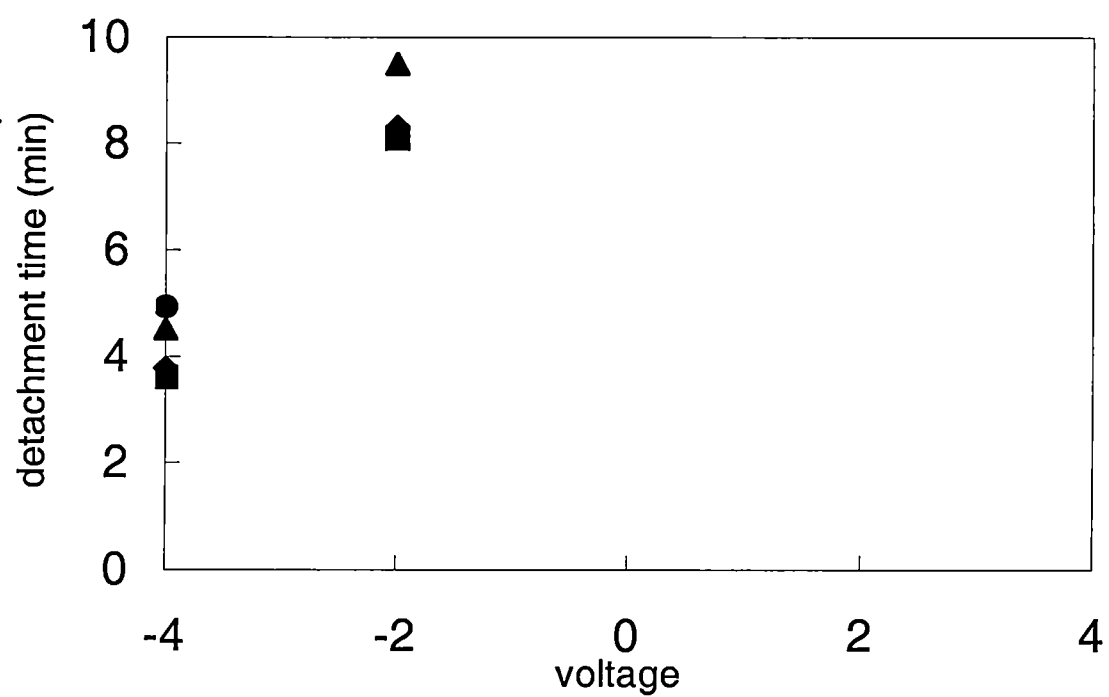


Figure 6. Effect of electrical potential on drop detachment in solutions of CTAB

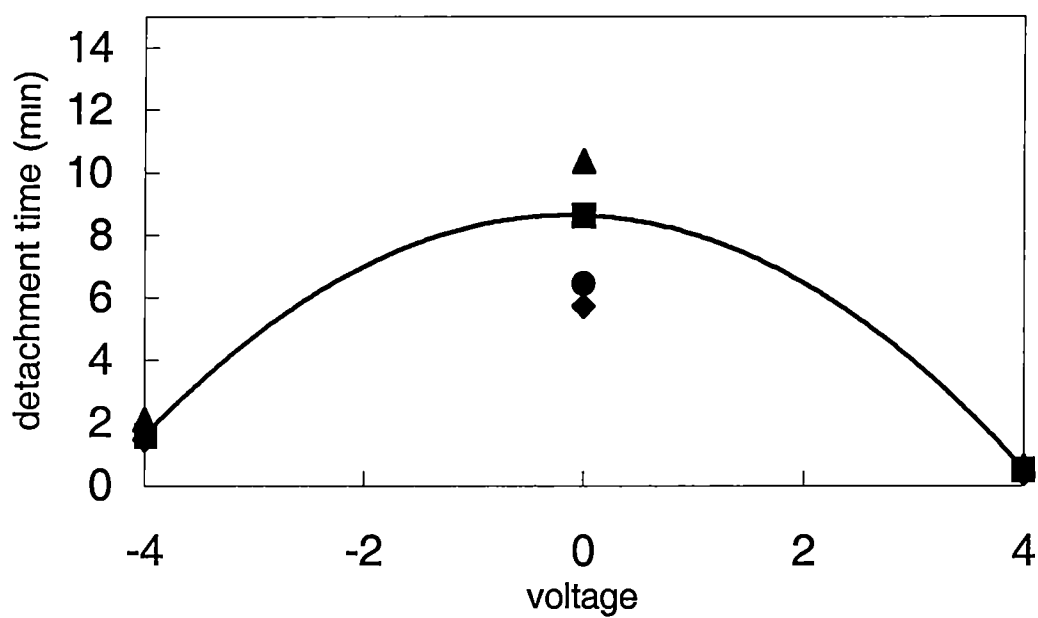


Figure 7. Effect of electrical potential on drop detachment in solutions of Chaps at a pH of 12.15

