8-2004

Prediction of Organic Droplet Behavior on a Solid Surface as Influenced by Aqueous Surfactant Solutions

Samuel Albert Morton III
University of Tennessee - Knoxville

Recommended Citation

Morton, Samuel Albert III, "Prediction of Organic Droplet Behavior on a Solid Surface as Influenced by Aqueous Surfactant Solutions. " PhD diss., University of Tennessee, 2004.
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To the Graduate Council:

I am submitting herewith a dissertation written by Samuel Albert Morton III entitled "Prediction of Organic Droplet Behavior on a Solid Surface as Influenced by Aqueous Surfactant Solutions." I have examined the final electronic copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Chemical Engineering.

Robert M. Counce, Major Professor

We have read this dissertation and recommend its acceptance:

David J. Keffer, David W. DaPaoli, Raymond A. Buchanan

Accepted for the Council:

Carolyn R. Hodges

Vice Provost and Dean of the Graduate School

(Original signatures are on file with official student records.)

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Accepted for the Council:

Anne Mayhew
Vice Chancellor and Dean of
Graduate Studies

PREDICTION OF ORGANIC DROPLET BEHAVIOR ON A SOLID SURFACE AS INFLUENCED BY AQUEOUS SURFACTANT SOLUTIONS

A Dissertation
Presented for the
Doctor of Philosophy
Degree
The University of Tennessee, Knoxville

Samuel Albert Morton III
August 2004

DEDICATION

This dissertation is dedicated to my family. Through years of support they have borne me to this moment in my life. More specifically I dedicate this work to my paternal grandfather, Samuel A Morton Sr., who attended this university for a brief time in the 1930's, was called home to help with the family farm, and went on to inspire me through his hard work, dedication, and personal strength.

ACKNOWLEDGEMENTS

This project was supported through Oak Ridge National Laboratory (ORNL), managed by UT-Battelle, LLC for the United States Department of Energy under contract DE-AC05-00OR22725 as well as through a grant from the American Electroplaters and Surface Finishers Society, Inc. Their support is greatly appreciated. I would like to thank the Department of Chemical Engineering at the University of Tennessee for allowing me to expand my academic experience beyond that of a simple dissertation. Special thanks are due to Dr. Pete Counce and Dr. David Keffer for much needed help and encouragement as well as the opportunities to travel and present my work to the larger scientific community. Additionally, I would like to thank the members of my committee, Dr. David DePaoli and Dr. Raymond Buchanan for providing guidance and reviews if this work. I am indebted to Alison Davis for her phenomena laboratory work as well as her friendship. Likewise I would like to thank Anne Wells for her assistance in the later portions of my laboratory work and encourage her to continue in the pursuit of her engineering degree. My special thanks go out to my parents, Samuel and Mary Morton, my brother Stephen Morton, my great-aunts, Louise Glover, Ann Bradshaw, and my grandfather, Samuel Morton Sr., for challenging me to succeed and helping to ensure that I did. Lastly, and most importantly, I would like to thank my wife, Laurie, for her temperance and patience when I was least deserving, for encouraging me when it seemed, to me, that things were going badly, and for being willing to be my companion through the challenges of the coming years.

ABSTRACT

This dissertation presents a model capable of predicting equilibrium oil droplet contact angles on a solid surface immersed in surfactant solution, a thorough discussion of the effects of surfactant concentration and salt addition on contact angles, and an experimental investigation into the impact of voltage application to the solid surface on oil droplet shape in an aqueous/organic/solid system. The work contained in this dissertation resulted in five journal articles and numerous presentations.

The model applies current theories of surfactant self-assembly, the quasi-chemical approximation for solid surface adsorption, and various aqueous/organic/solid system properties to determine organic droplet contact angles. The computational methodology employed by the model requires the description of the aqueous/organic/solid system by selected component balances and through numerical techniques determines the equilibrium component distribution and the organic droplet contact angle for the specific system. Results from the model are compared to experimental contact angle data for various surfactants, surfactant concentrations, salt concentrations, and surface materials.

The investigation into the effects of low magnitude applied voltage on droplet phenomena and oil removal determined that significant changes in droplet shape and removal efficiency can occur for voltages between ±3.0 volts. These changes in droplet shape where then compared to observed improvements in ultrasonic oil removal from metal surfaces in aqueous solutions. Employing the theoretical understanding of aqueous/organic/solid systems a discussion of controlling phenomena and mechanisms was presented.

I have shown that (1) organic droplet contact angles on solid surfaces in aqueous/organic/solid systems are significantly affected by aqueous/ solid interfacial surfactant aggregation, (2) this impact is due to changes in the structure of the surfactant aggregate itself, (3) these changes are heavily impacted by surfactant concentration and the addition of low concentration salt to the aqueous surfactant solution, (4) the type of salt added to the solution is of greater relevance than indicated in the existing literature, and (5) that the application of low voltage applied potentials can significantly effect droplet shape and oil removal efficiency in an aqueous/oil/solid system.

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NOMENCLATURE

PART II

Symbol	Definition	Units
$A_{effective}$	Area of surface per surfactant monomer	m^2/molecule
$A_{micelle}$	Surface area of micelle hydrophobic core	m^2
A_{mon}	Area of surfactant footprint	m^2/molecule
C_i	Concentration of species i	molecule /m^3
Cp_i	Heat capacity of species i	J/(molecule ·K)
E	Packing parameter	–
e_c	Unit charge (1.602177×10^{-19})	C
E_i	Adsorption interaction parameter	J/molecule
h_{cap}	Maximum height of spherical cap	m
k_b	Boltzmann constant (1.38083×10^{-23})	J/(molecule ·K)
K_i	Equilibrium constant for balance i	–
$N_{aggregation}$	Micelle aggregation number	–
N_{aq_ion}	Number of ions in solution	molecules
N_C	Number of carbons in surfactant tail chain	
N_i	Number of molecules of species i	molecules
N_{moles_i}	Number of moles of species i	moles
N_{sites}	Number of available adsorption sites	–
R	Ideal gas constant (1.38083×10^{-23})	J/(molecule ·K)
$R_{micelle}$	Radius of micelle hydrophobic core	m
R_{sphere}	Radius of theoretical sphere	m
S	Dimensionless surface charge density	–
T	System temperature	K
V_i	Volume of species i	m^3
$V_{i,adsorbed}$	Free volume of adsorbed species i	m^3
$V_{i,bulk}$	Free volume of species i in bulk phase	m^3
ΔG_{CH2}	Free energy for transfer of CH_2 groups	J/molecule
ΔG_{CH3}	Free energy for transfer of CH_2 groups	J/molecule
ΔG_i	Gibbs free energy change of balance i	J/molecule
ΔH_i	Enthalpy change for adsorbing balance i	J/molecule
ΔS_i	Entropy change for adsorbing balance i	J/molecule
$\alpha_{micelle}$	Restrictive/steric correction factor	J/molecule
ε_{H2O}	Dielectric constant for water	–
ε_v	Permittivity of a vacuum (8.85419×10^{-12})	C/(J·m)
$\gamma_{micelle}$	Surface tension of micelle core	J/(molecule ·K)
κ	Inverse Debye-Huckel screening length	m^{-1}
Θ	Contact angle	radians

θ_i	Fractional surface coverage for species i	–
τ	Surfactant tail penetration depth in organic	m

PART III

A	Interfacial tension contribution constant	–
A_{drop}	Surface area of organic/solution interface	m^2
$A_{effective}$	Area of surface per surfactant monomer	m^2/molecule
$A_{headgroup}$	Cross sectional area of surfactant headgroup	m^2/molecule
$A_{hydrophobic}$	Area of the hydrophobic micelle core	m^2
B	Interfacial tension contribution constant	–
C	Interfacial tension contribution constant	–
C_i	Concentration of species i	molecule/m^3
C_p	Heat capacity of species i	J/(molecule ·K)
D_{surf}	Diameter of surfactant headgroup	m
e_c	Unit charge (1.602177×10^{-19})	C
$E_{packing}$	Packing parameter	–
h_{cap}	Height of spherical cap droplet	m
k_b	Boltzmann constant (1.38083×10^{-23})	J/(molecule ·K)
k_i	Equilibrium constant for balance i	–
K_i	Overall equilibrium constant for balance i	–
$L_{tailchain}$	Length of surfactant tail chain	m
$N_{avagadro}$	Avagadro's number (6.022×10^{23})	molecule/mole
N_i	Number of molecules of species i	–
$N_{i,j}$	Number of molecules of species i in state j	molecule
N_{ions}	Number of free ions in solution	molecule
N_{sites}	Number of adsorption sites	–
N_{TailC}	Number of carbons in surfactant tail chain	–
R_{core}	Radius of micelle core	m
R_{dropeq}	Radius of equivalent droplet	m
R_{sphere}	Radius of spherical cap theoretical sphere	m
S	Dimensionless surface charge density	–
T	Temperature	K
$V_{headgroup}$	Volume of surfactant headgroup	m^3
V_i	Volume of phase, layer, or species i	m^3
$V_{tailchain}$	Volume of surfactant tail chain	m^3
X_i	Mole fraction of species i	–
ΔG_{CH2}	Free energy for transfer of CH_2 groups	J/molecule
ΔG_{CH3}	Free energy for transfer of CH_2 groups	J/molecule
ΔG_i	Gibbs free energy change for balance i	J/molecule
ΔH_i	Enthalpy change for balance i	J/molecule
ΔS_i	Entropy change for balance i	J/ molecule

α	Generic component identifier	–
β	Generic component identifier	–
ε	Dielectric constant for solution	$C/(J\cdot m)$
Γ	Adsorbed moles of surfactant	$moles/m^2$
κ	Inverse Debye-Huckel screening length	m^{-1}
σ_{core}	Micelle core interfacial tension	$J/(molecule\cdot K)$
σ_{tail}	Contribution to σ_{core} from surfactant tail	$J/(molecule\cdot K)$
σ_{water}	Contribution to σ_{core} from water	$J/(molecule\cdot K)$
θ_i	Fractional surface coverage for species i	–
τ	Thickness of hydrocarbon layer	m
ψ	Micelle core interfacial tension parameter	–

PART IV

A	Szyzkowski adsorption constant	mM
$C_{surfactant}$	Concentration of surfactant in solution	mM
c	Number of possible neighbor sites	–
g	Configurational degeneracy term	–
k_b	Boltzmann constant (1.38083×10^{-23})	$J/(molecule\cdot K)$
M	Number of sites	–
N_i	Fraction of sites occupied by species i	–
N_{ij}	Number of species i –species j interactions	–
q_i	Intra-site partition function for species i	–
q_N	Nearest neighbor interaction term	–
q_S	Intra-site partition term	–
Q	Total partition function	–
R	Ideal gas constant (1.38083×10^{-23})	$J/(molecule\cdot K)$
T	Temperature	K
U_i	Solid interaction parameter of species i	J/molecule
V_{site}	Approximate volume of an adsorption suite	m^3
w_{ij}	Lateral interaction parameter for species i-j	J/molecule
x_s	Mole fraction of surfactant molecules in bulk	–
x_w	Mole fraction of water molecules in bulk	–
Γ^{∞}	Adsorbed surface excess at saturation	$molecule/m^2$
$\gamma_{s/a}$	Surface tension of solid/aqueous interface	J/m^2
$\gamma_{s/l}$	Surface tension of solid/liquid interface	J/m^2
$\gamma_{l/a}$	Surface tension of liquid/aqueous interface	J/m^2
Λ_i	Thermal de Broglie wavelength for species i	m^3
μ_i^{ad}	Chemical potential of adsorbed species i	J/molecule
μ_i^{bulk}	Chemical potential of species i in the bulk	J/molecule
θ	Contact angle	degrees

PART V

a	Constant from empirical relationships	–
A_{RC}	Empirical constant for $w_{22\text{-}RC}$	–
b	Constant from empirical relationships	–
B_{RC}	Empirical constant for $w_{22\text{-}RC}$	–
c	Constant from empirical relationships	–
CMC	Critical micelle concentration	mM
C_i	Concentration of species i	mM
k_b	Boltzmann constant (1.38083×10^{-23})	J/(molecule·K)
n_c	Number of carbon in surfactant tail chain	–
T	Temperature	K
U_2	Solid-surfactant interaction parameter	J/molecule
$w_{22\text{-}RC}$	Region C surfactant lateral interaction	J/molecule
ΔG_{def}	Gibbs free energy change from deformation	J/molecule
Φ_{CMC}	Salt dependent CMC parameter	–
Φ_{U2}	Salt dependent U_2 parameter	–

PART VI

W_B	Coupon basis weight	g
W_C	Coupon cleaned weight	g
W_O	Coupon oily weight	g
η_{OR}	Oil removal efficiency	–

PART I

Introduction

1. Overview

The objective of this research is to develop a classical thermodynamic model to aid in the prediction of aqueous surfactant-based, solid-surface cleaning performance while accounting for the effects of various cleaning system variables and adjustments. The research will include the development of a model, verification with experiment, comparison to cleaning efficiency using a prototypic cleaning system.

1.1. Motivation

Concern for the effects of industrial processes on human health and the environment has increased in the past few decades. One area of much interest is the improvement of surface cleaning and degreasing. As environmental regulation limits the use of organic solvents, the use of aqueous cleaning solutions has become a focus for improving industrial cleaning and degreasing processes. Due to this interest, a series of studies was performed to determine the techniques and methods that can be utilized to help improve the environmental performance of aqueous cleaning. These investigations concentrate on the modification of cleaning system parameters and their effect on cleaning performance. Previous research work has shown that the contact angle and shape of an oil droplet on a solid surface can be used to predict the effect of system parameter changes on cleaning [1-10]. Building upon the understanding of the oil-removal process gleaned from those works, a model was developed to predict the equilibrium contact angle of organic droplets on various surfaces. Additionally, the wealth of research into surfactant self-assembly provides the model with a selection of firm theoretical approaches to analyzing the behavior of surfactant in solution and subsequent effects on cleaning. As a result the model incorporates an understanding of oil removal from surfaces and relative surfactant adsorption/self-assembly theory into a thermodynamic model that could be used to assist in the optimization of industrial cleaning processes.

1.2. Methodology

The model utilizes information gained from a combination of surfactant self-assembly behavior and cleaning system properties. These properties include but are not limited to oil type, surfactant type, temperature, solution alkalinity, and solid surface type. It has been shown that controlled manipulation of these parameters can provide insight into surface cleaning [2-9]. The model combines minimization of free energy, pertinent mass balances describing the movement of species within the studied system, and the behavior of surfactant monomers during self-assembly processes to provide a methodology for the prediction of the efficiency of cleaning. The aggregation of surfactants in the bulk solution and at the various interfaces plays a demonstrative role on the processes for the removal of liquid organic contaminants from the solid surface being cleaned.

The model was developed based on a simplified cleaning system. This system is composed of a solid surface contaminated with an organic droplet immersed in an aqueous cleaning solution. The organic droplet is assumed to behave like a spherical cap, which means it can be approximated to be a portion of a complete sphere truncated by the surface being cleaned. Another assumption is that system components will adsorb to the limited solid surface area in a competitive manner.

Additionally, the system is assumed to be at equilibrium, which allows for the development of a system of component balances. As a result the modeling approach is to:

1. write component balances to describe a three phase system characteristic of aqueous cleaning,
2. develop equilibrium constants for each balance,
3. utilize numerical method based computational techniques to determine component distribution,
4. and determine the contact angle of the droplet.

The predictive capabilities of the model can be verified by comparison to various macroscopic experimental results, including surface tension, interfacial adsorption, and organic droplet contact angle.

1.3. Results

This work has the stated goal of providing a theoretical approach to the prediction of organic-droplet/solid/solution contact angles. The model incorporates the effects of surfactant concentration, solution ionic strength, and applied electric potential. The work is unique in its extension of surfactant self-assembly to multiple interfaces simultaneously and that it will model contact angles with limited empirical manipulation. This work will be extendable to a broad range of surfaces, organics, and surfactants provided adequate descriptive information is present. Additionally, it will lay the groundwork for a more detailed molecular thermodynamic modeling effort in the future. In addition to theoretical work, experimental investigations of the effect of low voltage applied potentials are included. This information is of particular interest as previous work indicated its dramatic effects but left significant gaps in our understanding of these phenomena.

2. Review of Previous Work

As indicated in the above section, the conceptual system analyzed in this dissertation was preceded by an extensive body of experimental work. This earlier work was the subject of several recent theses [4, 7, 10] that resulted in numerous peer-reviewed journal articles [1, 2, 5, 6, 8, 9]. A brief review of this work is provided in chronological order in the following subsections to assist the reader in understanding the larger dissertation subject material as well as the model that was developed.

2.1. Byron A. Starkweather (1996-1998)

Byron Starkweather evaluated the effects of surfactant solution pH and solid surface type on the displacement of oil from a solid surface. The first article [1] was concerned with the effects of solution pH and surfactant concentration on the removal of oil from a steel surface. Starkweather et al. performed experiments to quantitatively determine the extent of this effect. He measured droplet contact angle as a function of time as a method of quantifying the displacement of the oil droplet. The oil used in this study was Mar-TEMP 355, a quench oil composed of a blend of several petroleum distillates, and the surfactant utilized was Triton X-100, a non-ionic surfactant. The study observed that there was a direct relationship between solution pH and oil displacement and between surfactant concentration and oil displacement. The second article [2] delved further into the changes in contact angle on surfaces as affected by pH and surfactant concentration. This study utilized two different surfaces, steel and glass, to measure the changes in contact angle for Mar-TEMP 355 in the presence of solution containing sodium dodecyl sulfate (SDS), an anionic surfactant. For a range of pH between 7.0 and 10.0, two different SDS concentrations, one at the critical micelle concentration (CMC) and one significantly above the CMC, were tested and the oil droplet contact angles and interfacial tensions were measured. The significant finding for this study was that at elevated pH and SDS concentrations the change in droplet contact angle was hindered on both surfaces. This revelation that the solution/solid interface contributed to droplet displacement was significant and contributed greatly to all the subsequent work. A third article [3], published in a trade journal, related the correlation of droplet contact angle to cleaning potential.

2.2. Anthony W. Rowe (1998-2000)

Anthony Rowe continued Starkweather's investigation into the effects of pH and surfactant concentration on droplet displacement as well as expanding to study the effects of applied potential. The first article [5] studied the effects of pH on the removal of oil droplets from a steel surface for a range of surfactant types: nonionic, ionic, and zwitterionic. This study evaluated the droplet displacement as a function of detachment time, finding that conditions that favored a faster detachment corresponded to high cleaning using an ultrasonic bath. The effects were noted for all surfactants, but the greatest impact was found for the ionic surfactants, SDS and cetyl trimethyl ammonium bromide (CTAB). Rowe and coworkers were able to hypothesize that the droplet phenomena changes were due to a combination of electrostatic interactions and solid surface hydrophobicity changes. This study also furthered the premise that equilibrium droplet measurements are predictors for prototypic surface cleaning. The second article [6] investigated the effects of applying an electric voltage directly to the metal surface. The results of this work showed that droplet detachment time could be significantly reduced for certain systems with the application of voltage. Similar to the previous report, the conditions of greatest change were found for solutions of SDS near the CMC. This work was a direct predecessor for the work presented in Part VI.