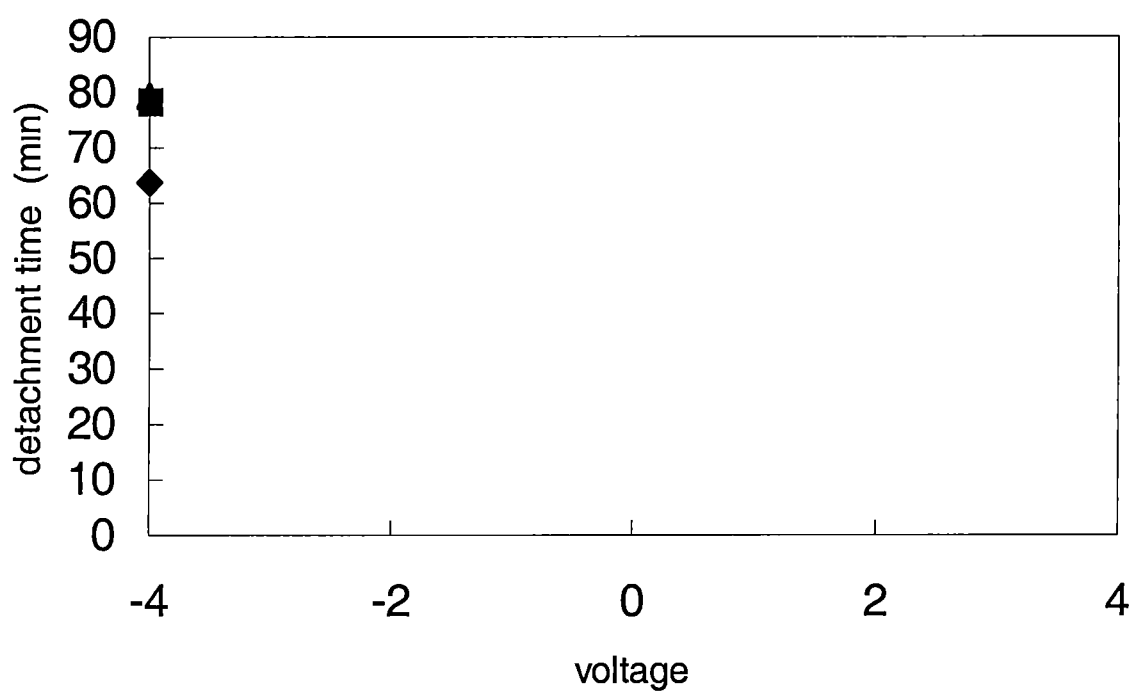


Figure 8. Effect of electrical potential on drop detachment in solutions of Chaps at a pH of 2.75

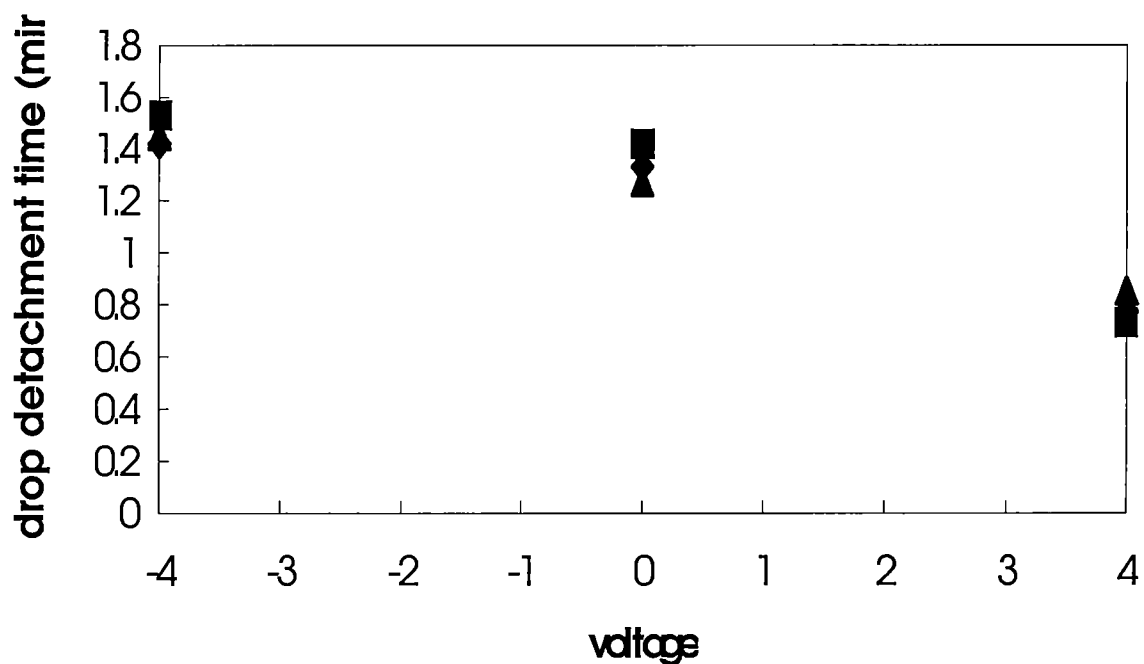


Figure 9. Effect of electrical potential on drop detachment in solutions of Chaps at a pH of 5.95

From the observed data trends in Figure 4, oil droplets show a more rapid detachment time in solutions of the anionic surfactant SDS when the magnitude of applied voltage delivered to the surface is either increased or decreased. The application of ± 4 volts decreases drop detachment time from the zero-voltage case by a factor greater than 50 relative to no surface potential modification. At an applied voltage of $-1.5V$ to the surface, there is a noticeable shoulder in the curve. It is hypothesized that as the

magnitude of applied voltage decreases toward zero there exists a local depletion of surfactant molecules at the surface/aqueous interface due to repulsion between the negatively charge surfactant molecules and the surface. As the magnitude of applied voltage increases past -1.5V there is sufficient repulsion between the oil drop (per zeta potential measurements) and the surface to overcome the surfactant depletion phenomena.