2.3. Alison N. Davis (2000-2002)

Alison Davis evaluated the effects of the addition of low concentrations of salt (<3 mM) on droplet contact angle for gold and steel surfaces. The first article [8] evaluated the effects of ionic strength manipulation for hexadecane droplets on gold in SDS and CTAB solutions. Ionic strength was manipulated through the addition of various concentrations of sodium chloride (NaCl) to solutions of various concentrations of the aforementioned surfactants. Davis was able to demonstrate, for hexadecane on gold, that the changes in ionic strength resulted in dramatic changes in droplet contact angle. Additionally, the study showed that the effect was most dramatic for NaCl concentrations of less than 0.5 mM, showing little change for greater concentrations that were studied. Davis postulated that these changes were due, not to organic/solution interfacial tension changes, but to changes in the surface charge and adsorption behavior of surfactants at the solid/solution interface. These changes resulted in a competition for limited solid surface area which precipitated an increase in droplet contact angles. The second article [9] continued this study, showing that the phenomena observed for hexadecane were also evident for Mar-TEMP 355 droplets on both gold an steel surfaces. Additionally, Davis performed the most extensive prototypic cleaning studies and was able to demonstrate that changes in contact angle also were directly relatable to cleaning performance. This work provided the experimental data for the analyses of ionic strength changes presented in Part V of this dissertation.

3. Composition of Dissertation

This dissertation is divided into seven parts. Part I provides an introduction to the material, the motivation for the research, a discussion of the methodologies employed, and a review of the previous research work related to the subject material of the dissertation. Parts II through VII present the experimental and theoretical results of this research as individual journal articles. These articles have been published or submitted for publication in peer reviewed journals and can be considered individually. Part II provides an introduction to the theoretical study of oil droplets on solid surfaces as well as an analysis of preliminary experimental results. Part III contains an exhaustive literature review, a detailed explanation of the development theory and model for the prediction of equilibrium oil on solid contact angles, and a more extensive comparison to experimental than presented in Part II. Part IV provides a discussion of a significant improvement to the model presented in Part III. Part V discusses the extension of the model, as revised in Part IV, to account for the impact of low concentration salt (<5 mM) to surfactant solutions and the subsequent effect on hexadecane contact angles on a gold surface. Part VI contains an experimental investigation of the effect of an applied voltage on oil droplets on a steel surface immersed in an ionic surfactant solution as well as a qualitative discussion of the controlling phenomena. Part VII contains a summary of the work presented in this dissertation.

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PART II

Thermodynamic Model for the Prediction of Contact Angles of Oil Droplets on Solid Surfaces in SDS Solutions

Part II of this dissertation is a slightly revised version of an article by the same name originally published in the journal *Separation Science and Technology* in 2003 by Samuel Morton III, David Keffer, Robert Counce, David DePaoli, and Michael Hu:

> Morton III, S.A., Keffer, D.J., Counce, R.M., DePaoli, D.W. and Hu, M.Z-C., *Thermodynamic model for the prediction of contact angle of oil droplets on solid surfaces in SDS solutions*. Separation Science and Technology. 2003, **38** *(12&13)*, 2815-2835.

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Abstract

The attachment of a droplet of oil to a solid surface in the presence of an aqueous surfactant solution may be quantified by contact angle measurements. A classical thermodynamic model has been developed to predict this characteristic contact angle. The model minimizes the Gibbs free energy for a system that includes five mass-transfer actions: micellization of surfactant monomer in aqueous solution, adsorption of surfactant at the solid/solution interface, adsorption of surfactant at the oil/solution interface, adsorption of the oil at the solid surface, and adsorption of water at the solid surface. Limitations in the model include empirical values for the energy of steric/restrictive interactions in micellization and the interfacial free energy term for adsorption of surfactant at the oil/solution interface; in addition, the free energies for adsorption of water, oil, and surfactant at the solid surface are adjustable parameters. The model has been validated by comparison with experimental values of contact angle measured for droplets of hexadecane on a gold surface. This approach allows for the use of published physical property data for the prediction of surfactant distribution and contact angle in a given system, and may be useful in guiding aqueous cleaning applications.

1. Introduction

Aqueous surfactant solutions are currently a topic of great interest in the field of environmentally benign cleaning technology. The application of these solutions to the removal of oils from solid surfaces is of heightened interest in recent years, due to the restrictions imposed on the use of chlorinated/fluorinated solvents. This paper presents preliminary work toward a thermodynamic model for the prediction of oil/solid contact angles in aqueous surfactant solutions for use in optimization of industrial cleaning processes and techniques.

The fundamental processes involved in the removal of oil from solid surfaces have been investigated and expanded upon over the last several decades. The removal of contaminating oils from solid surfaces can be separated into three main mechanisms. The first of these mechanisms is the ‘rolling-up’ of the droplet, where the oil is observed to decrease its area of contact with the solid surface while still maintaining a nearly spherical shape. If this process continues, the droplet’s contact angle, the angle between the solid surface and the inside edge of the droplet, increases with time and eventually approaches 180 degrees, at which time the droplet will detach. The second mechanism is that of ‘necking’, where the oil droplet seems to form an inverted tear shape with a slender ‘neck’ maintaining attachment to the oil still in contact with the solid surface. At some point buoyancy effects, due to the differences in the densities of the oil and solution, cause the neck to break and a portion of the droplet to detach. Despite the dramatic removal process of ‘necking’, a substantial portion of the organic remains on the surface and subsequent removal of residual organics is markedly more difficult. The ‘roll-up’ mechanism usually occurs at lower concentrations and the ‘necking’ mechanism primarily at higher concentrations. A third mechanism for oil removal, solubilization, is related to the movement of the oil species into the solution due to concentration gradients. This mechanism is normally observed to be a function of time and surfactant concentration. A basic assumption for the model presented is that the mechanism for oil removal will be the 'roll-up' mechanism. This assumption is grounded in the knowledge that 'roll-up' results in a cleaner surface than 'necking' and occurs on a faster time scale than solubilization.

Many researchers have investigated these processes and it is possible to find a discussion of the above phenomena in any number of colloid and surface chemistry texts [1-5]. In addition to published textbook sources, the early work of Mankowich [6], into the effects of surfactant solutions on hard surface detergency, provides a good foundation upon which to build a study of surfactant-enhanced removal of organic contaminants. The aforementioned study determined that an increase in detergency, or amount of soils removed from the surface, could be directly correlated to an increase in surfactant concentration in the aqueous solution. Additionally it demonstrated that detergency reaches a maximum point at and above the particular surfactant's critical micelle concentration (CMC). The CMC is a characteristic of the surfactant and is normally defined as the aqueous surfactant concentration above which surfactant molecules self-assemble into micelles. Kao *et al* discussed the mechanisms of organic removal in anionic surfactant solutions where micelles were expected to be present [7]. Kao and coworkers observed the separation of organic droplets from a silica surface and suggested that a combination of the roll-up and diffusional, where water and surfactant diffuse between the interface of the organic and the solid surface, mechanisms were operating to remove the organic droplets. More recently Matveenko *et al* reported on the removal of organics from a porous solid and correlated the displacement of organics, interfacial tension of the aqueous solution and the contact angles of wetting species [8]. It was concluded that the recovery of oil was greater for increased surfactant concentration. The recovery of oil was seen to exhibit behavior similar to that reported by Mankowich and reached a maximum value above the CMC. Aveyard *et al* concluded, in a report on oil removal from capillaries [9], that the main mechanism for oil removal was not solubilization or mass transfer of surfactant across the oil/water interface. Instead, the displacement was due to changes in the interfacial tension between the oil and water phases. Notice that these are characteristics similar to the 'necking' mechanism.

In the system considered in this article an anionic surfactant was used and its concentration varied. Since this surfactant is of an ionic nature the electrostatic properties of the solution become important in determining the CMC. Typically an increase in non-surfactant electrolyte causes a decrease in the CMC for ionic surfactants. This decrease in the CMC would result in 'necking' occurring at a lower overall surfactant concentration. The work of Starkweather *et al* indicated that the 'necking' mechanism was dominant in the study of the removal of industrial quench oil from metal and glass surfaces [10, 11]. The Starkweather study focused on the changes in droplet attachment as modified by changes in non-ionic surfactant concentrations and increased pH. They concluded that for Triton X-100, a nonionic surfactant, increases in pH had a more dramatic effect than changes in concentration. In later work Starkweather hypothesized that changes in interfacial tension, in the case of altered pH, could be explained by chemical changes to the interfacial layer of the organic phase [12]. A series of studies into the effects of ionic strength, pH, and surfactant concentration was undertaken by Rowe *et al* [13, 14]. Rowe and coworkers observed the removal through ‘necking’ in some of their experiments, however it was concluded that due to the presence of the ‘roll-up’ mechanism that surface adsorption of surfactants onto the solid surfaces was of importance. A major result from both the work of Starkweather [12] and Rowe [13] was the correlation of the efficacy of oil removal in an industrial type cleaning process to the easily observed changes in the contact angle of the oil on the surface material in question. From this relationship it becomes possible to measure the contact angle of a droplet and indicate whether or not oil removal is improved by a permutation of some characteristic of the system studied. Most recently Chatterjee has indicated that for a static system ‘necking’ will be the primary mechanism for the removal of organics over ‘roll-up’ [15]. Through an exhaustive analysis it was demonstrated that changes in the interfacial tension of the oil droplets, when combined with buoyancy forces, result in oil removal. The article provides an excellent documentation of droplet changes due to both ‘roll-up’ and ‘necking’, and can be used to understand the differences in the two mechanisms and any resulting droplet breakup/detachment. The choice of the ‘roll-up’ mechanism for the current study is that the physical system studied demonstrated a dominance of ‘roll-up’ over ‘necking’ in preliminary tests. It is assumed in the current work that the qualitative correlations of Starkweather and Rowe will remain valid. Their work into correlating non-static prototypic industrial cleaning processes to droplet behavior in a static system provides validation for relating the qualitative information garnered from the static system model presented here and non-static industrial cleaning systems.

Some of the more complex actions involved in aqueous cleaning processes are related to the aggregation behavior of the surfactants. There are several aspects of aggregation that are of concern for the modeling effort presented here. The first process is the formation of solution-based aggregates, or micelles. Micelles form at and above the CMC, which usually indicates the overall concentration at which all other surfactant aggregation processes reach a maximum. The 'Dressed Micelle' model of Evans and Wennerstrom [3] is the basis for the treatment of micellization in this paper. The basic features of the 'Dressed Micelle' model, developed in the early 1980s, are described by Evans and Ninham [16], and Evans *et al* [17]. Evans and coworkers' approach treats the micellization process as an adsorption process in which the overall free energy of adsorption can be subdivided into several terms. These terms allow for the positive/negative affects on free energy changes due to various separable physical/electrochemical interactions involved in the self-assembly process. Nagaragan and Ruckenstien [18] expanded on the work of Evans and coworkers and provide an excellent explanation of the micellization model and the summed contribution modeling approach. The summed contribution approach has also been applied to the modeling of surfactant aggregation at solid/liquid and air/liquid interfaces. Li and Ruckenstien [19] applied a similar theoretical approach to the formation of surfactant aggregates at the solid/liquid interface. Further discussion into the effects of pH, ionic strength, and temperature on such surfactant aggregation is presented by Pavan *et al* [20], where an investigation into the effects of system parameters on the adsorption of sodium dodecyl sulfate (SDS) onto a hydrotalcite clay surface was performed. Hines provides an excellent discussion of such a model for air/liquid self-assembly [21]. When combined with the experimental results from Gillap *et al* [22] the summed contributional approach is shown to be satisfactory for description of simple surfactant aggregation at solution interfaces.

Another surfactant aggregation process relevant to the current modeling work is the formation of aggregates at the oil/water interface. However, unlike micellization, solid/liquid adsorption, or air/liquid adsorption, this process is not well covered in the literature and to the best of the authors' current knowledge no summed contribution approach to modeling such adsorption exists. Gillap *et al* [23] and Staples *et al* [24] provide experimental information regarding the adsorption of SDS to a hexadecane/solution interface. Comparison of those results to studies on solid/liquid and air/liquid interfacial surfactant aggregation indicates that the expansion of the summed contribution approach to modeling of oil/solution interfacial aggregation may be fruitful.

The purpose of this article is to present a model for the prediction of contact angles of oils on solid surfaces. The model could be used to assist in the determination of industrial scale cleaning/degreasing systems' operation parameters. Such an improvement in the use of materials in these cleaning systems will have a beneficial impact on the environment in that less waste materials will be generated for treatment and disposal. The article presents a theoretical investigation into the effects of surfactant concentrations on oil droplet contact angles on solid surfaces, which have been shown to be an indicator for the degree of oil removal for a cleaning system.

2. Theory

The system being modeled is that of an organic droplet in contact with a solid surface immersed in an aqueous surfactant solution. The current model is based on an assumption that the response of the equilibrium contact angle will be useful in understanding the mechanisms of oil detachment, where at steady state a system of mass transfer equations are at equilibrium. With this assumption it is possible to determine the distribution of the system components and the resulting contact angle. Therefore the approach is to write mass balances for each component transfer action, determine equilibrium constants for the mass transfer actions, utilize computational techniques to find the overall distribution of components, and predict the contact angle of the droplet.

2.1. Mass Balances

The system components being studied are surfactant, water, organic, and solid. It is assumed that the solid is stable in solution and therefore is a separable component. The surfactant can be divided into free solution monomer, micellized solution monomer, monomer adsorbed at the oil/solution interface, and monomer adsorbed at the solid/solution interface. The organic component is either adsorbed to the solid surface or free in a contiguous phase separate from the aqueous solution. Lastly the water is either adsorbed to the solid surface or free in the solution. To describe the model process it was determined that at equilibrium the following five mass-transfer actions are sufficient to describe the system:

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

where the term in parenthesis indicates the location of the respective component. Surfactant is found free in solution, bound in solution aggregates or micelles, adsorbed to the oil/solution interface, or absorbed to the solid/solution interface. Oil is found either free in a liquid phase separate from the solution or adsorbed to the solid/oil interface. Water is found either free in solution or adsorbed to the solution/solid interface.

First consider the formation of micelles, self-assembling surfactant aggregates, from free monomer in solution, which occurs at and above the critical micelle concentration (CMC). In this work the CMC is defined to be the point at which micellization is the dominant surfactant mass transfer action, above which any additional monomer added to the system will be incorporated into micelles. The second accounts for the movement of monomer from solution to an adsorbed phase at the solid/solution interface. This is the classical adsorption of surfactant to a solid surface, and is discussed in depth in most surface chemistry/surface phenomena texts. The third describes the transfer of monomer from solution to an adsorbed phase at the oil/solution interface. The single equation for the oil component describes the adsorption to or desorption from the solid surface. We assume that the oil is of a known and constant volume, and that no solubilzation or partitioning of oil into the solution due to the diffusional mechanism, occurs; therefore any oil not adsorbed to the solid surface will be in the free liquid state. The last describes the water molecules adsorption to or desorption from the solid.

2.2. Equilibrium Constraints

With these equilibriums relationships written, we next move to the establishment of equilibrium constraints. From classical thermodynamics, the above equations, when considered at equilibrium, can be partitioned between the involved components through the use of an equilibrium constant, K_i, where *i* indicates the mass action under consideration. This equilibrium constant is the ratio of the concentration of one component to the concentration of another component, respective to the balance considered. The following equation shows the form of the equilibrium constant, $K_{\alpha\rightarrow\beta}$, for the transfer of molecules of component in the α state to the β state:

$$K_{\alpha\rightarrow\beta} = \frac{\left[N_{molecules\beta}\right]}{\left[N_{molecules\alpha}\right]} \tag{1}$$

where the concentration is replaced by either the number of molecules, $N_{molecules,j}$, as in the above equation, or mole fractions. The equilibrium constant of a process is related to the change in the free energy, ΔG, by:

$$RT\ \ln\left[K_{\alpha\rightarrow\beta}\right] = -\Delta G_{\alpha\rightarrow\beta} \tag{2}$$

Rearranging the above equation and substituting for the equilibrium constant gives us a relationship that can be used to determine the partitioning of components between states in the model system:

$$\frac{\left[N_{molecules\beta}\right]}{\left[N_{molecules\alpha}\right]} = \exp\left(\frac{-\Delta G_{\alpha\rightarrow\beta}}{RT}\right) \tag{3}$$

where R is the ideal gas constant in appropriate units, and T is temperature in Kelvin. Hence in this approach the change in free energy can be estimated as a function of any of the system variable parameters: solution pH, ionic strength, temperature, surfactant type, solid type, and organic type. To determine the change in free energy, a method, respective to each particular equilibrium equation, is needed that accounts for interactions between the components of a phase and/or the components at the interfaces where adsorption occurs. Each balance in considered in the following sections.

2.3. Micellization

First begin with the formation of micelles from free surfactant in solution. A great deal of work has been performed over the past several decades that has expanded the understanding of the micellization process. The current approach will utilize the 'Dressed Micelle' model (DMM) put forward by Evans and coworkers [3, 16, 17] to represent this process. This model presents a method for determining the free energy change in forming a spherical micelle comprised of a known number of surfactant monomers. This number of surfactant monomer called the aggregation number, $N_{aggregation}$, has been measured experimentally and can be found for several surfactants in any number of colloidal science texts [1-5]. The DMM states that the change in free energy of the self-assembling formation of a micelle can be related to a summation of several contributing terms:

$$\Delta G_{micelle} = \Delta G_{hydrophobic} + \Delta G_{restrictive/steric} + \Delta G_{electrostatic} \quad (4)$$

The first term on the right hand side of the equation, $\Delta G_{hydrophobic}$, is due to the hydrophobic nature of the surfactant tail chains. This favorable term describes the energy benefit from moving the surfactant tail from solution to the hydrocarbon like core of the micelle. The second contribution, $\Delta G_{restrictive/steric}$, is the unfavorable restriction of the tail groups in the limited volume of the micelle core combined with the steric interaction between surfactant headgroups at the micelle core surface. These two interactions are linked through their mutual dependence on the surface of the micelle core and consequently the surface tension of the micelle core. The third term, $\Delta G_{electrostatic}$, is the unfavorable electrostatic interaction between the surfactant headgroups at the micelle surface and between the surfactant headgroups and the electrolytes in the solution. The electrostatic term is an approximate curvature-corrected solution to the Possion-Boltzmann equation from electric double layer theory. These terms are shown in the following equations [3, 16, 17]:

$$\Delta G_{\text{hydrophobic}} = \Delta G_{\text{CH}_2}(\text{Nc} - 1) + \Delta G_{\text{CH}_3} \tag{5}$$

$$\Delta G_{\text{restrictive/steric}} = \left(\frac{A_{\text{micelle}}}{N_{\text{aggreagation}}} \right) \gamma_{\text{micelle}} + \alpha_{\text{micelle}} \tag{6}$$

$$\begin{aligned} \Delta G_{\text{electrostatic}} = 2k_b T \Bigg(& \ln\left[\tfrac{S}{2} + \sqrt{1 + \left(\tfrac{S}{2}\right)^2} \right] - \left(\frac{2}{S} \right) \left(\sqrt{1 + \left(\tfrac{S}{2}\right)^2} - 1 \right) \\ & + \left(\frac{4}{\kappa R_{\text{micelle}} S} \right) \ln\left[\tfrac{1}{2} + \frac{\sqrt{1 + \left(\tfrac{S}{2}\right)^2}}{2} \right] \Bigg) \end{aligned} \tag{7}$$

$$\kappa = \sqrt{\frac{2 N_{\text{aq ion}} e_c^2}{\varepsilon_{H_2O} \varepsilon_V k_b T}} \tag{8}$$

$$S = \left(\frac{e_c^2}{\varepsilon_{H_2O} \varepsilon_V \kappa A_{\text{effective}} k_b T} \right) \tag{9}$$

where the variables and constants used are listed, with units and values (where applicable), in the nomenclature section of this dissertation.

2.4. Oil/Solution Interfacial Surfactant Adsorption

The next task is to describe the free energy change from the movement of free surfactant from solution to the oil/solution interface. Following the format for the free energy change from micellization, separating the steric and restrictive terms, and adding a separate term for the interfacial tension change from adsorption, we get the following equation:

$$\Delta G_{\text{soln/oil ads}} = \Delta G_{\text{hydrophobic}} + \Delta G_{\text{steric}} + \Delta G_{\text{restrictive}} + \Delta G_{\text{electrostatic}} + \Delta G_{\text{interfacial}} \quad (10)$$

This form was chosen following not only the format from the work of Evans and coworkers, but also the similar work of Nagarajan and Ruckenstien [18], Li and Ruckenstien [19], and J.D. Hines [21].

The first term, $\Delta G_{\text{hydrophobic}}$, is the same as shown in Equation 5 for micellization above. The second or steric term, ΔG_{steric}, results from the conformational interactions between the adsorbed surfactant headgroups. The restrictive term, $\Delta G_{\text{restrictive}}$, results from the conformation interactions between the adsorbed surfactant tail chains. It should be noted that due to the relative size of the adsorption interface compared to the individual size of a surfactant monomer the terms are indeed separable. The steric interaction will be essentially negligible until very high surfactant loading at the interface. The restrictive term will also essentially be negligible from the fact that the tail chains are far less restricted as the large volume of the oil phase allows for considerable variation in arrangement. The electrostatic term, $\Delta G_{\text{electrostatic}}$, is similar to the one from the micellization development with the obvious exception that it can be well approximated at the molecular level by a pure planar term, rather than a curvature-corrected term as was used for micellization. The last term, $\Delta G_{\text{interfacial}}$, results from changes in interfacial tension due to the adsorption of surfactant at the oil/water interface. This term will decrease in magnitude as adsorption reaches a maximum value at the CMC for the respective surfactant. Several different suggestions have been made in the literature for terms of this type [18-20]; however, none are completely satisfactory for the model at its current state of development, and as such, we utilize an empirical relationship for the interfacial tension related free energy change will be utilized. These terms are shown in the following equations:

$$\Delta G_{\text{hydrophobic}} = \Delta G_{CH_2}\left(Nc - 1\right) + \Delta G_{CH_3} \tag{5}$$

$$\Delta G_{\text{steric}} = -k_b T \ln\left(1 - \frac{A_{\text{mon}}}{A_{\text{effective}}}\right) \tag{11}$$

$$\Delta G_{\text{restrictive}} = k_b T\left(\frac{10\pi^2}{80E}\right)\left(\frac{\tau}{A_{\text{mon}} N_{\text{sites}}}\right) \tag{12}$$

$$\Delta G_{\text{electrostatic}} = 2k_b T\left(\ln\left[\tfrac{S}{2} + \sqrt{1 + \left(\tfrac{S}{2}\right)^2}\right] - \left(\frac{2}{S}\right)\left(\sqrt{1 + \left(\tfrac{S}{2}\right)^2} - 1\right)\right) \tag{13}$$

$$\begin{aligned}\Delta G_{\text{interfacial}} = 13.724 &- \left(2.092 \times 10^{21}\right)\left(N_{\text{moles surfactant at oil/water interface}}\right)^2 \\ &- \left(1.230 \times 10^{10}\right)\left(N_{\text{moles surfactant at oil/water interface}}\right)\end{aligned} \tag{14}$$

2.5. Solid/Solution Competitive Adsorption

Next, the adsorption of components to the solid/solution interface will be considered. The three components adsorbing to the solid are competing with one another for the available solid surface area. Since the available solid surface area is set to a fixed value, it becomes possible to develop an adsorption methodology that reflects this fact. It is assumed that each species will adsorb in a fashion such that the fractional area of coverage, $\theta_{\alpha\rightarrow\beta}$, of that species can be described by a Langmuir isotherm:

$$\theta_{\alpha\to\beta} = \frac{K_{\alpha\to\beta}\left[C_\alpha\right]}{1 + K_{\alpha\to\beta}\left[C_\alpha\right]} \tag{15}$$

which relates the fractional area of solid surface coverage by a component when it adsorbs from phase α to phase β. Since there are three separable species adsorbing, water, surfactant, and oil, it becomes necessary to develop an extension of the Langmuir isotherm that can account for the increase/decrease of an adsorbed species by the adsorption/desorption of the other species. It is assumed that the surfactant will follow the Langmuir isotherm, increasing as concentration increases to a maximum value at the CMC. This allows for the assumption that the other two components will also follow a similar adsorption profile. Writing equations for the adsorption of the components, and simplifying results in the following equations:

$$\theta_{H_2O} = \frac{K_{H_2O} N_{H_2O}}{V_{aq} + K_{H_2O} N_{H_2O_{aq}} + K_S N_{S_{aq}} + K_{Oil} N_{Oil}\left({}^{V_{aq}}\!/\!{}_{V_{Oil}}\right)} \tag{16}$$

$$\theta_{Surfactant} = \frac{K_S N_{S_{aq}}}{V_{aq} + K_{H_2O} N_{H_2O_{aq}} + K_S N_{S_{aq}} + K_{Oil} N_{Oil}\left({}^{V_{aq}}\!/\!{}_{V_{Oil}}\right)} \tag{17}$$

$$\theta_{Oil} = \frac{K_{Oil} N_{Oil}}{V_{Oil} + K_{H_2O} N_{H_2O}\left({}^{V_{Oil}}\!/\!{}_{V_{aq}}\right) + K_S N_{S_{aq}}\left({}^{V_{Oil}}\!/\!{}_{V_{aq}}\right) + K_{Oil} N_{Oil}} \tag{18}$$

with the constraint that:

$$\theta_{Total} = \theta_{H_2O} + \theta_{Oil} + \theta_{Surfactant} \tag{19}$$

With the relation of the surface coverage to the equilibrium constant, all that remains undefined is three equilibrium constants for the adsorption processes. The equilibrium constants shown in Equations 14 through 17, K_{H2O}, K_S, K_{Oil}, can be related to free energy change as stated previously. It is know that the change in free energy contains an enthalpic and entropic contribution:

$$\Delta G = \Delta H - T\Delta S \tag{20}$$

An approximation for the entropic contribution is utilized that accounts for changes in aqueous concentration due to an increase in surfactant concentration. Equation 21 shows this entropic approximation for the surfactant component:

$$\Delta S = R\ln\left(\frac{V_{\text{surfactant adsorbed}}}{V_{\text{surfactant bulk}}}\right) \tag{21}$$

The contribution to free energy from enthalpic changes can be related to the heat capacity and an adjustable parameter describing the energy change from interactions between the component molecule and the solid surface. The following equation shows this contribution:

$$\Delta H = E_{\text{surfactant}} - \tfrac{1}{2} Cp_{\text{surfactant}} \left(T - T_{\text{ref}}\right) \tag{22}$$

Since the entropic contribution is determined by changes in solution properties and the heat capacity portion of the enthalpic contribution is based on known properties, the remaining interaction energy term can be used as an empirical parameter in the model.

2.6. Determination of Contact Angle

Lastly, a value for the contact angle of the droplet on the solid surface needs to be calculated. Since as a function of this model we determine the solid surface contact area of the oil droplet, it is possible to determine the contact angle geometrically. Neglecting buoyancy effects and assuming that the droplet is by nature a spherical cap and that no organic is found free in the aqueous solution, the contact angle can be calculated as follows:

$$\Theta = \cos^{-1}\left(\frac{\left(R_{sphere} - h_{cap}\right)}{R_{sphere}}\right) \tag{23}$$

where the relationships between contact angle, cap height, and theoretical sphere radius are shown in Figure 1: The dark line passing through the sphere represents the location of the solid surface and size of the spherical cap with respect to the theoretical sphere. As seen from the Figure 1, the height of the cap at its apex will be less than the theoretical sphere radius for droplets with contact angles less than 90°, and greater than the radius for droplets with contact angles greater than 90°.

3. Experimental Method

The experimental data, for comparison to model results, were collected using static shapes of sessile hexadecane droplets on gold surfaces in aqueous surfactant solutions. Contact angle measurements were performed using a Tantec Contact Angle Meter and the droplets observed via a Xybion Electronic Systems CCD camera (Model SVC-90) for verification of equilibrium. Figure 2 shows the experimental setup.

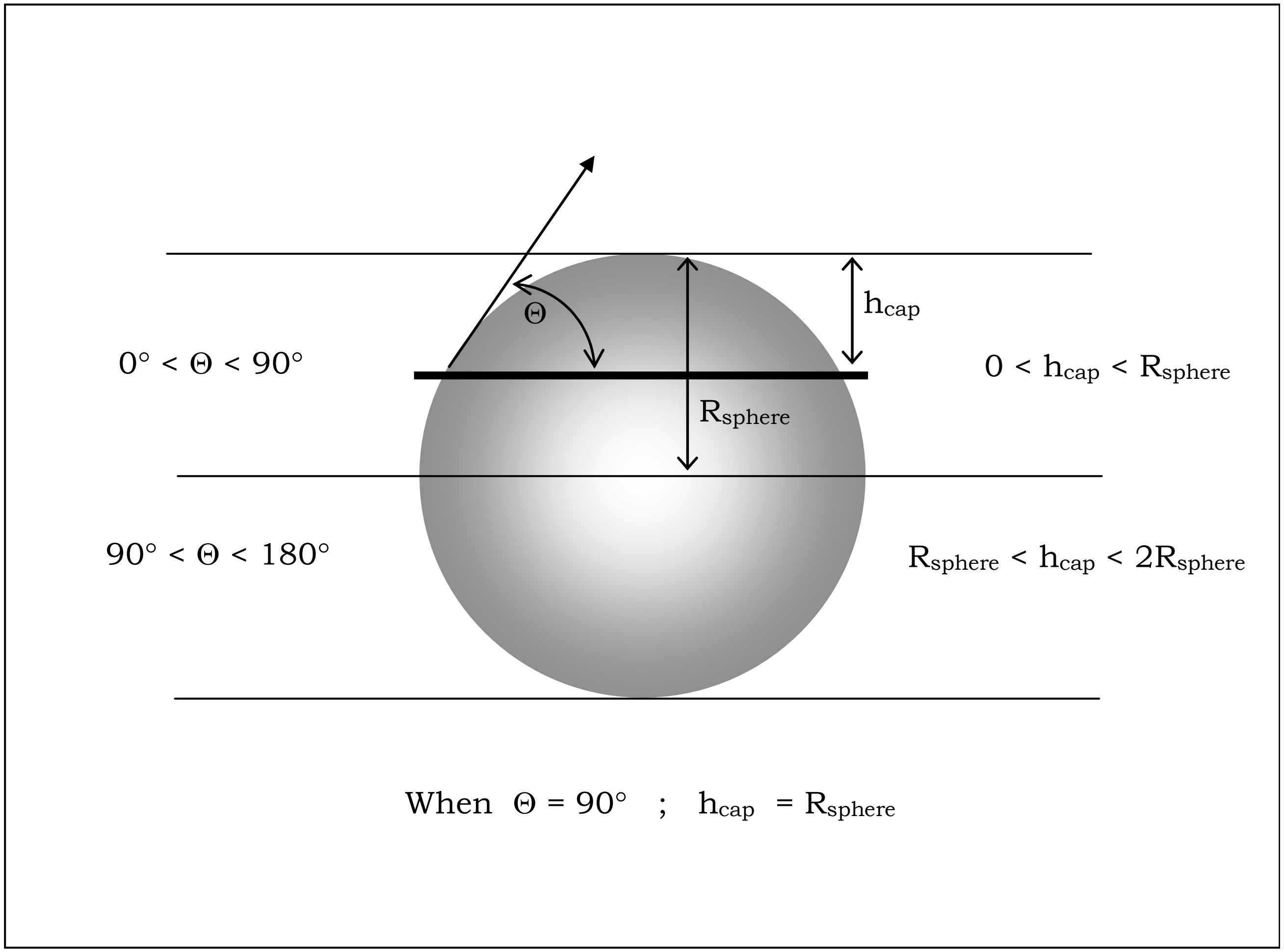

Figure 1: Droplet Geometric Relationships

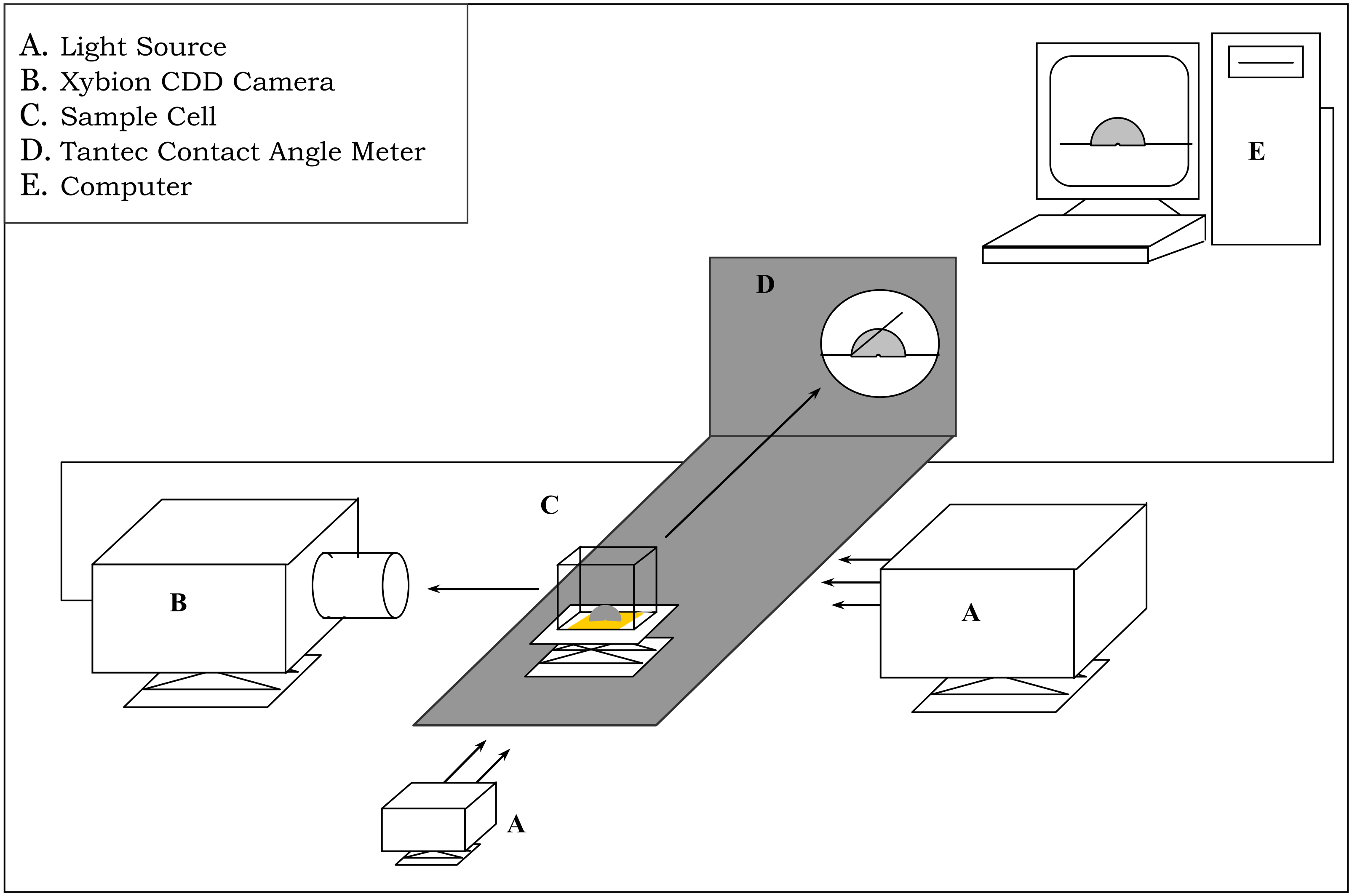

Figure 2: Contact Angle Study Apparatus

Experiments were performed using sodium dodecyl sulfate (SDS) for the surfactant, a gold-coated microscope slide for the solid surface, deionized water, and hexadecane for the oil species. The SDS surfactant was purchased from J.T. Baker, (CAS 151-21-3), with a reported purity of 100%. The gold-coated microscope slide was purchased from Asylum Research, (Gold 200C), with a reported roughness of ±20 Angstroms. The hexadecane was purchased from Aldrich, (CAS 544-76-3), with a reported purity of 99%, and specific gravity of 0.773. The temperature during testing was 22°C (±0.5) and negligible heat was added to the contact angle apparatus by the light source.

The gold slide was repeatedly washed with acetone and deionized water to remove any contaminants from handling and to insure consistent wetting of the gold surface by the hexadecane. The cleaned slide was allowed to equilibrate with room temperature and cleaned again with pressurized air to remove any lint and airborne debris, such as dust. After a sufficient length of time, a 2 μL droplet of hexadecane was placed, using a micropipetter, on the gold surface and allowed to spread until it reached its maximum degree of wetting in air. This was visually determined as the point after which the droplet ceased to spread on the solid surface when exposed to air. During the time allotted for the spreading of the droplet, a 200 mL surfactant solution, made by mixing the predetermined amount of dry surfactant in a 250 mL Erlenmeyer flask with 200 mL of deionized water, of appropriate concentration was placed in an optical quality glass colorimeter vis cell manufactured by Spectrocell. Using the same technique as Carroll [25], Starkweather and coworkers [10-12], and Rowe and coworkers [13, 14]) the slide was lowered into the surfactant solution and allowed to come to a state of equilibrium. The droplet was observed using a CCD camera connected to a personal computer and, when equilibrium appeared to have been achieved, the contact angle was measured using the Tantec angle meter. Equilibrium was determined as the point when the droplet visually stopped contracting. This was readily apparent as the center height of the droplet and the area of solid surface contact ceased changing.

Aqueous surfactant solutions are currently a topic of great interest in the field of environmentally benign cleaning technology. The application of these solutions to the removal of oils from solid surfaces is of heightened interest in recent years, due to the restrictions imposed on the use of chlorinated/fluorinated solvents. This paper presents preliminary work toward a thermodynamic model for the prediction of oil/solid contact angles in aqueous surfactant solutions for use in optimization of industrial cleaning processes and techniques.

4. Results and Discussion

4.1. Comparison with Experimental Data

The change in contact angle of the droplet on the gold surface was measured as a function of total surfactant concentration. The drop was viewed with the CCD camera until equilibrium appeared to have been achieved. Figure 3 shows a typical droplet on the gold surface in aqueous surfactant solution. Several equilibrium contact angles were measured, two at SDS concentrations above the CMC, and four below the CMC value of 8.3 mM. As can be seen from Figure 4, the values predicted by the model are in good agreement with the experimental data.