From Figure 5, oil droplets on the surface submerged in solutions of the nonionic surfactant Triton X-100 exhibit a monotonic decrease in detachment time as voltage is increased from negative to positive polarity. Also observed is that the application of negative polarity to the surface results in an increase in detachment time as opposed to the neutral condition. Application of $+4$ volts results in a 3-fold decrease in detachment time relative to the no-voltage condition (no voltage is applied) while application of -4 volts results in a 2-fold increase in oil detachment time.

From Figure 6, oil droplets on the surface submerged in solutions of the cationic surfactant CTAB exhibit a quicker detachment time as negative voltage is applied to the substrate. The oil droplets showed no detachment from the surface in a 2-hour period unless -4 volts were applied to the surface. Oil drops on the substrate at neutral or positive potentials do not show an increase in contact angle evolution for the 2-hour period nor a tendency to detach.

Since Chaps is a zwitterionic surfactant, the ionic character of the surfactant changes as the pH of the solution is varied in order for trends to be compared with those

of nonionic, anionic, and cationic surfactants. Oil drop detachment data is measured for a cleaning solution of pH 12.15, 7.0 and 2.75. These drop detachment data are shown in Figures 7-9. For a pH of 2.75 oil drops detach from the substrate only when a negative voltage is applied only. There is no detachment in a 2-hour period for the positive or neutrally charged substrate. This follows the same qualitative trend as observed for CTAB thereby supporting the proposed model based on electrical interactions since at low pH Chaps acts as a cationic surfactant. On the other hand, when the solution pH is increased to a value of 12.15 a trend similar to SDS solutions is observed where either a decrease or an increase in the magnitude of applied voltage delivered to the surface results in a decrease in detachment time. The application of ± 4 volts results in a 7-fold decrease in detachment time. At an intermediate pH value of 5.95 application of +4 volts results in a decrease in drop detachment time by a factor of 2 while the application of -4 volts results in a slight increase in drop detachment, similar to the trends obtained for the nonionic Triton X-100.

Cleaning Effectiveness Experiment

The effect of voltage on cleaning effectiveness in an ultrasonic bath is shown in Figures 10-12.

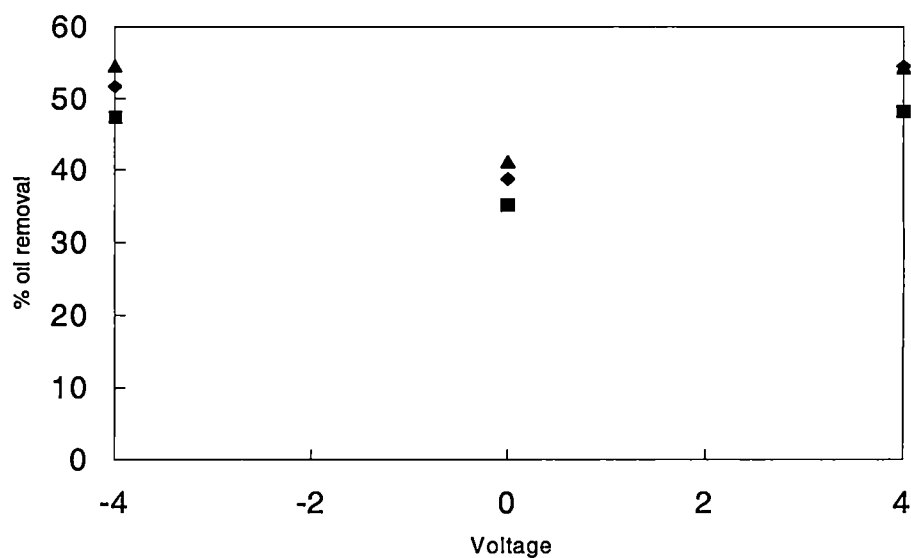


Figure 10. Effect of electrical potential on cleaning effectiveness in solutions of SDS

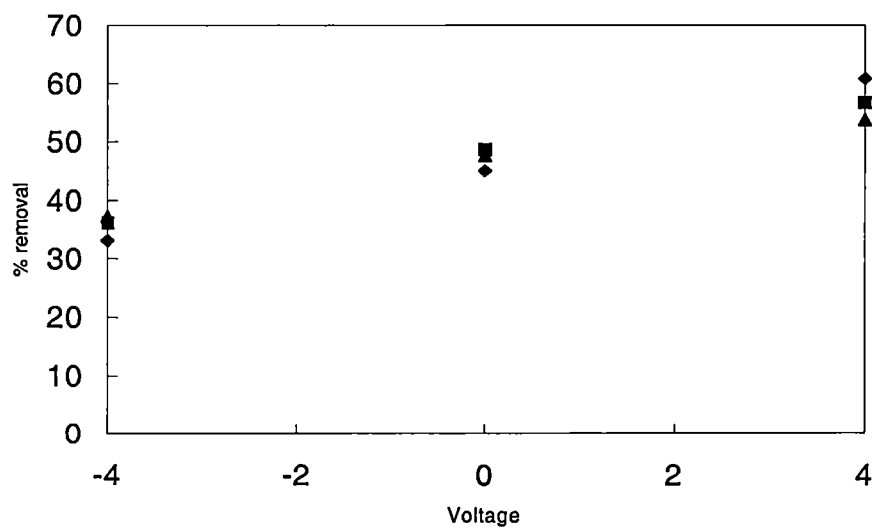


Figure 11. Effect of electrical potential on cleaning effectiveness in solutions of Triton X-100