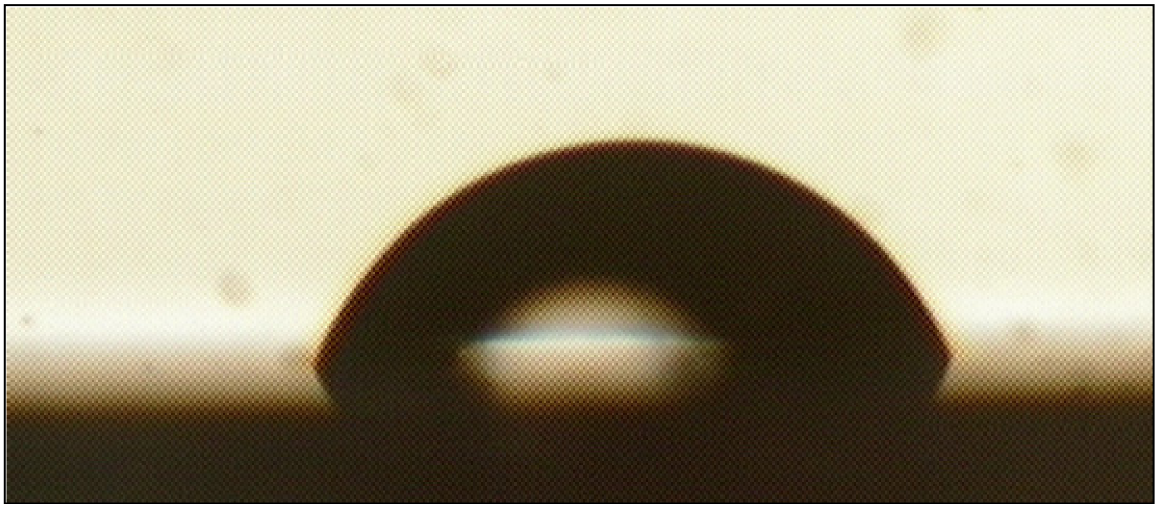

Figure 3. Hexadecane Droplet on Gold Surface in 5 mM SDS Solution

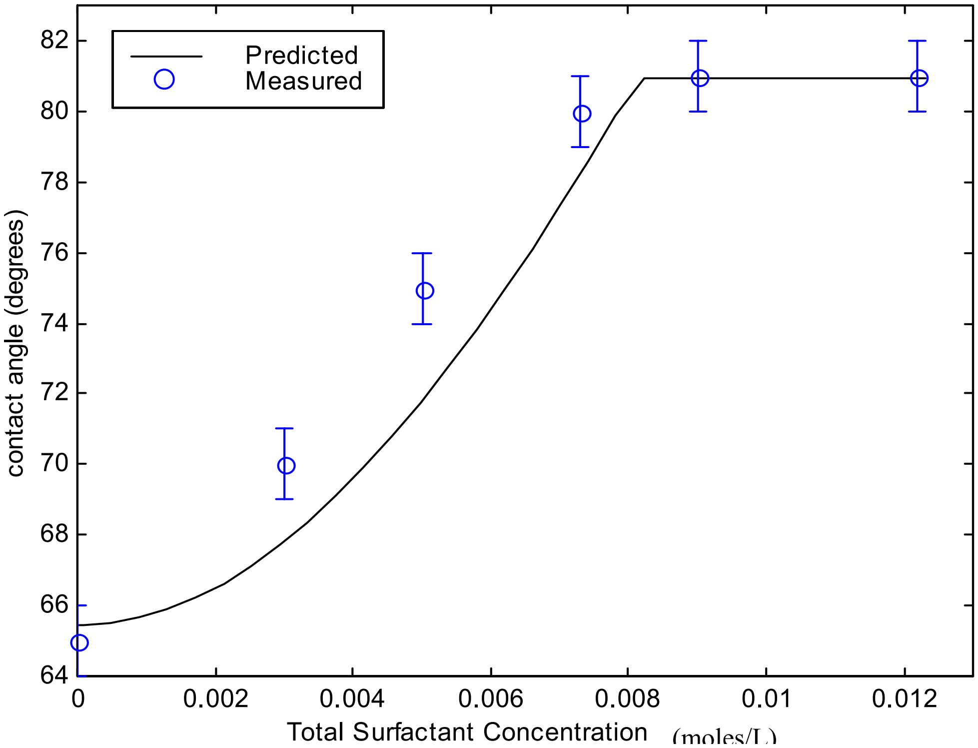

Figure 4. Comparison of Predicted and Measured Contact Angle

As expected, an increase in total surfactant concentration in the system resulted in increased adsorption of surfactant to the solid surface below the CMC. This increase in adsorption resulted in competition for available surface area between the surfactant, organic, and water species. The end results show, since the adsorption of surfactant is known to be affected by the concentration of surfactant in solution, that the adsorption of organic and water displayed an inverse relationship to the solid/solution interfacial adsorbed surfactant concentration. The values of the energetic interaction parameters, E_i, used in the calculation of the change in free energy of adsorption, resulting in the best correlation to the experimental data are shown in Table 1.

As the interaction parameters indicate the wetting of gold by the oil species is less than the value for the wetting of gold by water. This is reasonable in that the oil spread to a larger extent in air and retracted when placed in a surfactant free solution system. This retraction provides a basis for comparing the changes in contact angle due to increases in solution surfactant concentration. Since the overall number of water molecules and organic molecules are unchanged as concentration of surfactant in solution increases, the magnitudes observed for the free energy of adsorption should be lower for water and oil than that for surfactant. Additionally the measured and predicted values for contact angle increase from an initial value of 65°, where no surfactant is present, to a constant value of 80°, above the CMC.

Table 1. Approximate Interaction Parameters

Interaction Parameter	Parameter Value
E_{Oil}	-0.761 kJ/mol
E_{Water}	-5.603 kJ/mol
$E_{Surfactant\ (solid/soln\ ads)}$	-39.27 kJ/mol

4.2. Discussion of Model Performance

Our current model predicts the distribution of surfactant between aqueous monomer, micelles, solid/solution interfacial adsorbed, and oil/solution interfacial adsorbed states. It also predicts the adsorption/desorption of oil and water species. Additionally, the contact angle of a droplet on a solid surface can be predicted, specific to our modeled system. A current limitation to our approach is that the 'Dressed Micelle' Model is only valid, in our application, for SDS surfactants due to the empirical nature of the correction factor in the free energy of steric/restrictive interactions term. A value of 1.2 kJ/mol will allow for the correct prediction of the CMC for SDS, however the same value may not be valid for other surfactants. Another limitation is the empirical nature of the interfacial free energy term in the adsorption of surfactant to the oil/solution interface. Work is proceeding now to develop a more fundamental theoretical method to describe this interaction.

5. Conclusions

A model for the prediction of contact angles of oil droplets on solid surfaces in aqueous surfactant solutions as a function of various systematic parameters (i.e. surfactant type, surfactant structure, temperature, oil type, solution ionic strength, solid type) has been presented. The model predicts the changes in contact angle related to the competitive adsorption of surfactant, oil, and water on the solid surface and reflects the anticipated behavior at and above the critical micelle concentration. This model has been shown to be in qualitative agreement with experimental results obtained for hexadecane droplets on gold surfaces in aqueous solutions of varying SDS concentration. This model has advantages over current predictive techniques because of its basis in classical thermodynamics. Additionally, the model as presented allows for the use of currently published physical properties for the components in the model system for the predictions of component distribution and consequently contact angle. Presently work is underway to expand the model and allow for its use in optimizing the operating conditions in industrial cleaning processes.

6. Acknowledgments

The authors thank Dr. Costas Tsouris, at Oak Ridge National Laboratory, and Larry Perkins, at the University of Tennessee, for their assistance and suggestions. This work was supported by the Environmental Management Science Program, U.S. Department of Energy, through a grant to the University of Tennessee and under contract DE-AC05-00OR22725 with UT-Batelle, LLC.

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PART III

Thermodynamic Method for Prediction of Surfactant Modified Oil Droplet Contact Angles

Part III of this dissertation is a slightly revised version of an article by the same name originally published in the *Journal of Colloid and Interface Science* in 2004 by Samuel Morton III, David Keffer, Robert Counce, David DePaoli, and Michael Hu:

> Morton III, S.A., Keffer, D.J., Counce, R.M., DePaoli, D.W. and Hu, M.Z-C.; *Thermodynamic method for prediction of surfactant modified oil droplet contact angles*. Journal of Colloid and Interface Science, 2004, **270**, 229-241.

The article is reproduced with permission from the journal. This work is in total the effort of Samuel Morton III. Co-authors provided assistance, advice, and review during the preparation and publication of this work.

Abstract

A model applying surfactant self-assembly theory and classical thermodynamics has been developed to aid in the prediction of solid surface cleaning by aqueous surfactant solutions. Information gained from a combination of surfactant self-assembly behavior and cleaning system parameters, such as oil species, surfactant type, temperature, alkalinity, and solid surface type has been shown to provide insight into surface cleaning. The model combines minimization of free energy, pertinent component distribution mechanisms, and surfactant self-assembly processes to provide a methodology for the predicting of oil droplet contact angles. Such predictive capabilities will allow for the development of beneficial environmental and economic changes to industrial and commercial surface cleaning and degreasing processes. Results from the model will be compared to experimental data to verify the capability of the theory to account for the effect of solutions parameters on oil droplet behavior. The model, while aproximate in nature, has shown a remarkable quanititative predictive abilty.

1. Introduction

As concern for the effects of industrial processes on the environment increases the improvement of such processes becomes a topic of much investigation. One such area of continued interest is the cleaning and degreasing of metal surfaces. Prior to the formulation of environmental regulations covering the cleaning of industrially produced surfaces cleaning and degreasing were primarily performed using organic solvents. In an effort to protect the natural environment, the use of such solvents has been dramatically curtailed. Aqueous surfactant solutions have been investigated as both an effective and environmentally benign cleaning alternative. These solutions have, in most cases, distinct environmental advantages over chlorinated/fluorinated solvents, however there are instances where chlorinated solvents are still the choice of necessity. Overall, opportunities to reduce the impact of all industrial cleaning solutions on the environment exist. The now regulated/banned solvents were effective at cleaning with minimal use of other natural resources such as water. On the contrary, aqueous surfactant solutions require heavy use of water. In addition to the substantial use of water, industrial cleaning/degreasing processes release large quantities of water contaminated with oils, metal debris, and the various components of the surfactant cleaning solutions. In an effort to improve the environmental performance of aqueous cleaning/degreasing processes, research has been performed to expand the understanding of the fundamental processes involved in the removal of oil from solid surfaces [1-6]. These studies have focused on the illumination of techniques and methods to modify the cleaning solutions through the manipulation of cleaning system parameters, including surfactant type, surfactant concentration, pH modifying agents, and water softeners. Contact angle and droplet shape changes have been shown to provide insight into the effectiveness of cleaning [1-6], to predict conditions of spontaneous droplet removal from surfaces [7-9], and can be used in the optimization of industrial cleaning processes. These changes have been shown to correlate to the relative changes in cleaning effectiveness, therefore, providing a basis for this work toward predicting these changes with minimal experimental effort. This paper details a thermodynamic model for the prediction of oil/solid contact angles in aqueous surfactant solutions.

2. Background

2.1. Surface Cleaning

A wealth of literature exists on the subject of surface cleaning. It is possible to find discussions concerning the effects of surfactants in any number of colloid and surface chemistry texts [10-12]. Additionally, there are a number of researchers who have contributed greatly to the understanding of solid surface cleaning. The early work of Mankowich into the effects of aqueous solution of surfactants on hard surface detergency is an excellent foundation upon which to construct an understanding of cleaning using surfactant solutions [13]. The study determined that the amount of soil removed from the surface, detergency, was directly related to the aqueous surfactant concentration. It was shown that detergency generally increased with increased surfactant concentration until reaching a maximum when the surfactant concentration in solution reached the critical micelle concentration (CMC). The CMC is surfactant specific and is defined as the concentration at and above which surfactant micelles spontaneously form. Matveenko *et al.* reported on the removal of liquid organics from a porous solid [14]. It was found that the displacement of the organic material, the organic/solution interfacial tension, and the organic/solid contact angle are related to the overall aqueous surfactant concentration. In this study, the removal and recovery of the organics was improved as surfactant concentration increased. This recovery and removal was seen to exhibit similar behavior to the work of Mankowich and stopped increasing above the CMC. Work carried out by Kao *et al.* into the effects of anionic surfactant solutions on the removal of organics provides insight into the mechanism of such removal [15]. Carroll gives an excellent discussion of the physical nature of detergency [16]. This work gives a quick overview of detergency and identifies a number of resources that exist if a deeper study is desired. In later work, Carroll initiated a study of oil removal from solid surfaces [17]. In this study, Carroll provided an experimental discussion of the study of cleaning. Building upon this work, a series of articles by Starkweather *et al.* provided a direct study into the effects of surfactant solution change on cleaning of solid surfaces [1, 2]. These studies investigated and correlated changes in static droplet behaviors, such as contact angles and detachment, to the cleaning of metal surfaces. More recently a pair of articles by Rowe *et al.* analyzed the cleaning of a metal surface as affected by cleaning system parameter changes [3, 4]. The first article investigated the effects of pH on oil detachment and correlated the droplet detachment time to the cleaning efficiency of a prototypical industrial ultrasonic cleaning bath. The second article studied the effects of applying an electric potential to the metal surface and noted its effects on cleaning. Both studies provide mechanistic interpretations to explain the experimentally observed effects on cleaning for a range of system conditions and surfactant types (nonionic, anionic, cationic, and zwitterionic). The work from the previously mentioned studies can provide insight into cleaning that will aid in the development of the model presented in the present work.

2.2. Modeling

In addition to covering the experimental aspects of cleaning, it is necessary to review the currently published modeling work covering surfactant assembly and surface cleaning so that a complete background of this presented modeling effort covering can be developed. In an aqueous cleaning solution, surfactant can form micelles in solution, aggregate at the air/solution and oil/solution interfaces, and adsorb to the solid/solution interface. Perhaps the most thoroughly studied of these is the formation of micelles in solution. The model presented in this article is based on the determination of equilibrium Gibbs free energy through a summed contribution approach. This approach accounts for various surfactant-surfactant, surfactant-solution, and surfactant-adsorbate interactions, summing both encouraging and discouraging terms to estimate overall free energy values. The modeling work concerning micellization pertinent to this article can be traced to the 'Dressed Micelle' model as developed by Evans *et al.* [12, 18, 19]. The work of Evans *et al.* in the early 1980s treats micellization as an adsorption process in which the overall free energy of adsorption is determined by the summed contribution approach [18, 19]. This model accounts for the affects of various separable physical/electrochemical interactions involved in the self-assembly process. Our earlier work [20] utilized the 'Dressed Micelle' model (DMM) and has been replaced in this article with a more expanded theory presented by Nagaragan and Ruckenstien [21]. This expansion of the work of Evans *et al.* [12, 18, 19], more effectively accounts for the interactions involved in micelle formation and gives a discussion of the effect of the shape of micelles on their formation. The work of Li and Ruckenstien applied this summed contribution approach to the study of surfactant aggregation at the solid/solution interface [22]. Pavan *et al.*, while not applying the summed contribution method, provide a discussion of the effects of pH, ionic strength, and temperature on surfactant aggregation at the solid/solution interface [23]. Another non-contribution approach to the determination of surfactant adsorption is given in the works of Mulqueen and Blankschtein [24, 25]. Hines has analyzed the air/solution interface using the summed contribution approach and provides an excellent discussion of surfactant aggregation at this interface [26]. When combined with experimental work, the summed contribution approach can be satisfactorily used to describe simple surfactant aggregation at solution interfaces. The remaining surfactant aggregation process relevant to our current work is that occurring at the organic/solution interface. Unlike micellization, solid/liquid aggregation, or air/liquid aggregation only our recent preliminary efforts have applied the summed contribution approach to the organic/liquid interface. Utilizing experimental results to provide insight into this interface, the earlier work of Morton *et al.* [20] indicates that the expansion of the summed contribution approach to modeling of the organic/solution interface is justified.

The purpose of this current article is to present a model for the prediction of droplet contact angles of organics on solid surfaces and to apply the model to a simple system. The model may be used to optimize and explain the performance of industrial cleaning/degreasing systems. Such optimization allows for the improvement of the economic and environmental performance of these industrial cleaning systems. In this article, the model will be applied to simple systems composed of ionic surfactant solutions, hexadecane droplets, and a gold or steel surface to demonstrate the capabilities of our theory and approach.

3. Proposed Model

The model presented in this article is based on a simplified cleaning system. As can be seen in Figure 1 the system is composed of a solid surface, an organic droplet contacting the solid, and the aqueous cleaning solution. We are assuming that the walls of the cleaning system have no effect on the result from the model and, therefore, can be assumed negligible. The organic droplet is assumed to behave like a spherical cap. This means that the observed droplet will appear as a portion of a sphere that is truncated by its contact with the solid surface being cleaned. It should also be noted that the solid surface is assumed to have a limited surface area for adsorption/desorption of oil, water, and surfactant. Additionally the system is considered to be at equilibrium, by which a system of component balance equations can be developed to explain the distribution of system components. Therefore the modeling approach is to:

1. write component balances to describe cleaning system,
2. develop equilibrium constants for each balance,
3. utilize numerical method based computational techniques to determine component distribution,
4. and determine the contact angle of the droplet.

A conceptual representation of the computational approach utilized in this work can be seen in Figure 2.

3.1. Equilibrium System Description

The cleaning system being studied in this article is composed of surfactant, water, an organic contaminant, and a solid surface. The

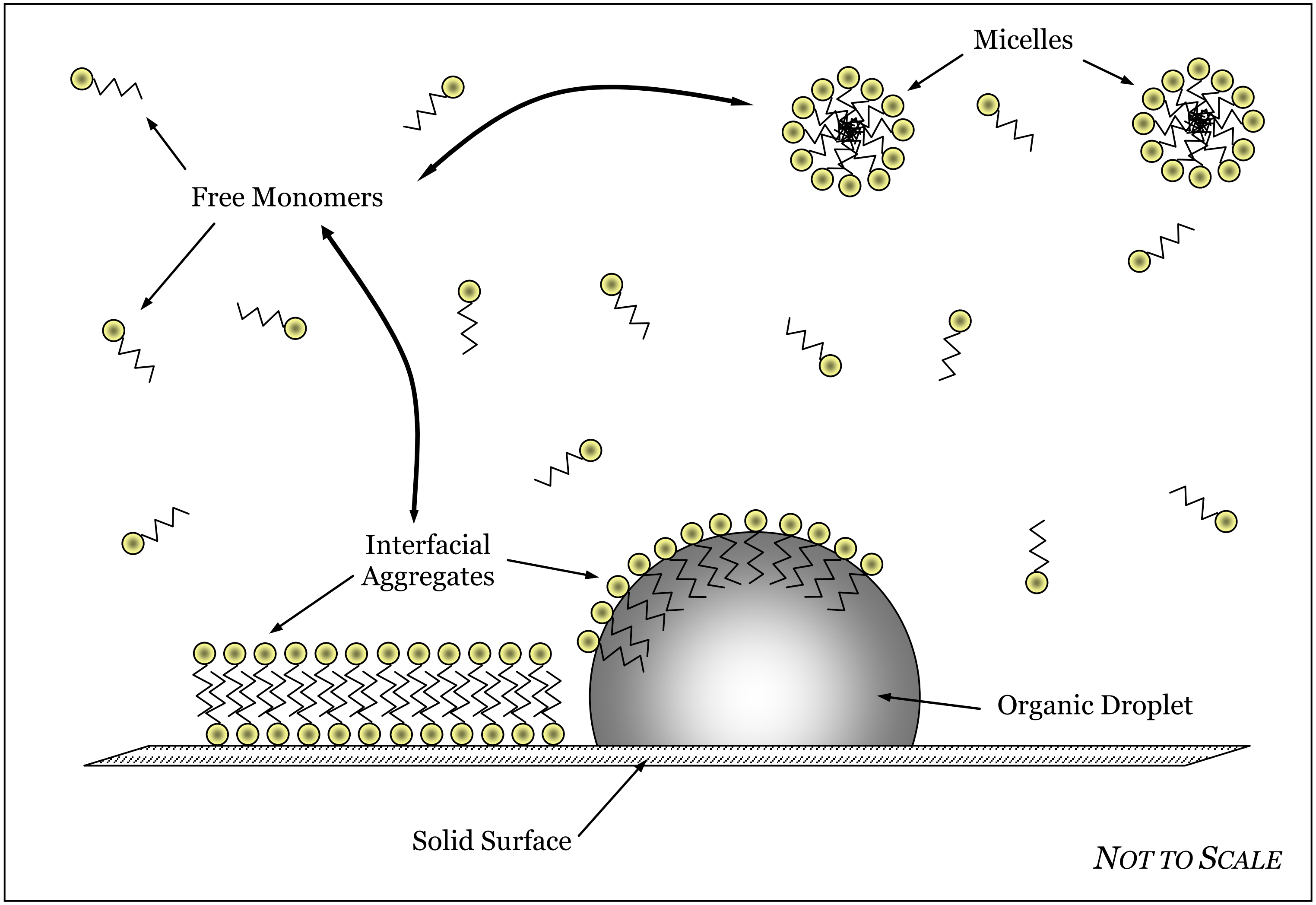

Figure 1. Simplified Surfactant Solution Cleaning System

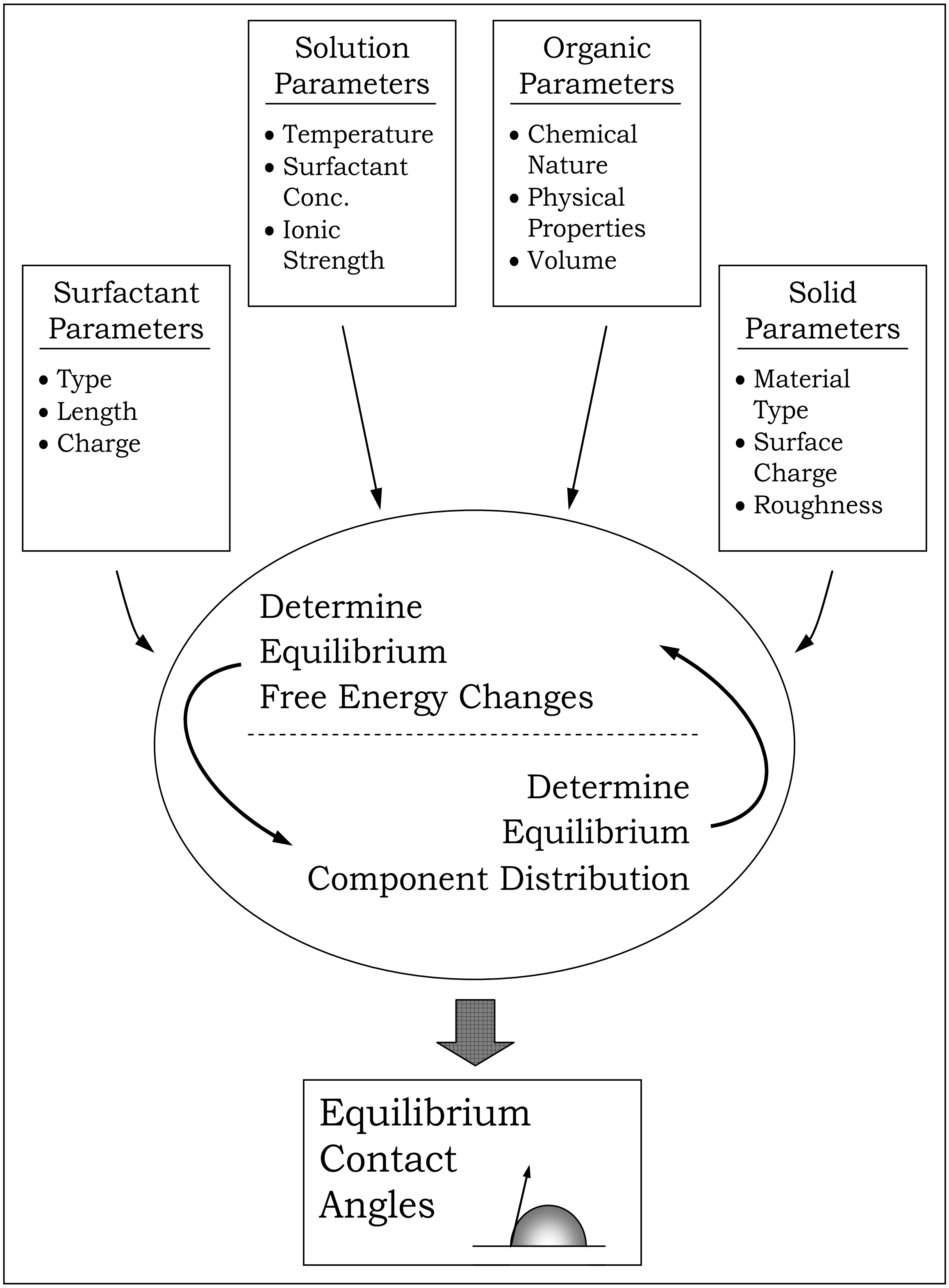

Figure 2. Conceptualization of Modeling Approach

model assumes a state of equilibrium and therefore the following five component balances can be used to describe the system:

Surfactant *(in solution)* ⇔ Surfactant *(in micelles)*
Surfactant *(in solution)* ⇔ Surfactant *(at organic/solution interface)*
Surfactant *(in solution)* ⇔ Surfactant *(at solid/solution interface)*
Organic *(free liquid)* ⇔ Organic *(in solid/organic interface)*
Water *(in solution)* ⇔ Water *(at solid/solution interface)*

The first three component balances cover the movement of surfactant monomers from the free state in solution to one of three possible aggregation destinations. The first balance describes the movement of surfactant between the solution and micelles, which are solution aggregates. The second balance describes the movement of surfactant between solution and an adsorbed state at the organic/solution interface. The third balance is concerned with the formation of surfactant aggregates at the solid/solution interface. The fourth balance covers the movement of organic molecules between a free contiguous liquid state and a state of adsorption at the solid/organic interface. In this model, the assumption is made that the organic maintains a separate phase from the aqueous solution. The organic is assumed to have a known and constant volume and, therefore, no organic molecules will be found free in the aqueous phase. The remaining balance describes the movement of water between the solution and the solid/solution interface.

Once the balances for the system have been determined, it becomes possible to utilize basic equilibrium theory and elementary thermodynamics to determine the form of the equilibrium constants. For the generic case of a reversible process:

$$\alpha \Leftrightarrow \beta \tag{1}$$

the forward and backward change in mass concentration can be shown as follows:

$$\frac{d[\beta]}{dt} = k_{\alpha\to\beta}[\alpha] \tag{2}$$

$$\frac{d[\alpha]}{dt} = k_{\beta\to\alpha}[\beta] \tag{3}$$

As a condition of equilibrium, the change in the mass concentration of α must be equal to the change in the mass concentration of β. Therefore, an overall component equilibrium constant, K_i, can be determined as follows:

$$K_{\alpha\leftrightarrow\beta} = \frac{k_{\beta\to\alpha}}{k_{\alpha\to\beta}} = \frac{[\alpha]}{[\beta]} \tag{4}$$

In the same manner surfactant self-assembly, which in its simplest form is an adsorption-desorption process, can be defined by modifying this equation as follows:

$$K_{self-assembly} = \frac{k_{desorption}}{k_{adsorption}} = \frac{[N_{\text{molecules, free state}}]}{[N_{\text{molecules, aggregate state}}]} \tag{5}$$

From classical thermodynamics the relationship between the equilibrium coefficient and the change in Gibbs free energy for a process can be described in the following manner:

$$\Delta G_{free \rightarrow aggregate} = -RT \ln\left(K_{self\text{-assembly}}\right) \qquad [6]$$

where R is the ideal gas constant, T is the equilibrium temperature of the process and ΔG represents the change in Gibbs free energy of aggregation/self-assembly. Combining Equations 5 and 6 results in a relationship that assists in the determination of the separation of components within the system being modeled:

$$\frac{\left[N_{\text{molecules, free state}}\right]}{\left[N_{\text{molecules, aggregate state}}\right]} = \exp\left(\frac{-\Delta G_{free \rightarrow \text{aggreate}}}{RT}\right) \qquad [7]$$

This relationship can be used to determine the molecular concentrations of free or adsorbed species, depending on which are unknown. This allows for the determination of the amount of a particular component in a particular state through the determination of the change in Gibbs free energy. Eq. [7] can be modified by the replacement of the molecular concentration terms with mole fractions. This change will be shown in the subsequent sections to be a function of a number of measurable system parameters, such as ionic strength, temperature, surfactant type, solid type, and the organic type.

3.2. Micellization Equilibrium Constant

Micellization is perhaps the most widely discussed type of aqueous based surfactant self-assembly in the available body of literature. A large portion of this work is devoted to experimental investigations into the effects of various solutions parameters on micellization and CMC. Over the past few decades, a significant body of literature has been published that presents various strategies for modeling and predicting the process of micellization. The work presented in this article is based on the use of a summed contribution approach to the determination of the free energy of micellization. These works were initially utilized as a foundation for our initial modeling work. The equation for the free energy of micellization, $\Delta G_{micellization}$, utilized in the DMM:

$$\Delta G_{\text{Micellization}} = \Delta G_{\text{Hydrophobic}} + \Delta G_{\text{Interfacial}} + \Delta G_{\text{Electrostatic}} \qquad [8]$$

accounts for the free energy changes due to the hydrophobic nature of the surfactant tail chains, $\Delta G_{hydrophobic}$, from variations in the nature of the interface between the solution and the micelle, $\Delta G_{interfacial}$, and from the electrostatic interactions between micellized surfactant headgroups and between these headgroups and free electrolytes in solution, $\Delta G_{electrostatic}$. The first term has a negative value, which favors micellization and in fact is the driving for most surfactant self-assembly. The remaining terms are typically positive in nature and provide a moderating effect on the self-assembly process. The equations for these terms are provided in an earlier work [20] and will not be review here. The main difficulty in utilizing Eq. [8] is found in the necessity for a constant in the interfacial term. This constant was not defined in the work of Evans *et al.* [12, 18, 19] and it appeared to provide a factor that would allow for the manipulation of the free energy of micellization to match the experimental values reported for various surfactants' CMC. This presented a difficulty in that the CMC would need to be hard-coded into the model and the robustness desired when analyzing experimental data for systems with little CMC data published would be compromised. As a result of these difficulties the more involved contributional approach presented in the work of Nagarajan and Ruckenstien [21] was determined to provide a better basis for the computer code portion of the present work. This approach relied on six free energy change terms:

$$\begin{aligned}\Delta G_{\text{micellization}} &= \Delta G_{\text{hydrophobic}} + \Delta G_{\text{steric}} + \Delta G_{\text{restricitve}} + \Delta G_{\text{interfacial}} \\ &\quad + \Delta G_{\text{electrostatic}} + \Delta G_{\text{dipole}}\end{aligned} \tag{9}$$

In addition to a term that accounts for the dipole-dipole interactions, ΔG_{dipole}, this approach breaks the interfacial term presented in the DMM into three separate terms. These terms account for the physical interactions between headgroups at the micelle/solution interface, ΔG_{steric}, the physical interactions between surfactant tail chains inside the micelle's hydrophobic core, $\Delta G_{\text{restrictive}}$, and the changes on the solution/core interfacial tension from solution composition changes, $\Delta G_{\text{interfacial}}$. In the current work only ionic surfactants will be considered thereby eliminating the need to incorporate the dipole interaction term, ΔG_{dipole}, as only zwitterionic surfactants have a need for this term. An additional benefit to the method presented by Nagarajan and Ruckenstien is the ability to account for surfactant aggregates that are not ideally spherical in nature [21]. Since their work provides an excellent discussion of the development of the individual terms, only the equations as utilized in the present effort will be shown. The reader should refer to their work for a detailed discussion of these terms. The hydrophobic term, $\Delta G_{\text{hydrophobic}}$, was derived from the work of Tanford [27] and can be found from the following equation:

$$\Delta G_{\text{hydrophobic}} = \Delta G_{\text{CH}_2}\left(N_{Tail\,C} - 1\right) + \Delta G_{\text{CH}_3} \qquad [10]$$

where the free energy change for the methlyene groups, $\Delta G_{CH2,}$ and the methyl groups, $\Delta G_{CH3,}$ in the tail chain of the surfactant are found from the following empirical relationships:

$$\Delta G_{\text{CH}_2} = k_b \cdot T\left(5.85\ln\left(T\right) + {}^{896}\!/_{T} - 36.15 - 0.0056T\right) \qquad [11]$$

$$\Delta G_{\text{CH}_3} = k_b \cdot T\left(3.38\ln\left(T\right) + {}^{4064}\!/_{T} - 44.13 - 0.02595T\right) \qquad [12]$$

relating the desire for the organic portion, tail chain, of the surfactants to phase separate from the water component in the solution. The steric term relating the inhibition of self-assembly from headgroup-headgroup interaction is simply the Van der Waals approach to the interactions of hard spheres. This equation:

$$\Delta G_{\text{steric}} = -k_b\,T\,\ln\left(1 - \frac{A_{\text{headgroup}}}{A_{\text{effective}}}\right) \qquad [13]$$

simply relates the cross sectional area of the surfactant headgroup, $A_{\text{headgroup}}$, to the effective area per monomer, $A_{\text{effective}}$, allowed for each surfactant based on the size of the hydrophobic core. The effective area per monomer is determined by dividing the estimated surface area of the hydrophobic core by the aggregation number for the surfactant of interest. The area of the hydrophobic core, $A_{\text{hydrophobic core}}$, is determined as follows:

$$\mathrm{A}_{\text{hydrophobic core}} = 4\pi\left(R_{core}\right)^2 \qquad [14]$$

where the radius of the micelle hydrophobic core, R_{core}, is based on the best estimate for the volume of the surfactant tail chain. The restrictive term describes the inhibition of the self-assembly process from the interactions between surfactant tail chains in the micelle hydrophobic core. This term is important since each tail chain is fixed at one end by the position of the headgroup at the micelle core surface and therefore has a limited possible arrangement respective of the other surfactant tail chains in the hydrophobic core. The empirical relationship utilized by Nagarajan and Ruckenstein [21]:

$$\Delta\mathrm{G}_{\text{restrictive}} = k_b\,T\left(-0.50 + 0.24 * N_{Tail\,C}\right) \qquad [15]$$

relates the free energy change to the number of carbons in the surfactant tail chain. The interfacial term seen in the following equation:

$$\Delta\mathrm{G}_{\text{interfacial}} = \sigma_{core}\left(A_{effective} - A_{headgroup}\right) \qquad [16]$$

where the interfacial tension of the hydrophobic core/solution interface, σ_{core}, is defined as follows:

$$\sigma_{core} = \sigma_{tail} + \sigma_{water} - 2.0\psi\sqrt{\sigma_{tail}\,\sigma_{water}} \qquad [17]$$

in which the surface tension of water and the surface tension of an organic molecule can be empirically related to temperature:

$$\sigma_{tail} = 35.0 - 325\left(M_{tail}\right)^{-2/3} - 0.098\left(T - 298\right) \qquad [18]$$

$$\sigma_{water} = 72.0 - 0.16\left(T - 298\right) \qquad [19]$$

with M_{tail} representing the molecular weight of the surfactant tail chain. A constant, ψ, present in Eq. [17], was set to values between 0.5 and 0.8 depending on surfactant type. The last crucial term for the current work describes the repulsive interactions between the headgroups at the micelle/solution interface and between micelles headgroup and electrolytes free in solution. The equations for this term remain essentially unchanged from those presented in the DMM. The DMM presents a solution to the problem of micelle surface curvature, which for the distances normally present in a micelle is of considerable concern. The reader should refer to the works of Evans *et al.* for a detailed derivation of this curvature approximation to the planar Possion-Boltzmann equation [12, 18, 19]. This approximation is as follows:

$$\Delta G_{electrostatic} = \Delta G_{electrostatic-planar} + \Delta G_{electrostatic-curvature} \qquad [20]$$

with the planar electrostatic term:

$$\Delta G_{electrostatic-planar} = 2k_b T\left(\ln\left(\frac{S}{2} + \sqrt{1 + \left(\frac{S}{2}\right)^2}\right) + \frac{2}{S}\left(1 - \sqrt{1 + \left(\frac{S}{2}\right)^2}\right)\right) \qquad [21]$$

and the curvature-corrected term:

$$\Delta G_{electrostatic-curvature} = 2k_b\,T\left(\frac{4}{\kappa R_{core} S}\right)\ln\left(\frac{1}{2}+\left(\frac{1}{2}\right)\sqrt{1+\left(\frac{S}{2}\right)^2}\right) \qquad [22]$$

displaying a dependence on the dimensionless surface charge density, S, and the inverse Debye screening length, κ. The dimensionless surface charge density is further found to be a function of Debye screening length as follows:

$$S = \frac{\left(e_c\right)^2}{\varepsilon \kappa\, A_{effective}\, k_b\, T} \qquad [23]$$

where the inverse screening length is defined as:

$$\kappa = \sqrt{\frac{2N_{ions}\left(e_c\right)^2}{\varepsilon k_b\, T}} \qquad [24]$$

and is a function of the temperature, T, the dielectric constant of the solution, ε, and the number of free ions in solution, N_{ions}.

With the terms that contribute to the free energy of micellization determined it becomes possible to find the equilibrium constant for the micellization process. Modifying Eq. [7] as is appropriate for micellization:

$$K_{micellization} = \frac{X_{\text{free surfactant}}}{X_{\text{micellized surfactant}}} = \exp\left(\frac{-\Delta \mathrm{G}_{micellization}}{\mathrm{RT}}\right) \qquad [25]$$

provides a way to determine the equilibrium constant and subsequently the distribution of surfactant between the free state and the micellized state. This equation can be further simplified by the assumption that surfactant monomers incorporated in micelles are no longer available in the free state and consequently the micelles constitute a separate phase. Put simply, the mole fraction of micellized surfactant can be set to unity which simplified the above equation in the following manner:

$$K_{micellization} = X_{\text{free surfactant}} = \exp\left(\frac{-\Delta \mathrm{G}_{micellization}}{\mathrm{RT}}\right) \qquad [26]$$

3.3. Organic/Solution Adsorption Equilibrium Constant

Since the driving force for the self-assembly is the hydrophobic nature of the surfactant tail chains it would seem reasonable to extend the theory presented in the discussion of micellization to the adsorption of surfactant monomers to the organic/solution interface. The hydrophobic nature of the organic phase provides the ideal destination for the hydrophobic surfactant tail chains as opposed to the free-state in solution. Unlike micellization there is no reported minimum required aqueous surfactant concentration for the adsorption of surfactant to the organic/solution interface. A review of the literature provides a further justification for the extension of the summed contribution approach to the adsorption of surfactant to this interface. J.D. Hines' extension [26] of the theory present in the DMM and the work of Nagaragan and Ruckenstien [21] to the air/solution interface provide insight into the additional considerations required for non-micellular self-assembly. Additional justification for this approach is evident in the work of Li and

Ruckenstein [22] which is concerned with the self-assembly of surfactants at the solid/solution interface.