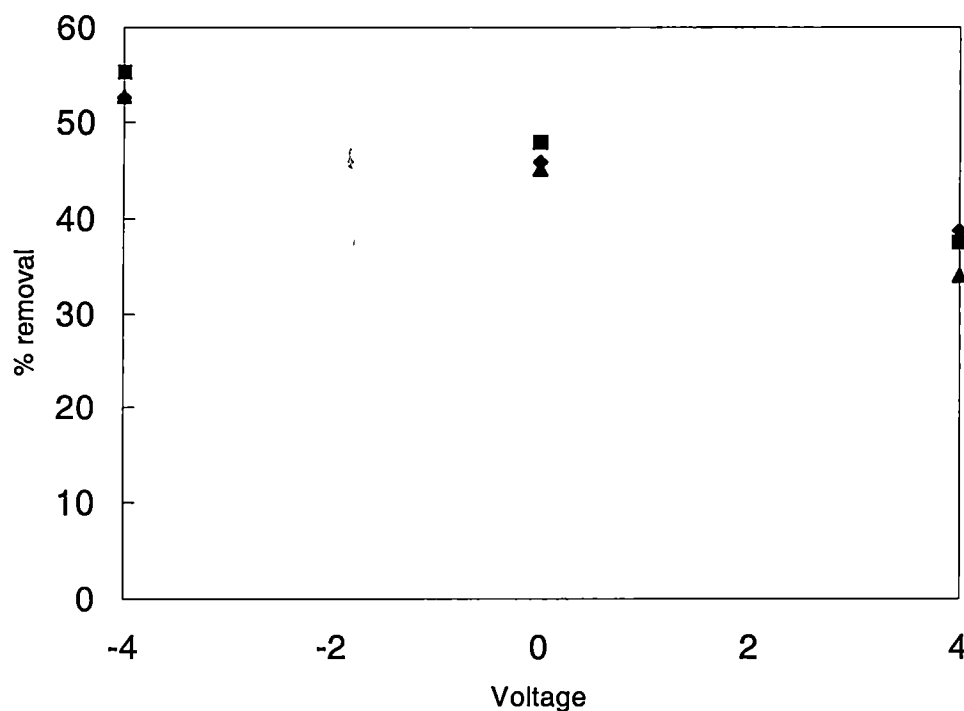


Figure 12. Effect of electrical potential on cleaning effectiveness in solutions of CTAB

In this experiment cleaning effectiveness in an ultrasonic bath is quantified as a function of applied electrical potential delivered to the surface. Figures 10-12 depict the effect of applied electrical potential on cleaning effectiveness in the ultrasonic bath.

The effect of applied voltage on cleaning effectiveness of SDS solutions is shown in Figure 10. An increase or decrease in the voltage from the no-voltage point resulted in a more-efficient cleaning process. For application of ± 4 volts to the substrate, an increase of nearly 15% in cleaning effectiveness is noted. This trend is consistent with the drop detachment time trend in Figure 2, giving a correlation between cleaning effectiveness and drop detachment time. Since cleaning effectiveness increased while drop detachment

time decreased, drop detachment time can be used as a simple indicator to predict ultrasonic cleaning bath results.

The effect of applied voltage on the cleaning effectiveness of Triton X-100 solutions is shown in Figure 11. The trend observed is a monotonic increase in cleaning effectiveness as voltage is increased from negative to positive polarity. The application of +4 volts to the substrate results in a 10% improvement in cleaning effectiveness relative to the no-voltage case, with the application of negative potential reducing the cleaning effectiveness. As with SDS solutions, this trend can be related to the drop detachment time trend in Figure 4

The effect of voltage on the cleaning effectiveness of CTAB solutions is shown in figure 12. The trend observed is a monotonic increase in cleaning effectiveness as voltage is decreased from positive to negative polarity. The application of -4 volts to the substrate results in nearly a 7% improvement in cleaning effectiveness over the no-voltage case with the application of positive potential reducing the cleaning effectiveness. As with solutions containing SDS and Triton X-100, this trend is consistent to the drop detachment time trend in Figure 5. Since no detachment occurred within a 2-hour period, it can be assumed from the ultrasonic bath data that a monotonic decrease in detachment time will likely occur as voltage is decreased from positive to negative polarity.

DISCUSSION

The proposed mechanism for removal of oil by the anionic surfactant SDS will be presented first (Figure 13a). As shown in Figure 4 an increase in the magnitude of voltage results in a significant increase in cleaning effectiveness. Drop detachment kinetics increase by 54 as applied voltage ranges from 0 to ± 4 volts. SDS, by zeta potential measurements, is shown to be highly negative resulting in a long-range repulsive force between the oil drop surface (due to adsorbed SDS molecules at the oil/aqueous interface) resulting in a rapid detachment of the oil drop from the surface. A point of inflection is observed at an electrical potential of -1.5 volts. Application of voltage below a magnitude of -1.5 volts is not large enough to provide a long-range electrical repulsive force between the drop and surface and only is expected to result in a local depletion of surfactant molecules at the surface/aqueous interface. When the applied voltage exceeds -1.5 volts, long-range repulsive forces overcome the local depletion of surfactants resulting in quick expulsion of the oil drop from the surface. This explains the reasoning for negative applied voltage to decrease drop detachment time. With the application of positive electrical potential on the surface, SDS molecules accumulate at the surface in an attempt to neutralize the positive charge. As more and more surfactant accumulate onto the surface, the surfactant aggregation is expected to preferentially wet the surface with respect to the oil therefore competing for surface area and removing the drop.

The proposed mechanism for removal of oil by the nonionic surfactant Triton X-100 will be presented next (Figure 13b). As shown in Figure 5 an increase in electrical potential from negative to positive results in an increase in cleaning effectiveness. Drop detachment kinetics increase by a factor of 6 as applied voltage ranges from -4 to +4 volts. Since Triton X-100 is nonionic, the charge of the hydrophilic group is expected to be neutral, however, zeta potential measurements reveal a slight negative charge [16]. When application of negative potential is applied to the surface, a small repulsive force exists between the surfactant head groups adsorbed at the oil/aqueous interface and the negatively charged substrate. Since the zeta potential measurements show a weak negative charge associated with the hydrophilic group of the surfactant, a limited repulsive force exists. This repulsive force results in the depletion of surfactant adsorbed at the surface which, in turn, does not affect the interfacial tension of the aqueous/solid interface. As voltage applied is increased in the negative direction, less Triton X-100 molecules are adsorbed to the surface thus not having any reducing effect on the interfacial tension. With the application of positive potential across the substrate, Triton X-100 molecules accumulate on the surface in an attempt to neutralize the positive charge. As more and more surfactant molecules accumulate onto the surface, the surfactant preferentially wets the surface with respect to the oil therefore removing it.

The proposed mechanism for removal of oil by the cationic surfactant CTAB will be presented next (Figure 13c). As shown in Figure 6 the only detachment of oil from the surface occurred at negative applied voltage. When application of positive potential is

applied to the substrate, this results in repulsion between the surfactant head groups adsorbed at the oil-aqueous interface and the positively charged substrate. Since the zeta potential measurements show a small positive charge associated with the hydrophilic group of the surfactant a repulsive force exists thus depleting the surrounding media of surfactant molecules. This explains the reasoning that positive applied voltage did not remove the oil drop. With the application of negative potential across the substrate, CTAB molecules accumulate at the surface in an attempt to neutralize the negative charge. As more and more surfactant accumulates onto the surface, the surfactant preferentially wets the surface with respect to the oil therefore displacing it.

The proposed mechanism for removal of oil by Chaps solutions is presented (Figure 13a, 13b, and 13c, depending on the pH). Since Chaps is a zwitterionic surfactant, an increase in solution pH should cause the surfactant to resemble an anionic surfactant while a decrease in pH is expected to modify the surfactant to a cationic. The results shown in Figures 7-9 depict what is to be expected. As with SDS solutions, at high pH an increase in the magnitude of applied voltage results in a decrease in detachment time. As with CTAB solutions, at low pH a negative applied voltage is the only condition of drop detachment. At intermediate pH values, Chaps is expected to be near its isoelectric point thereby mimicking a nonionic surfactant. Comparison of the trends of Chaps solutions to Triton X-100 solutions show a direct correlation.

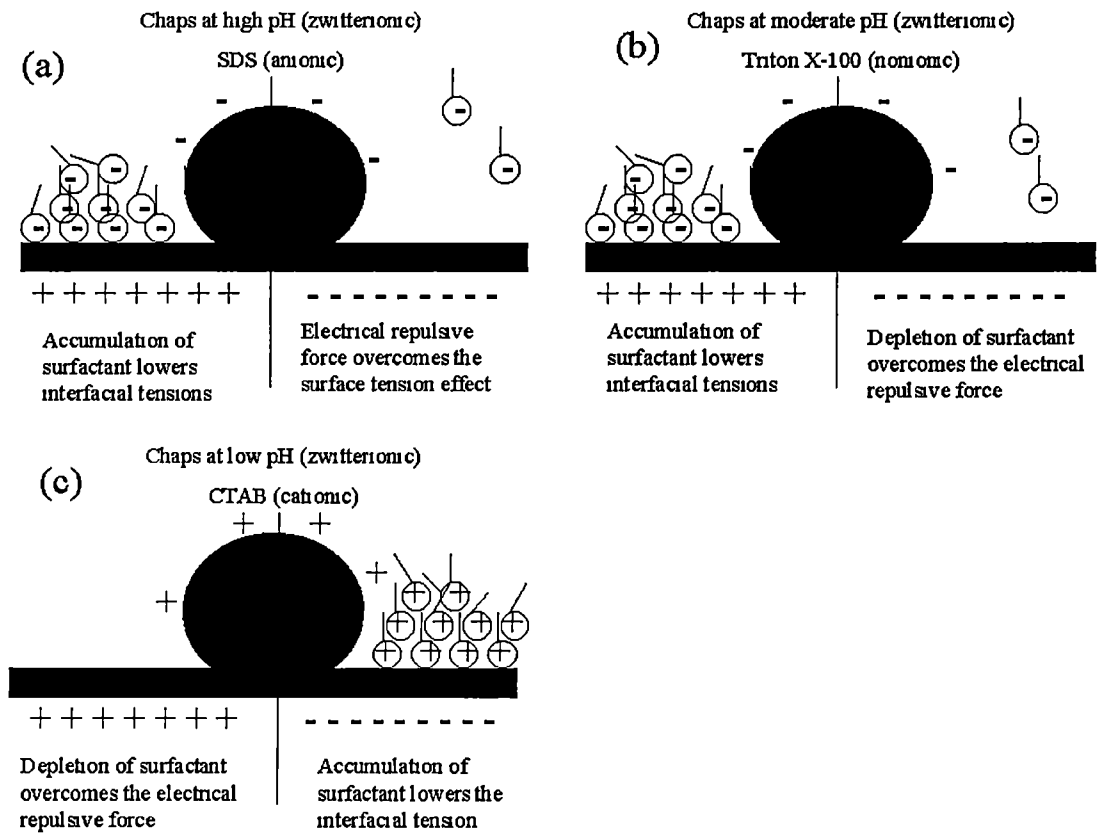


Figure 13. Detailed illustration of electrical potential effect on oil detachment from solid surfaces.