First Eq. [9] must be modified by the removal of the dipole contribution:

$$\Delta G_{\text{organic/solution adsorption}} = \Delta G_{\text{hydrophobic}} + \Delta G_{\text{steric}} + \Delta G_{\text{restricitve}} + \Delta G_{\text{interfacial}} + \Delta G_{\text{electrostatic}} \quad [27]$$

since this present work is not concerned with zwitterionic surfactants. A benefit inherent in the extension of the micellization approach is that a number of the previously defined contributions will be utilized in the determination of the equilibrium constant for the organic/solution interfacial adsorption. Eq. [10] describing the hydrophobic contribution is assumed to hold valid for this process. Additionally the form of the equation for the steric contribution will also hold true, however, the value for the effective area per surfactant monomers, $A_{effective}$, will be based on the organic/solution interfacial area. The determination of the value for this interfacial area is grounded in one of the primary assumptions of the current approach. It is assumed that the organic droplet will maintain a spherical shape, ranging from a spherical cap up to a full spherical droplet. As this definition implies, the actual value for the organic/solution area has the possibility of variation from equilibrium state to equilibrium state. While a spherical shape is used in this model there exist an additional shape, a buoyancy-driven inverse teardrop, which merits mention. Chatterjee has presented the results of a modeling effort concerning such droplets and can be referred to for further information on the subject [28]. The assumption of a spherical shapes was based on experimental studies indicated earlier and has proven to be valid for the systems studied. A visual description of the droplet's assumed shapes is shown in Figure 3. The spherical cap is assumed for contact angles between 0° and 90°. A fractional spherical shape will be assumed for contact angles between 90° and 180°. Contact angles greater than 180° are not possible, as the droplet would have detached from the solid surface. A discussion of contact angles and their analysis can be found in the works of Kwok and Neumann [29, 30]. This work provides an in-depth discussion of contact angles and the validity of their use in certain situations. As can be seen in Figure 3, the contact angle used in the model is interpreted geometrically where the value for the height of the center of the spherical cap, h_{cap}, is determined based on the amount of solid surface area occupied by the organic component. The method for determining the organic droplets 'footprint' will be in a later section. However, with the height of the spherical cap determined it becomes possible to calculate a value for the radius of a sphere, R_{sphere}, large enough to incorporate the spherical cap:

$$R_{sphere} = \frac{1}{3}\left(\frac{3V_{organic} + \pi \left(h_{cap}\right)^3}{\pi \left(h_{cap}\right)^2} \right) \qquad [28]$$

where $V_{organic}$ is the known volume of the organic phase. This volume is a constant value for a particular droplet due to the assumption that the organic and aqueous phases remain separate. Using this equivalent radius the contact angle of incidence between the droplet and the solid, Θ, can be determined as follows:

$$\Theta = \cos^{-1}\left(\frac{R_{sphere} - h_{cap}}{R_{sphere}} \right) \qquad [29]$$

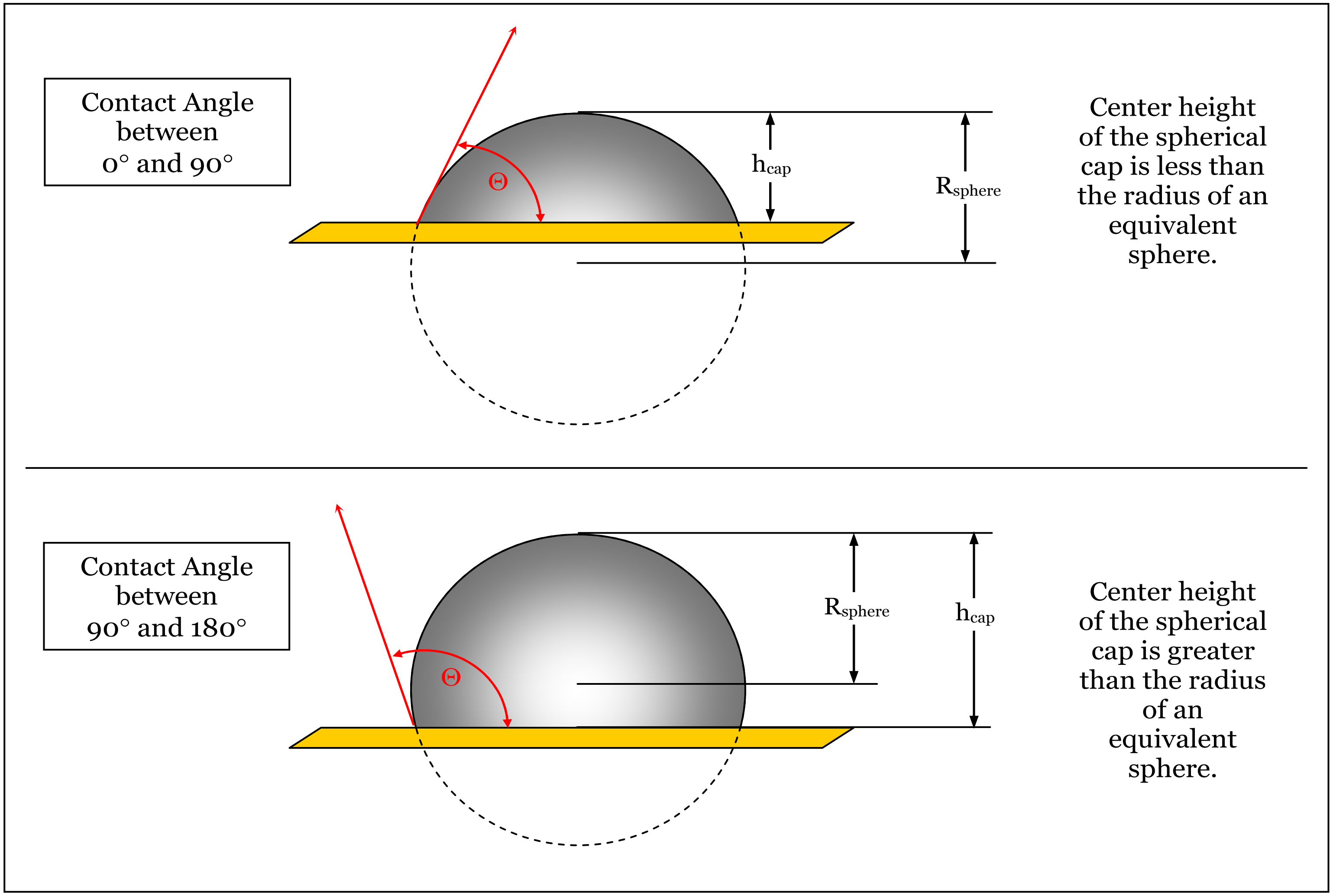

Figure 3. Organic Droplet Contact Angle Visualization

where units of Θ are radians. From a geometric analysis of the assumed droplet shape, it becomes evident that the contact angle is equal to the fraction of the surface of the equivalent sphere in contact with the solution. As a result the area of the interface between the organic droplet and the solution, A_{drop}, is:

$$A_{drop} = 4\left(R_{sphere}\right)^2\left(Surface\,Fraction\right) \qquad [30]$$

and consequently the effective area per surfactant monomer, $A_{effective}$, becomes:

$$A_{effective} = \frac{A_{drop}}{N_{Surf,O/S}} \qquad [31]$$

with $N_{surf,\,O/S}$, being the number of surfactant monomers present at the organic/solution interface. The contribution from the restriction of the surfactant tail chains, $\Delta G_{\text{restrictive}}$, can be approximated by applying the same technique that was used for the air/solution interface as described by Hines (26):

$$\Delta G_{\text{restrictive}} = k_b T\left(\frac{10\pi}{80E_{packing}}\right)\left(\frac{\tau^2}{A_{headgroup}N_{sites}}\right) \qquad [32]$$

This relationship was used for a molecular model of the air/solution interface however it is extendable to this work with a few simplifications. The first is that the thickness of the hydrocarbon layer, τ, will be assumed to only extend as far a the fully extended length of the surfactant tail chain, $L_{tail\ chain}$, as determined by the following equation [21]:

$$L_{tail\,chain} = \left(0.15 + 0.126 N_{Tail\,C}\right) \qquad [33]$$

which results in a length in nanometers and should be converted to meters for use in the computational model. The second simplification is that the packing parameter, $E_{packing}$, which describes the general orientation of the monomer in the adsorbed layer can be stated so that:

$$E_{packing} = \frac{A_{effective} L_{tail\,chain}}{V_{tail\,chain}} \qquad [34]$$

where $V_{tail\ chain}$ is the approximate volume of the surfactant tail chain. The packing parameter approaches unity at its minimum and is an indication of the effect of the restrictive contribution on the overall free energy change. Lastly, the number of available interfacial adsorption sites, N_{sites}, for the remaining solution based surfactant monomer can be determined as follows:

$$N_{sites} = \frac{A_{drop} - \left(A_{headgroup} N_{Surf,O/S}\right)}{A_{headgroup}} \qquad [35]$$

Since the organic/solution interfacial area is very large with respect to the area of an individual surfactant headgroup, the values for the packing parameter and the number of available adsorption sites will minimize the effect of the restrictive contribution on the overall free energy change. This will hold true until the organic/solution interfacial region nears the physical saturation limit for adsorption. This occurs when the summed area of the adsorbed surfactant headgroups nears the value of the organic/solution interfacial area. The term for the contribution of surfactant adsorption on the change in free energy, $\Delta G_{\text{interfacial}}$, was not as elegant as the one given for micellization. Utilizing published adsorption and/or organic/solution interfacial tension data, an empirical relationship can be developed to have the following form:

$$\Delta G_{\text{interfacial}} = \left(C - B\Gamma - A\Gamma^2 \right) \Big/ N_{Avagadro} \qquad [36]$$

where A, B, and C are constants, and Γ is equal to the adsorbed moles of surfactant. Since the interfacial tension is relative to the number of monomers adsorbed to the interface this relationship must reflect the free energy change for a specific adsorption state. This is done so that the model is not rigidly fixed to a certain adsorption profile. As the constants will be system specific, the actual values used in this current work will be discussed later. However, it is worth noting here that the same constants were satisfactory for the three systems analyzed later in this article. The electrostatic contribution will be determined using only Eq. [21]. The curvature correction term developed for the DMM is unnecessary despite the obvious curvature of the organic droplet. This is because the droplet is so large with respect to each individual surfactant monomer that the curvature of the droplet is negligible since each monomer effectively perceives a planar surface. An additional difference from the micellization section is that the value of the dimensionless surface charge density, S, is now based on the effective area per monomer as defined for the organic/solution interface.

With the individual contributions defined the change in free energy for the adsorption of surfactant monomers to the organic/solution interface can be calculated using Eq. [27]. Modification of Eq. [7] for this process:

$$K_{\mathrm{organic/soltuion\,adsorption}} = \frac{X_{\mathrm{adsorbed\,surfactant}}}{X_{\mathrm{free\,surfactant}}} = \exp\left(\frac{-\Delta \mathrm{G}_{\mathrm{organic/solution\ adsorption}}}{\mathrm{RT}}\right) \qquad [37]$$

identifies that some additional information regarding the adsorption interface is required. Since the number of surfactant monomers adsorbed at the organic/solution interface will typically be insignificant to shield the organic phase from the solution an approximation is required to determine the concentration of monomers at this interface. When no surfactant is present, the solution and the organic will have a defined interface. This does not hold true for solutions with surfactants present, since only the hydrophobic moiety of the surfactant will penetrate the organic phase. In order to satisfy the assumption of phase separation, but still determine the interfacial surfactant concentration, a series of layers will be used to approximate the actual organic/solution interface when surfactants are bridging this interface. The model assumes four layers are present. The first layer is composed of only aqueous surfactant solution. The second layer contains the hydrophilic surfactant headgroups and an appropriate amount of aqueous solution to avoid the mistake of allowing unfilled spaces between headgroups. The third layer is made up of the hydrophobic surfactant tail chains and a requisite amount of the organic phase to prevent unfilled space. The final layer is that of the organic droplet. A further simplification unites the second and third layers into a single layer that represents the interfacial adsorption layer. Obviously to determine the concentration of surfactants in this interfacial adsorption layer approximations need to be made so that the components volumes can be approximated. The volume of the surfactant headgroup/solution layer, V_{SSL}, can be approximated from the equivalent drop radius, $R_{drop\ eq}$, and the diameter of a surfactant headgroup, D_{surf}. The volume is defined as:

$$V_{SSL} = \tfrac{4}{3}\pi\left(\left(R_{drop\,eq} + D_{surf}\right)^3 - \left(R_{drop\,eq}\right)^3\right) \qquad [38]$$

where the equivalent drop radius is approximated from the calculated organic/solution area.

The volume for the surfactant tail chain/organic layer, V_{SOL}, is determined in a similar fashion with the thickness of the layer set equal to the length of the tail chain. Therefore the equation to determine this volume is:

$$V_{SOL} = \tfrac{4}{3}\pi\left(\left(R_{drop\,eq}\right)^3 - \left(R_{drop\,eq} - L_{tail\,chain}\right)^3\right) \qquad [39]$$

With the volumes of the second and third layer determined, it becomes simple to determine the volume of the layers not occupied by either a headgroup or a tail chain. As a result, the volume of the second layer allocated to water molecules, V_{WAL}, and the volume of the third layer allocated to organic molecules, V_{OAL}, is calculated as follows:

$$V_{WAL} = V_{SSL} - N_{Surf,O/S}\, V_{headgroup} \qquad [40]$$

$$V_{OAL} = V_{SOL} - N_{Surf,O/S}\, V_{tail\,chain} \qquad [41]$$

With estimations for the volume per molecule for the water and organic components, it is simple to determine the number of molecules of these two components in the combined adsorption layer. When combined with the number of molecules of surfactant adsorbed to this layer the required surfactant mole fraction for the organic/solution interface can be found as is necessary for the iterative solution process employed in this model.

3.4. Solid/Solution Adsorption Equilibrium Constant

The remaining mass balances are concerned with the competition for the limited area of the solid surface. This competitive adsorption/desorption requires that when surfactant adsorbs to the surface one of the other two system components must desorb. For this stage of the work an assumption that each species will adsorb/desorb in a manner consistent with a Langmuir isotherm:

$$\theta = \frac{K_{free \to ads}\left[C_{free}\right]}{1 + K_{free \to ads}\left[C_{free}\right]} \qquad [42]$$

where the fractional surface coverage, θ, of a particular component is a function of the free concentration of that component in the solution, $[C_{free}]$, and the equilibrium constant of adsorption, $K_{free \to ads}$. Since in the current work there are three distinct species adsorbing to the surface, the Langmuir isotherm must be modified to account for the relative movement of each species. The primary justification for this is that each species either occupies or vacates an adsorption site. It has been shown that the surfactant will adsorb to the surface therefore either the water or organic molecules will desorb to make room for the monomers. As a result, each equation necessary to describe the adsorption and desorption of any one of the three species will become a function of the adsoprtion behavior of the remaining two. These equations:

$$\theta_{H_2O} = \frac{K_{H_2O_{\text{ad}}} N_{H_2O_{\text{soln}}}}{V_{\text{soln}} + K_{H_2O_{\text{ad}}} N_{H_2O_{\text{soln}}} + K_{S_{\text{ad}}} N_{S_{\text{soln}}} + K_{org_{\text{ad}}} N_{org_{\text{free}}} \left(\frac{V_{\text{soln}}}{V_{\text{organic}}}\right)} \qquad [43]$$

$$\theta_{surf} = \frac{K_{surf_{ad}} N_{surf_{\text{soln}}}}{V_{\text{soln}} + K_{H_2O_{ad}} N_{H_2O_{\text{soln}}} + K_{surf_{ad}} N_{surf_{\text{soln}}} + K_{org_{ad}} N_{org_{free}} \left(\frac{V_{\text{soln}}}{V_{\text{organic}}}\right)} \qquad [44]$$

$$\theta_{organic} = \frac{K_{org_{ad}} N_{org_{free}}}{V_{\text{organic}} + K_{H_2O_{ad}} N_{H_2O_{\text{soln}}} \left(\frac{V_{\text{organic}}}{V_{\text{soln}}}\right) + K_{surf_{ad}} N_{surf_{\text{soln}}} \left(\frac{V_{\text{organic}}}{V_{\text{soln}}}\right) + K_{org_{ad}} N_{org_{free}}} \qquad [45]$$

when summed must equal unity, since a vacuum cannot be present on the surface. The three equilibrium constants in the above equations, K_{H2O}, K_{surf} , and K_{org}, must be determined by approximating the changes in free energy for each component respectively. From elementary thermodynamics it is known that:

$$\Delta G = \Delta H - T\Delta S \qquad [46]$$

which simply states that the change in free energy is related to the change in enthalpy, ΔH, and the temperature relative change in entropy, ΔS. The enthalpic portion of the above equation can be approximated in the following manner:

$$\Delta H = \varepsilon - \tfrac{1}{2} C_p \left(T - T_{ref}\right) \qquad [47]$$

which accounts for the enthalpy changes due to changes in the temperature through the use of a heat capacity, C_p, contribution and an adjustable interaction parameter, ε, relating the attraction of the component to the surface, which will be used as a component specific empirical term. The entropic portion of the free energy term will be approximated as follows:

$$\Delta S = R\ln\left(\frac{V_{ads}}{V_{free}}\right) \tag{48}$$

where the change in entropy is related to the volume of the adsorbed component, V_{ads}, relative to the volume of the free component, V_{free}.

Since the purpose of this model was to predict contact angles and their respective concentration dependent trends the model returns to the definition of contact angles described in Figure 3 and Eq. [28] and Eq. [29]. With the model equations defined it becomes possible to compare the performance of the model to experimental contact angle data. The model is based on the utilization of known properties for each component and five empirical features, one per mass balance. It lends itself to being tuned and improved through the use of experimental measurements. The empirical features imbedded in the micellization model can be tuned through comparison to published CMC data, which effectively removes it from consideration. The empirical relationship required by the interfacial term for the adsorption of surfactant to the organic/solution interface can be determined by comparison to experimental interfacial tension data. The remaining empirical constants for each of the solid surface adsorptions terms can be determined from experimental contact angle data.

4. Results and Discussion

The experimental data used for comparison with the model was from the work of Davis *et al.* [5, 6]. A complete compilation of this data, experimental methods used in its acquisition, and the data pertinent to the origin of the system components can be found in these articles. The data for the contact angles of hexadecane on a gold surface immersed in sodium dodecyl sulfate (SDS), an anionic surfactant with a published CMC of 8.2 mM [12], and cetyl trimethyl ammonium bromide (CTAB), a cationic surfactant with a published CMC range of 0.7 to 1.0 mM [4], solutions and for hexadecane on a polished steel surface immersed in CTAB solutions is used for comparison in this current work. These contact angles were measured using a Tantec commercial contact angle meter. Figure 4 shows a schematic of the data acquisition setup. The data acquired by Davis *et al.* provides a range of surfactant concentrations extending from no surfactant present to concentrations above the published CMCs [5, 6]. The following sections documents the empirical parameters used in the model and a comparison of the predicted contact angle values and trend to the aforementioned contact angle data.

As mentioned earlier an empirical relationship, Eq. [36], is required for the determination of the interfacial contribution for the adsorption of surfactant to the organic/solution interface. Utilizing experimental data from Staples *et al.* [31] for the adsorption of SDS to hexadecane droplets and Knock *et al.* [32] for the adsorption of CTAB to hexadecane droplets

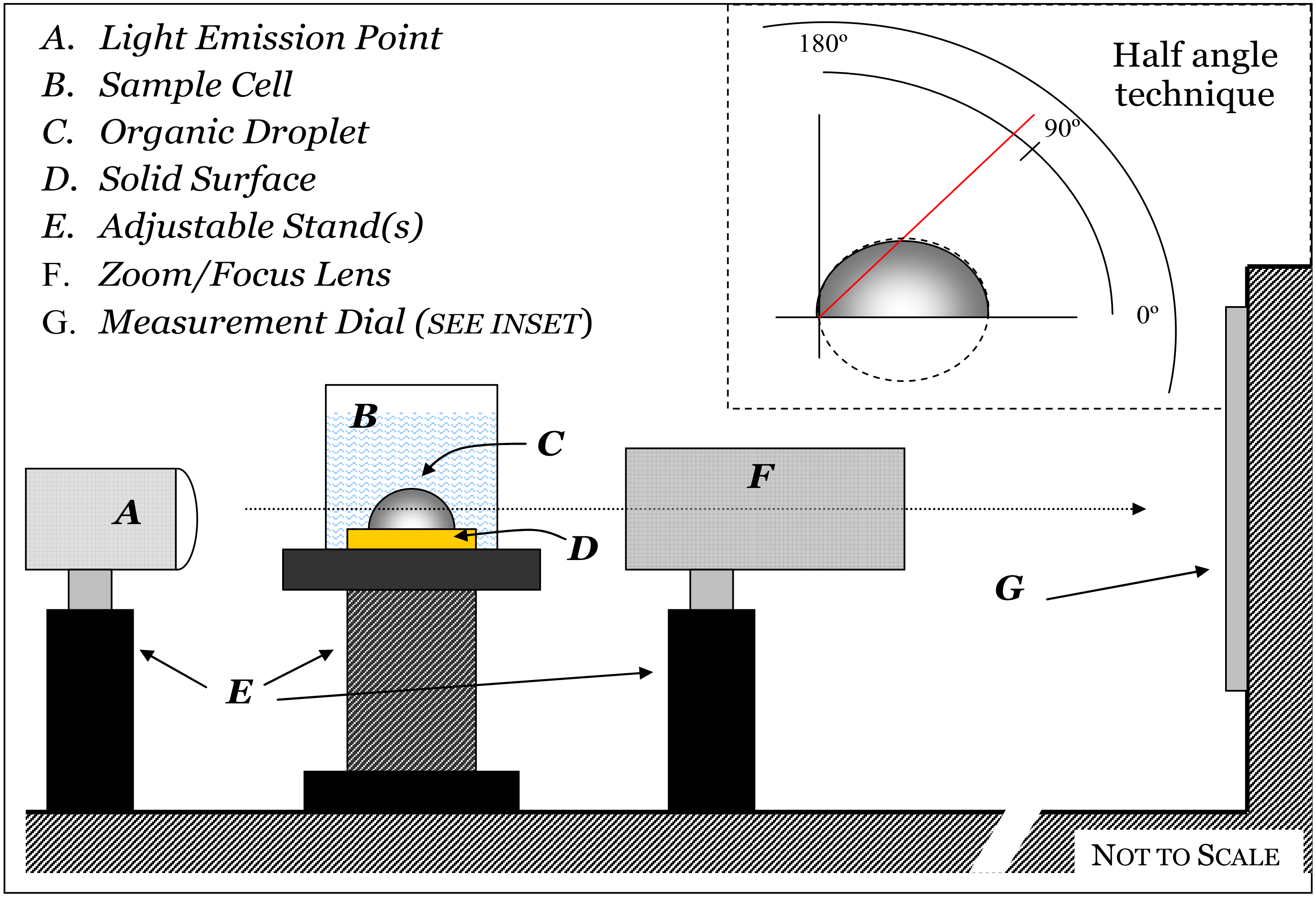

Figure 4. Contact Angle Measurement Apparatus

values for the three constants were determined and are shown in Table 1. These values were found to be satisfactory for both surfactants.

However, they provide a better correlation to SDS than CTAB. This seemingly counterintuitive result could be due to the fact that the interfacial term is more concerned with the surfactant tail chains and the two surfactants are close in total tail carbons, with twelve for SDS and fourteen for CTAB. Additionally, the oil/solution interfacial tensions of both surfactants over their respective range of concentrations observed are very close in value. As the model is improved in the future, these empirical values can be determined more precisely for each surfactant where desired and the contribution term could potentially be altered by an improved theoretical understanding.

The first experimental data analyzed was for hexadecane droplets on a gold surface in solutions of SDS. Figure 5 shows a comparison of the predicted trend to the experimental data. As expected, the prediction and the experimental data display an increase until the CMC is reached, since above the CMC any addition surfactant added to the solution is directed to the formation of micelles. The prediction has an overall average error of 1.07 percent compared to this experimental dataset. The empirical parameters required for the determination of the equilibrium constants for component adsorption to the solid surface were tuned to

Table 1. Empirical Constants for Equation [36]

Constant	Value	Units
A	-2.092×10^{21}	kJ/mol
B	-1.230×10^{10}	kJ/mol
C	13.724	kJ/mol

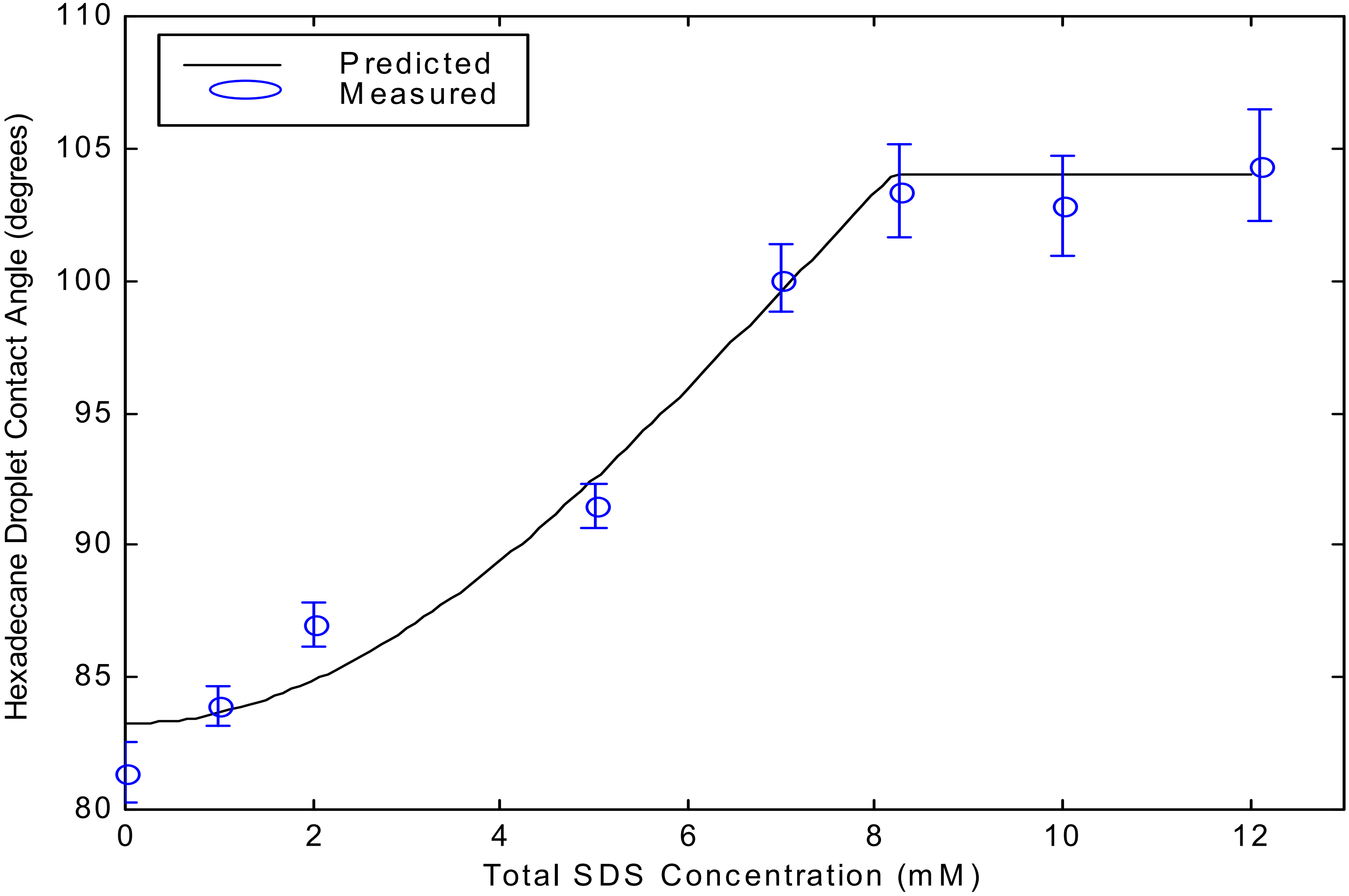

Figure 5. Hexadecane Droplets on Gold Surface in SDS Solutions

the data shown in Figure 5. The interaction parameters required for determination of the equilibrium constants in Eq. [47], were determined to be -6.151 kJ/mol for water, –41.015 kJ/mol for the surfactant, and –0.582 kJ/mol for the organic species respectively. The relative values are consistent with the expected trends that the organic is least attracted to the surface, and the surfactant is most attracted.

The next experimental data set analyzed was for hexadecane droplets on a gold surface in solutions of CTAB. Figure 6 shows a comparison of the predicted trend to the experimental data. As with the first comparison the model finds a satisfactory value for the CMC that falls within the report range. This prediction has an overall average error of 3.40 percent relative to the experimental dataset. This error is higher than the comparison to the SDS data. However, since the only compositional difference between the two systems is the surfactant, the values for the interaction parameters for the organic and water components were not changed from those used in the SDS comparison. Therefore, the remaining interaction parameter for solid surface adsorption, for the adsorption of CTAB to the solid, was found to be –46.974 kJ/mol.

The final data set analyzed was for hexadecane droplets on a steel surface in solutions of CTAB. The steel surface was hand polished; however, no measurement of roughness was made. It can be assumed that the roughness of the steel surface is considerable greater than the 200 angstrom roughness reported for the gold surface. As a result, the contact angle measurements would be expected to be initially lower and have a smaller overall change. This is due to the effect that surface roughness exhibits on the wetting and subsequent dewetting of the organic on the surface. Figure 7 shows the comparison of the predicted

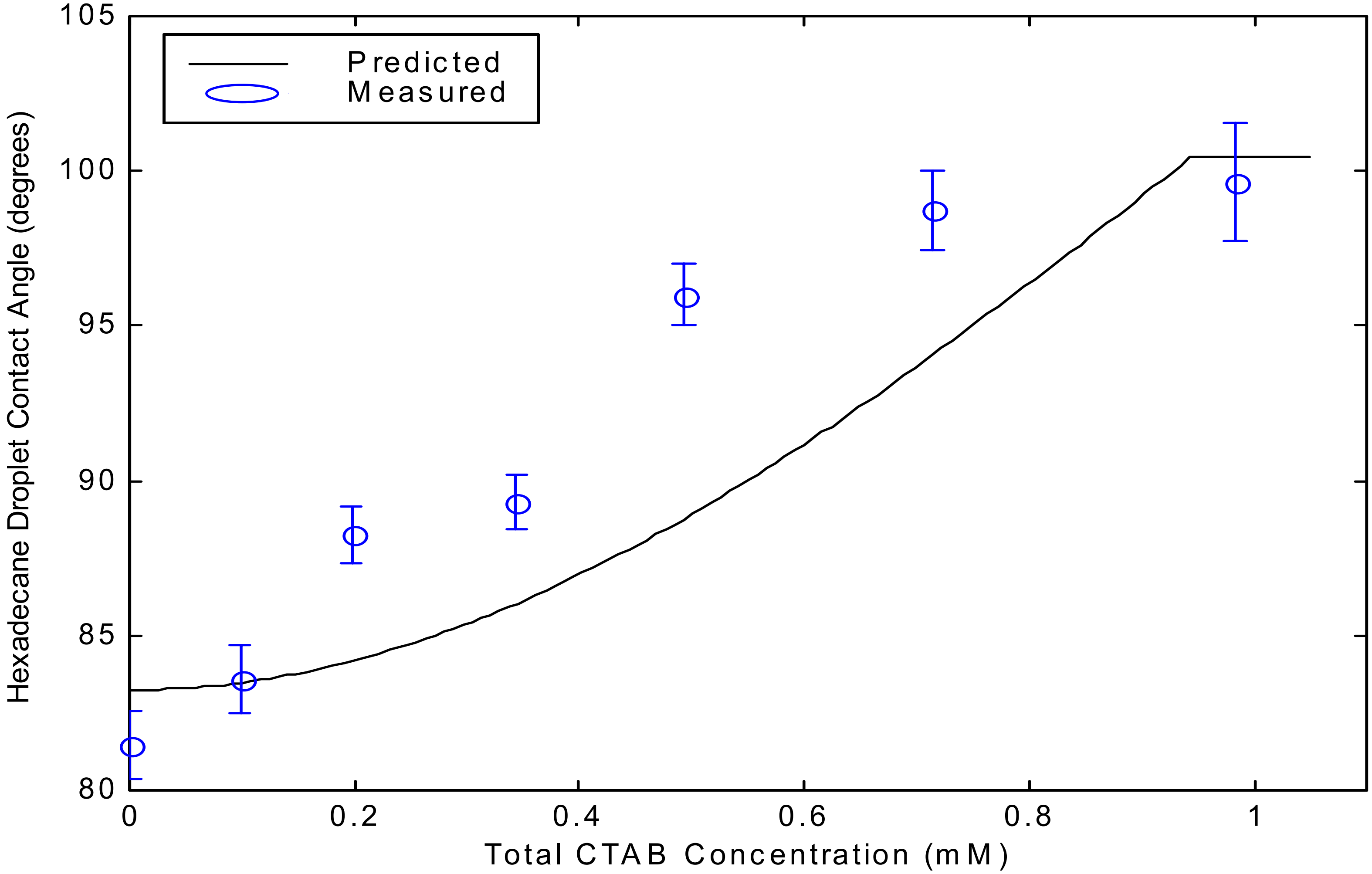

Figure 6. Hexadecane Droplets on Gold Surface in CTAB Solutions

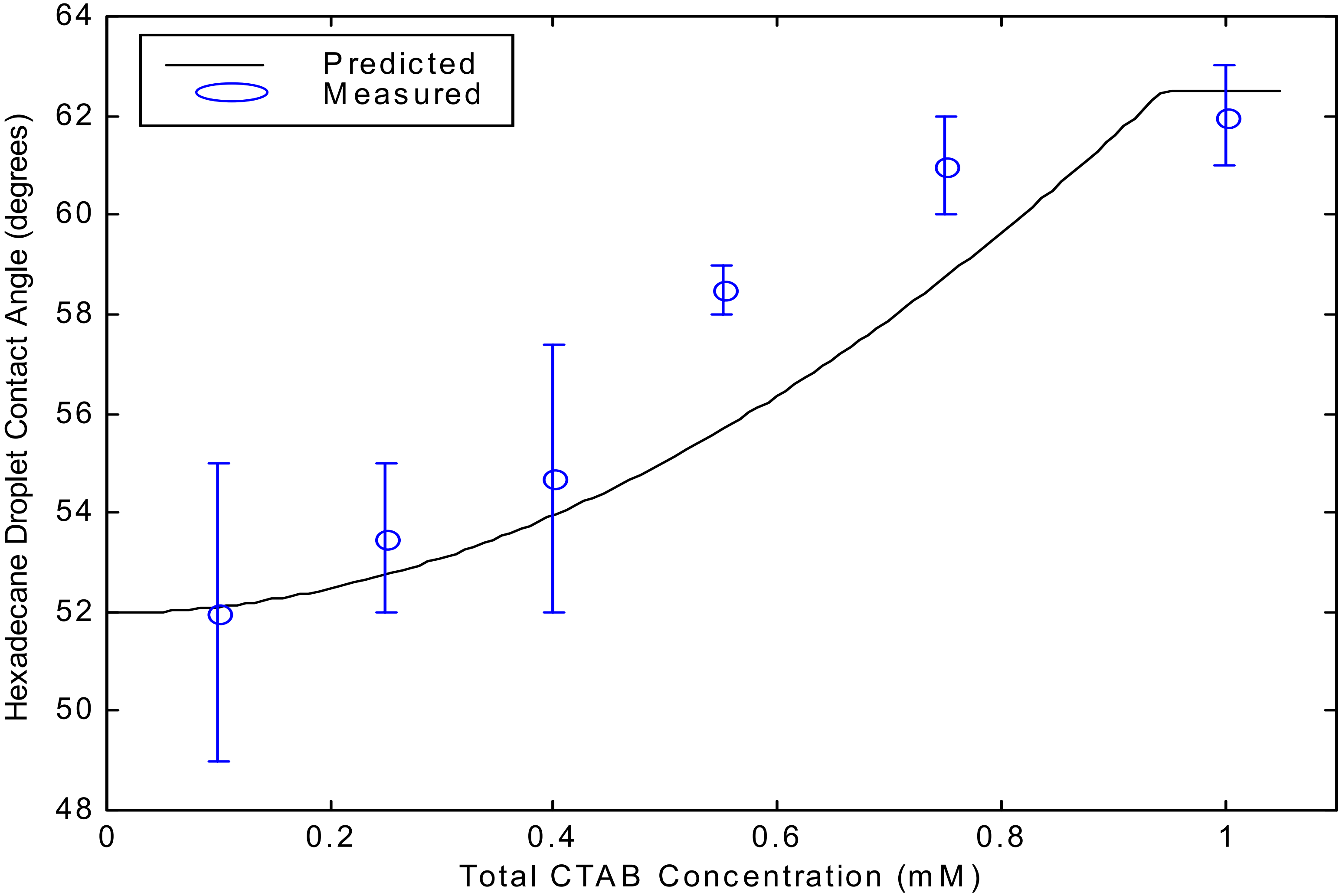

Figure 7. **Hexadecane Droplets on Steel Surface in CTAB Solutions**

trend to the experimental data. Again the model finds a satisfactory value for the CMC that falls within the report range. This prediction has an overall average error of 2.24 percent relative to the experimental dataset. This error is higher than the comparison to the SDS/hexadecane/gold data, but is lower that the CTAB/hexadecane/gold system. The lower error is likely a result of the flexibility returned to the model since of all three solid surface adsorption interaction parameters can again be adjusted. These parameters were determined to be -5.936 kJ/mol for water, and –45.187 kJ/mol for the surfactant, and –1.654 kJ/mol for the organic species, which again follows the expected magnitude trend.