SUMMARY

The effect of electrical potential on oil removal is studied in the presence four types of surfactant solutions. A mechanistic model of oil drop removal from a surface based on the magnitude and polarity of electrical potential delivered to the metal surface in the presence of four types of surfactants was proposed. The electrical potential delivered to the surface is believed to provide a similar effect on surfactant adsorption to the solid/aqueous interface as modification of solution pH. Trends of oil drop detachment as a function of surfactant type and applied potential were observed and correlated well with cleaning effectiveness in an ultrasonic bath. That is, conditions for which oil drops detach more rapid result in a higher cleaning effectiveness than those conditions for which oil drops detach more slowly. Nonionic surfactant solutions provided more rapid oil drop detachment as the magnitude of voltage applied to the surface increased in the direction of positive polarity. Anionic surfactant solutions provided quicker drop detachment as the magnitude of voltage applied to the surface increased regardless of polarity. Cationic surfactant solutions yielded more rapid oil drop detachment as the magnitude of applied voltage increases in the direction of negative polarity. Zwitterionic surfactant solutions compared well with trends for nonionic, cationic, and anionic surfactant solutions depending on the solution pH.

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PART V

SUMMARY AND FUTURE WORK

This experimental work was performed to better understand the cleaning process at more fundamental level. Despite the importance of oil fouling and cleaning in industry, very little attention has been paid to fundamental studies of oil detachment mechanisms. This work follows that of Starkweather et al. in which the removal of an oil drop from a solid surface was studied as the cleaning solution pH was adjusted. The authors were able to model drop detachment results with trends of interfacial tension at the aqueous/oil interface as a function of pH. That is, trends of interfacial tension decreasing with increasing pH were consistent with quicker drop detachment times. There still remains an inadequate amount of literature on how changes at the solid/aqueous interface impact the kinetics of oil drop removal. This study finds adsorption of surfactant ions at this interface to be as important as adsorption at the oil/aqueous interface. A consistent model of drop detachment trends as a function of cleaning solution pH is developed. Since altering the cleaning solution pH has an impact on the surface charge, it was hypothesized that application of a small electrostatic potential would provide the same effect without rendering problems that acidic and basic media cause. Experiments involving the application of a small voltage to the surface during the cleaning process provided distinct trends of drop detachment and cleaning effectiveness results. A similar model with some modification was used to explain the observed trends. Development of a simple screening procedure for predicting industrial

cleaning was developed during the course of this work. Conditions that favor quicker drop detachment also show a higher cleaning effectiveness.

In Part II, the effect of the adjustment of cleaning solution pH and cleaning effectiveness is studied. From this study, trends of oil removal are found to be a function of both surfactant type and solution pH. Anionic, nonionic, and zwitterionic surfactant solutions are found to be more effective at oil removal as the solution pH increases. Cationic surfactants, on the other hand, are more effective in oil removal as the solution pH decreases. The observed trends are modeled by proposing an electrostatic attraction/repulsion mechanism between a monolayer of adsorbed surfactant molecules and the oil drop surface. Depending on the orientation of surfactant ions at the surface, the oil drop is expected to either spread over the surface (when the surfactant molecules are adsorbed to the solid/aqueous interface by their head groups) or be repulsed away from the surface (when surfactant molecules are adsorbed to the solid/aqueous interface by their tail groups). The model fits the data continuously.

In Part III, a simple screening procedure of predicting industrial-scale cleaning from laboratory drop detachment studies is presented. The idea of a simple laboratory drop detachment experiment at predicting the cleaning effectiveness in an industrial-scale ultrasonic bath is supported by data collected for three different types of cleaners. For each case, cleaning solution conditions that favor rapid oil displacement also favor a higher cleaning effectiveness in the ultrasonic bath.

In Part IV, a refined mechanistic model from the previous case, where solution pH was altered, was developed to interpret the trends of applying a small direct electrical potential on the contaminated surface while monitoring oil removal. Oil removal is found to be a strong function of surfactant type as well electrical potential. For cationic surfactants, the cleaning effectiveness increases as applied voltage to the surface decreased from positive to negative polarity. Anionic surfactants exhibited trends of higher cleaning effectiveness as the magnitude of applied voltage increased, nearly independent of polarity. Nonionic surfactants are found to clean the surface better as applied voltage is increased from negative to positive polarity. The trends of cleaning effectiveness in zwitterionic surfactants support the previous three situations. That is, depending on solution pH, cleaning effectiveness trends in the zwitterionic surfactant follow those of cationic (low pH), anionic (high pH), and nonionic (moderate pH) surfactants. A mechanistic model based upon surfactant accumulation/depletion at the solid/aqueous interface is proposed to explain the observed trends. This finding may prove valuable to industry which relies heavily upon alkaline aqueous cleaners since similar cleaning effectiveness can be achieved by directly introducing an electrical potential to the surface. This will alleviate both the corrosivity problems of cleaning baths and environmental concerns, notably additional wastewater problems.

Further fundamental studies are needed on the absolute orientation of surfactant molecules at the solid/aqueous interface. So far, the proposed mechanism of oil removal consistently follows the mechanistic model based on either a surfactant monolayer or

surfactant accumulation at the solid/aqueous interface; however, spectroscopic measurements should be made in support of this model. Contact angles of water droplets on a hydrophilic surface previously flushed with surfactant solution at a particular pH can give some indication as to the orientation of surfactant molecules at the top of the layer. For instance, if the water droplet forms a high contact angle with the surface, a hydrophobic layer of surfactant tail groups are extended outward from the surface.

Further studies need to be made on the interfacial tension of the aqueous/oil interface while under the influence of an electric field. Also, the interfacial tension of oil drops in solutions of CTAB and Chaps should be made under various pH conditions.

Oil drop detachment time as a function of both electrical potential and solution ionic strength may provide a more thorough understanding of the voltage effect. It is thought that increasing the solution ionic strength may cause shielding of the charge delivered to the surface, therefore hampering the electrical potential effect. Some work has already been performed at UT/ORNL on the detachment time of oil drops as a function of ionic strength. From the trends, it is shown that increasing only the ionic strength of the cleaning solution can drastically increase the cleaning effectiveness of a surface.

APPENDICES

Appendix for Part II

Figure 2

pH	2.75	7.13	12.15	3.91	9.62
CHAPS	120	7.89	8.23	120	19.88
pH	4.31	10.33	1.97	6.95	12.86
CTAB	9.32	40.011	12.45	21.92	63.19
pH	2.12	6.6	10.23	3.16	12.33
SDS	28.28	6.5	0.45	26.79	4.27
pH	1.32	6.23	12.16	4.26	9.93
Triton	17.14	3.87	3.25	10.19	4.533
X-100					

Figure 3

pH	2.08	5.96	12.45		
CHAPS	24.86	40.05	38.96		
pH	2.08	6.95	11	4.93	10.21
SDS	13.7	15.6	32.9	24.4	35.9
pH	2.38	4.14	6.77	10.02	11.16
Triton	37.8	45	41.5	48	50
X-100					
pH	1.78	4.83	6.78	10.04	12.53
CTAB	29.3	26.1	26.3	13.4	14.2

Figure 4

Triton X-100

	0	0.25	0.5	0.75	1
12.01	35	34	43.5	57.5	50.5
5.48	16.5	21.5	32.5	45.5	39

Chaps

	0	0.25	0.5	0.75	1
7.3	19.5	35.5	41.5	44	42.5
12.06	46	57.5	66.5	67	50

CTAB

	0	0.25	0.5	0.75	1
12.2	17.5	20	33.5	36.5	44
3.04	17	34.5	58	67	56.5
5.45	21.5	33.5	46.5	54	48

SDS

	0	0.136	0.19	0.29	0.37	0.43	0.57	0.6	0.84	1
pH=6.0	1		0.994	0.784		0.67	0.62			0.55
pH=9.8	1	1.04			1.03			0.99	0.93	

Figure 5

Oil/water emulsion

pH	trial	Zeta potential				average
7.14	-35.8	-36.6	-34.7	-33.6	-34.8	-35.1
10.25	-58.6	-56.7	-58.2	-57.9	-58.5	-57.98
11.84	-68.9	-70.5	-70.5	-69.4	-70.5	-69.96
1.82	-57.7	-62.9	-63.7	-58.6	-58.7	-60.32
3.03	-57	-53.9	-55.7	-58.1	-56.3	-56.2

Oil/water/Chaps

pH	trial	Zeta potential				average
6.08	-24.5	-26.7	-30.2	-24.9	-27.2	-26.7
8.35	-50	-53.4	-51.2	-57.3	-51.4	-52.66
9.65	-62.8	-55.8	-61.4	-66.4	-58.2	-60.92
2.55	-66.7	-70	-66.1	-68.2	-72.9	-68.78

Oil/water/CTAB

pH	trial	Zeta potential				average
2.86	82.3	83.2	84.7	91	86.3	85.5
6.23	55.9	58.2	55.9	61.7	61.9	58.72
7.45	75.2	75.4	76.2	72.9	77.5	75.44
10.92	69.8	69.6	65.7	69.3	66.2	68.12
11.57	75.9	76.2	81.2	77.5	77.4	77.64

Oil/water/SDS

pH	trial	Zeta potential				average
6.02	-108.5	-106.8	-108.1	-108.5	-108.5	-108.08
1.2	-108.5	-108.5	-108.2	-108.5	-107.6	-108.26
11.08	-103.6	-102.1	-104.2	-104.6	-103.3	-103.56

Appendix for Part III

<u>drop detachment time (min)</u>	<u>cleaning effectiveness (%)</u>	<u>cleaner</u>	<u>variable</u>
0.8	58.4	1	1
2.9	47.6	1	1
5.9	37.1	1	1
127.5	38.6	1	2
2.48	51.4	1	2
2.53	51.8	1	2
11.9	28.8	2	1
20.2	25.4	2	1
40	12.6	2	1
0.35	69	2	2
0.5	40	2	2
2.75	38.7	2	2
0.45	35.9	3	1
6.5	15.6	3	1
28.28	13.7	3	1
3.25	50	3	2
4.53	48	3	2
10.19	45	3	2
17.14	37.8	3	2

Appendix for Part IV

Figure 2

voltage	avg									
-4	2.5333	1.95	2.12	2.51	2.78	2.86	2.98			
-2	19.396	23.06	18.87	18.17	18.12	18.8	19.18	18.45	19.88	20.03
-1.5	83.73	79.23	79.88	92.08						
-1	98.82	94.75	99.08	102.63						
0	127.57	108.35	124.5	134.67	134.85	135.5				
1	23.96	23.75	24.1	24.03						
1.5	5.7167	5.63	5.67	5.85						
2	4.152	3.33	2.17	3.3	2.03	3.97	4.43	5.33	5.37	5.77
4	2.4767	2.05	2.2	3.7	2.12	2.34	2.45			

Figure 3

voltage	Ave. time (min)
-4	5.9
-2	3.8
-1.5	4.2
-1	4
0	2.9
1	3
1.5	2
2	1.8
4	0.8

Figure 4

-4	0	4
3.77	None	None
4.93	None	None
4.52	None	None

Figure 5

pH	12.15	<u>detachment time</u> <u>(min)</u>	
<u>volts</u>	<u>trial 1</u>	<u>trial 2</u>	<u>trial 3</u>
4	0.4	0.5333	0.6333
0	5.75	8.633	10.35
-4	1.467	1.6	2.1

Figure 6

4	None	None
0	None	None
-4	63.65	78.21

Figure 7

-4	1.53	1.45	1.42
0	1.27	1.33	1.42
4	0.85	0.77	0.73

Figure 8

<u>SDS</u>		<u>wt. of oil</u> <u>adhering</u> <u>to surface</u>	<u>post-wash</u>	<u>fraction of</u> <u>removal</u>	<u>V</u>	<u>%</u> <u>removal</u>
<u>clean</u>	<u>contam.</u>					
70.1083	70.198	0.0896	70.1516	0.516741071	-4	51.67411
69.9995	70.084	0.0842	70.0511	0.387173397	0	38.71734
70.1827	70.27	0.0874	70.2225	0.544622426	4	54.46224
70.1134	70.189	0.0758	70.1533	0.473614776	-4	47.36148
70.1838	70.262	0.0777	70.2342	0.351351351	0	35.13514
70.0001	70.082	0.0822	70.0427	0.481751825	4	48.17518
69.9955	70.079	0.0837	70.0336	0.544802867	-4	54.48029
70.1126	70.193	0.0803	70.1599	0.410958904	0	41.09589
70.1831	70.268	0.0853	70.2221	0.542790152	4	54.27902

Triton X-100						
<u>clean</u>	<u>contam.</u>	<u>wt. of oil</u> <u>adhering to</u> <u>surface</u>	<u>post-</u> <u>wash</u>	<u>fraction of</u> <u>removal</u>	<u>V</u>	<u>%</u> <u>removal</u>
70.1841	70.265	0.0807	70.2381	0.330855019	-4	33.0855
70	70.079	0.0791	70.0435	0.450063211	0	45.00632
70.1132	70.192	0.0786	70.144	0.608142494	4	60.81425
69.9991	70.073	0.0743	70.0464	0.363391655	-4	36.33917
70.1136	70.187	0.0733	70.1513	0.485675307	0	48.56753
70.1837	70.262	0.0785	70.2177	0.566878981	4	56.6879
70.0002	70.08	0.0802	70.0506	0.371571072	-4	37.15711
70.1836	70.267	0.0832	70.2273	0.474759615	0	47.47596
70.1128	70.19	0.0774	70.1486	0.5374677	4	53.74677

CTAB						
<u>clean</u>	<u>contam.</u>	<u>wt. of oil</u> <u>adhering to</u> <u>surface</u>	<u>post-wash</u>	<u>fraction of</u> <u>removal</u>	<u>voltage</u>	<u>%</u> <u>removal</u>
70.013	70.09	0.0751	70.049	0.525965379	-4	52.597
70.112	70.19	0.076	70.154	0.457894737	0	45.789
70.188	70.26	0.0718	70.232	0.38718663	4	38.719
70.11	70.19	0.0804	70.146	0.553482587	-4	55.348
70.013	70.09	0.0789	70.055	0.479087452	0	47.909
70.187	70.27	0.0827	70.239	0.374848851	4	37.485
70.012	70.09	0.07962	70.049	0.526500879	-4	52.65
70.11	70.18	0.0711	70.149	0.451476793	0	45.148
70.188	70.26	0.0753	70.238	0.33997344	4	33.997

Vita

Anthony W Rowe was born in Middlesboro, Kentucky on July 5, 1976. He has lived in Tazewell, Tennessee all his life. He attended public schools in Claiborne County where he graduated with an Honors Diploma from Claiborne County High School. He graduated from Walter's State Community College in May of 1998 with an Associate of Science Degree majoring in pre-medicine. He graduated from Lincoln Memorial University *summa cum laude* in May of 1998 with a Bachelor of Science Degree majoring in chemistry and biology. During the course of his undergraduate degree, he was a member of the *Phi Theta Kappa* Honor's Society and received the Whitaker-Schnider Science Award. In August of 1998, he enrolled in the University in Tennessee in Knoxville to pursue a Master's Degree in Chemical Engineering conducting research on the enhancement of aqueous cleaning by introduction of electrostatic potential. During his graduate studies, he has worked as graduate research assistant with University of Tennessee and the (ORNL) Oak Ridge National Laboratory.