The correlation of cleaning to droplet shape has been demonstrated in the work of Starkweather *et al.* [1, 2], Rowe *et al.* [3, 4], and Davis et al [6]. However, insufficient experimental work has been presented to date to derive a quantitative correlation between the cleaning efficiency of a solution and the static solution contact angle at equilibrium. Despite this limitation, a qualitative relationship can be proposed that states that the larger the contact angle for a particular cleaning system the greater the efficiency of cleaning. Therefore, the presented modeling work provides a method to enhance the interpretation of cleaning system research, and to qualitatively predict the effects of system parameter changes on the behavior of the contact angles for a particular contaminant on a particular solid. The resulting increase or decrease in contact angle could be used to predict whether the cleaning process will benefit from the proposed changes.

5. Summary

A method for the prediction of aqueous immersed organic droplet contact angles has been developed. This model can, with minimal experimental input, predict solid/organic contact angles and any changes due to alterations in the solution composition. Additionally, the model has been demonstrated to perform satisfactorily for two different surface materials. The primary goal for this modeling effort was to develop a predictive technique. This goal has been met to the satisfaction of the authors and more importantly the model has a quantitative performance with less than five percent average error. Despite the encouraging results presented in this article, the model still has avenues for improvement. The empirical relationship required for the determination of the interfacial contribution for the adsorption of surfactant to the organic/solution interface merits further theoretical study. An additional area is the concavity of the contact angle curves. The experimental data appears to have a concave downward shape, while the model predicts a more concave upward shape. A number of factors could be influencing this with the most probable being the assumption of an adsorption profile similar to that for the Langmuir isotherm. Another potential avenue for improvement is the consideration of solid surface aggregate shape. Overall, the predictions of contact angle changes from the model agree reasonably well with experimental data. These predictions could be used to direct the simplification and improvement of industrial cleaning processes with openly published information and minimal experimental effort.

6. Acknowledgements

The authors would like to acknowledge the financial support of the Environmental Management Science Program, U.S. Department of Energy, through a grant to the University of Tennessee through contract DE-AC05-00OR22725 with UT-Batelle, LLC. Additional financial support from the American Electroplaters and Surface Finishers Society is greatly appreciated. The assistance of Dr. Costas Tsouris at Oak Ridge National Laboratory and Alison N. Davis at the University of Tennessee was greatly appreciated and aided in the completion of this work.

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PART IV

Influence of Aqueous/Solid Interactions on Organic Droplet Shape in Aqueous/Organic/Solid Systems

Part IV of this dissertation is a copy of an article by the same name originally submitted for publication in the *Journal of Colloid and Interface Science* in 2004 by Samuel Morton III, David Keffer, Robert Counce,:

> Morton III, S.A., Keffer, D.J., Counce, R.M.; *Influence of aqueous/ solid interactions on organic droplet shape in aqueous/organic/solid systems*, Submitted for Consideration in **2004** Journal of Colloid and Interface Science.

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Abstract

We report the results of our study of the complex phenomena relating to contact angle changes for hexadecane droplets on a gold surface in aqueous solutions of anionic and cationic surfactant. First an analysis of an experimental procedure demonstrating that observed features in contact angle for an aqueous/organic/solid sytem as impacted by surfactant concentration can be attributed to changes in the nanoscale surfactant structures formed at the aqueous/solid interface. Additionally a theoretical method is devised that incorporates a conceptual understanding of these interfacial surfactant changes into our existing thermodynamic model for aqueous/organic/solid system. This approach improves on this earilier model through use of the quasi-chemical approximation which allows for adsorbate clustering and adsorbate-adsorbate lateral interactions. The theoretical predictions are tested using previously published data regarding the contact angle of hexadecane on gold in sodium dodecyl sulfate (SDS) and cetyl trimethyl ammonium bromide (CTAB) solutions. In all cases presented the theoretical predictions correspond satisfactorily to the experimental data.

1. Introduction

Contact angle measurements play an important role in the study of interfacial phenomena. Such measurements can be used to determine numerous surface characteristics such as surface cleanliness, surface roughness, and solid/vapor or solid/liquid interfacial tensions. Contact angles are dependent on the droplet shape of the particular liquid being studied and the manner in which the droplet evolved. Two main droplet shapes, elongated and spherical, are commonly observed in the study of contact angles in aqueous/organic/solid systems. A discussion of these shapes is presented in Morton *et al.*. [1]. An example of a aqueous/organic/solid system can be found where organic droplets are contacting metal surfaces while immersed in aqueous surfactant solutions.

Spherical droplets can be analyzed using the Young's equation:

$$\cos(\theta) = \frac{\gamma_{s/a} - \gamma_{s/l}}{\gamma_{l/a}} \qquad [1]$$

where θ is the contact angle, $\gamma_{s/a}$ is the aqueous/solid interfacial tension, $\gamma_{s/l}$ is the organic/solid interfacial tension, and $\gamma_{l/a}$ is the aqueous/organic interfacial tension. Contact angles are routinely measured for elongated droplets through the use of asymmetric drop shape analysis (ADSA) techniques, which fits the shape of the drop numerically using the Young-Laplace equation. Chatterjee [2] discusses such droplets and provides an analytical approach to drop shape and links this to detachment. Another resource for ADSA can be found in the work of Kwok and coworkers [3, 4]. For droplets examined in this present article only spherical shapes were observed and as a result only Young's equation [Eq. 1] is required for analysis.

In addition to ADSA, Kwok *et al.* (1996) [5] utilize dynamic contact angle data to evaluate solid interfacial tensions in a liquid/vapor/solid system. Building on this work, Kwok and Neumann [6] re-evaluate literature contact angle data giving significant insight into the reliability and use of published contact angle data. Their work validates the premise that contact angle data can be used to determine solid surface interfacial tensions for liquid/vapor/solid systems.

Whereas the work of Kwok and coworkers [4-6] pertained to liquid-vapor-solid systems, our previous work [1, 7-10] has investigated phenomena in aqueous/organic/solid systems. This body of work is concerned with aqueous surfactant cleaning solutions and the removal of organic contaminants from metal surfaces. Using the model presented in Morton *et al.* [10] and the contact angle data reported by Davis *et al.* [9] an analysis of the aqueous/solid and organic/solid interfacial phenomena can be performed. The bulk of these studies have concentrated on aqueous solutions of ionic surfactants. Assuming Young's equation to be as valid for liquid/liquid/solid systems as it is for liquid/vapor/solid system an analysis of solid surface phenomena presented in the hexadecane/surfactant/gold systems reported in Davis *et al.* [9] and Morton *et al.* [10] can be performed.

2. Contact Angle and Interfacial Tension

From Young's equation, the inversely proportional relationship between the cosine of the contact angle and the interfacial tension at the organic/solution interface is obvious. It should be possible to determine if droplet shape changes are due simply to changes in aqueous/organic interfacial tension or if other factors, such as aqueous/solid interfacial adsorption and surfactant aggregate structuring at the interface, exhibit a demonstrative effect. Such a determination could then validate the use of contact angle data to interpret aqueous/solid interfacial phenomena in aqueous/organic/solid systems. While statements have been made indicating the unsuitability of contact angle measurements for use in interpreting aqueous/solid phenomena [3], we feel that an experimental method has been devised [9] that alleviates this unsuitability.

Contact angle data for hexadecane droplets on gold are available in the literature [9] for solutions of an anionic surfactant, sodium dodecyl sulfate (SDS), and a cationic surfactant, cetyl trimethyl ammonium bromide (CTAB). Additionally hexadecane/solution interfacial tension data can be found in the literature. Oh and Shah [11] present interfacial tension data for hexadecane/SDS solutions while interfacial tension data for hexadecane/CTAB solutions can be found in both the work of Medrzycka and Zwierzykowski [12] and the work of Knock *et al.* [13].

Figure 1 shows the reported contact angle and interfacial tension data for hexadecane droplets in an aqueous SDS solution while Figure 2 shows the reported data for hexadecane in aqueous CTAB solutions. From these figures it is obvious that a general inverse relationship exists between contact angle and interfacial tension. It is important to note that the curve shape of the contact angle data set does not mirror the shape of the interfacial tension data set. By rearranging Young’s equation as follows:

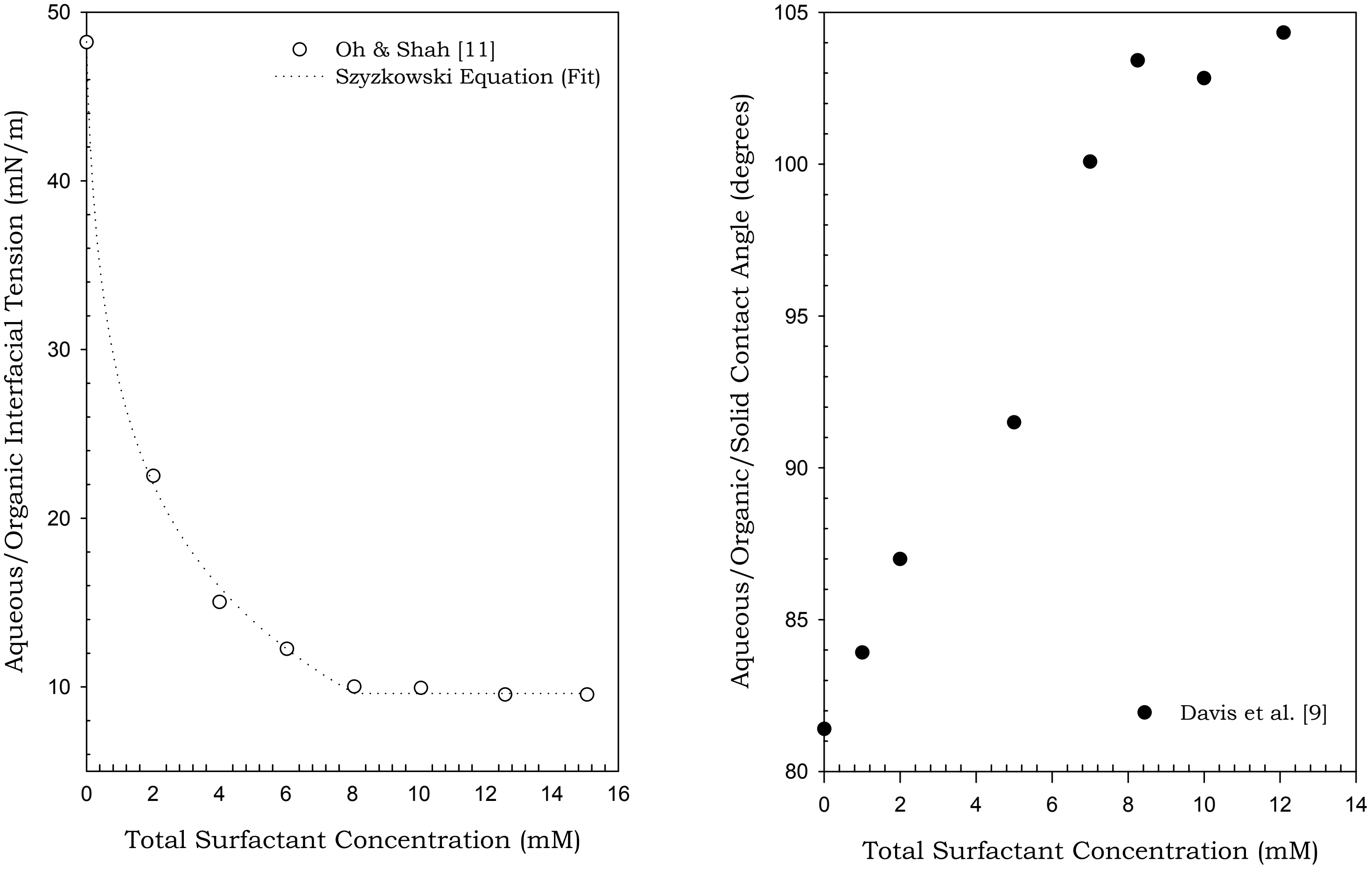

Figure 1. Interfacial Tension and Contact Angle Data for Hexadecane/SDS Solution

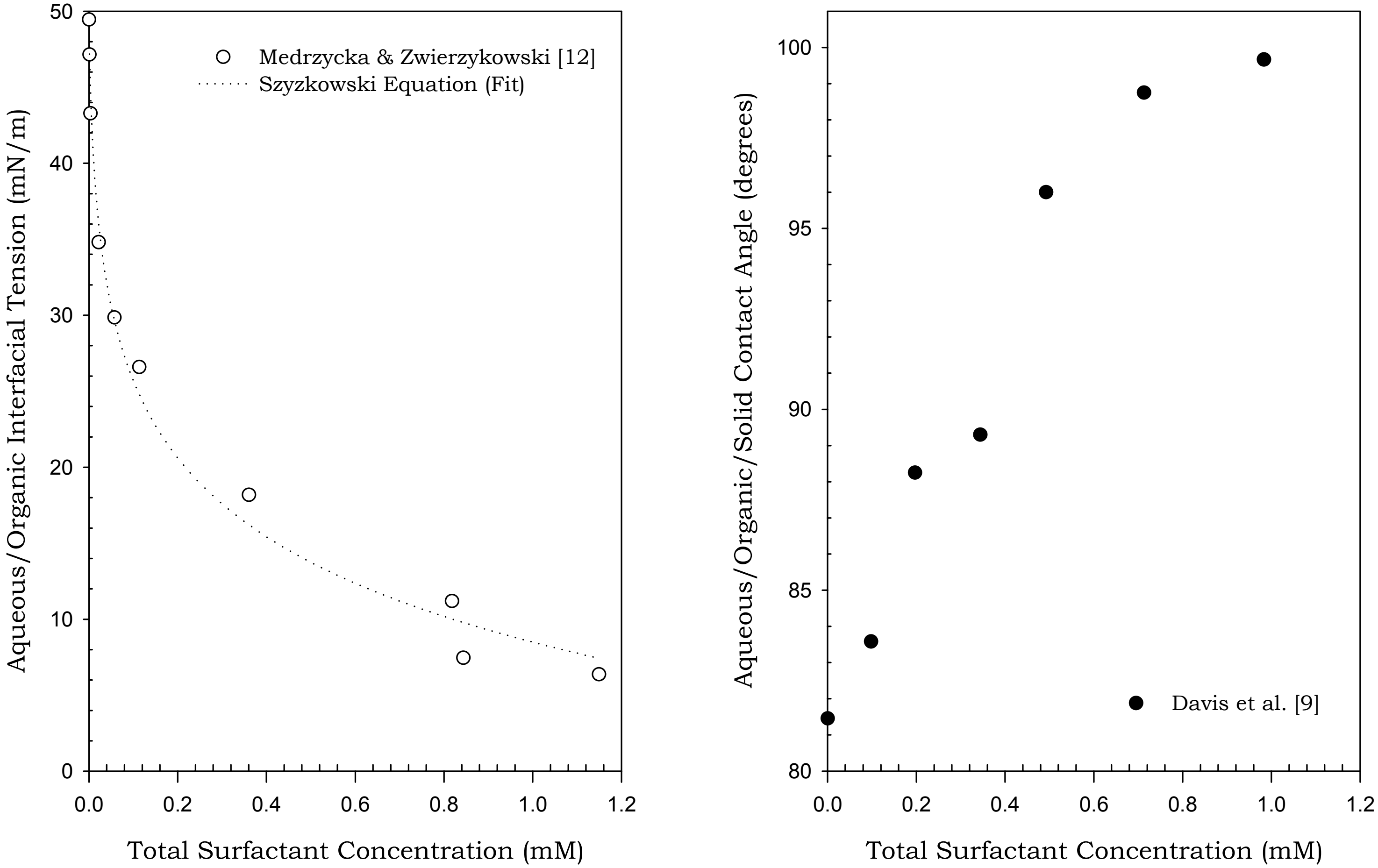

Figure 2. Interfacial Tension and Contact Angle Data for Hexadecane/CTAB Solution

$$\gamma_{s/a} - \gamma_{s/l} = \cos(\theta)\gamma_{l/a} \qquad [2]$$

a relationship which relates the contact angle and aqueous/organic interfacial tension data to the interfacial tension of the aqueous/solid and organic/solid interface is determined. Since the contact angle data and the interfacial tension data were not acquired at the same surfactant concentrations, comparison would be difficult without a numeric technique to predict the corresponding data points. This problem is resolved due to the fact that the aqueous/organic interfacial tension data can be modeled using the Szyzkowski equation:

$$\gamma_{l/a} = \gamma^{o}_{l/a} - RT\,\Gamma^{\infty} \ln\left(1 + \frac{c}{A}\right) \qquad [3]$$

where $\gamma_{l/a}$ is the aqueous/organic interfacial tension at a particular surfactant concentration, $\gamma^{o}_{l/a}$ is the aqueous/organic interfacial tension in the absence of surfactant, Γ^{∞} is the adsorbed surfactant surface excess at saturation, c is the concentration of surfactant in aqueous solution, and A is the Szyzkowski adsorption constant. Table 1 lists the fitted parameters for each type of hexadecane/ionic surfactant solution dataset.

Table 1. Szyzkowski Equation Parameters for SDS/Hexadecane and CTAB/Hexadecane Interfacial Tension Data

Parameters for Hexadecane/SDS Interface		
γ°	48.2303	mN/m
Γ^{∞}	0.0037	moles/m^2
A	0.1260	mM
Parameters for Hexadecane/CTAB Interface		
γ°	48.6381	mN/m
Γ^{∞}	0.0031	moles/m^2
A	0.0052	mM

After including the contact angle and aqueous/organic interfacial tension data into the modified form of Young's equation (Eq. 2) the effect of surfactant concentration on the aqueous/solid interfacial tensions can be determined. Figure 3 shows the left-hand side of Equation 2 for both the SDS and CTAB datasets. From this figure it is evident that the trend observed in the contact angle data is manifested in the difference between the aqueous/solid interfacial tensions. Davis *et al.* [9] first introduced the organic to the solid surface, allowed time for wetting, and then immersed the solid in the aqueous surfactant solution. The benefit from this procedure is that the organic/solid interfacial tension, $\gamma_{s/l}$, may be assumed to be essentially constant, therefore the inflection observed in the contact angle data must be due to a subsequent inflection in the aqueous/solid interfacial tension, $\gamma_{s/a}$. Such an inflection would be logically due to a change in the adsorbed surfactant aggregate structure and increased competition for adsorption sites with the organic. This phase change in the adsorbed surfactant aggregate is supported by the work of Fan *et al.* [14], Goloub and Koopal [15], Somasundaran and Krisknakumar [16], and Drelich [17]. These representative articles discuss the phenomena related to the adsorption of surfactants to various surfaces.

Fan *et al.* [14] discuss the adsorption of surfactant in terms of the reverse orientation model. This model, first proposed by Somasundaran and Fuerstenau [18], separates the adsorption of surfactant into four regions. In Region A, surfactants adsorb to the surfaces due to electrostatic considerations and display no obvious aggregation behavior. Region B surfactant adsorption shows the first indication of self-assembly behavior with progression toward a monolayer near the onset of Region C. Surfactants continue the self-assembly behavior in Region C progressing

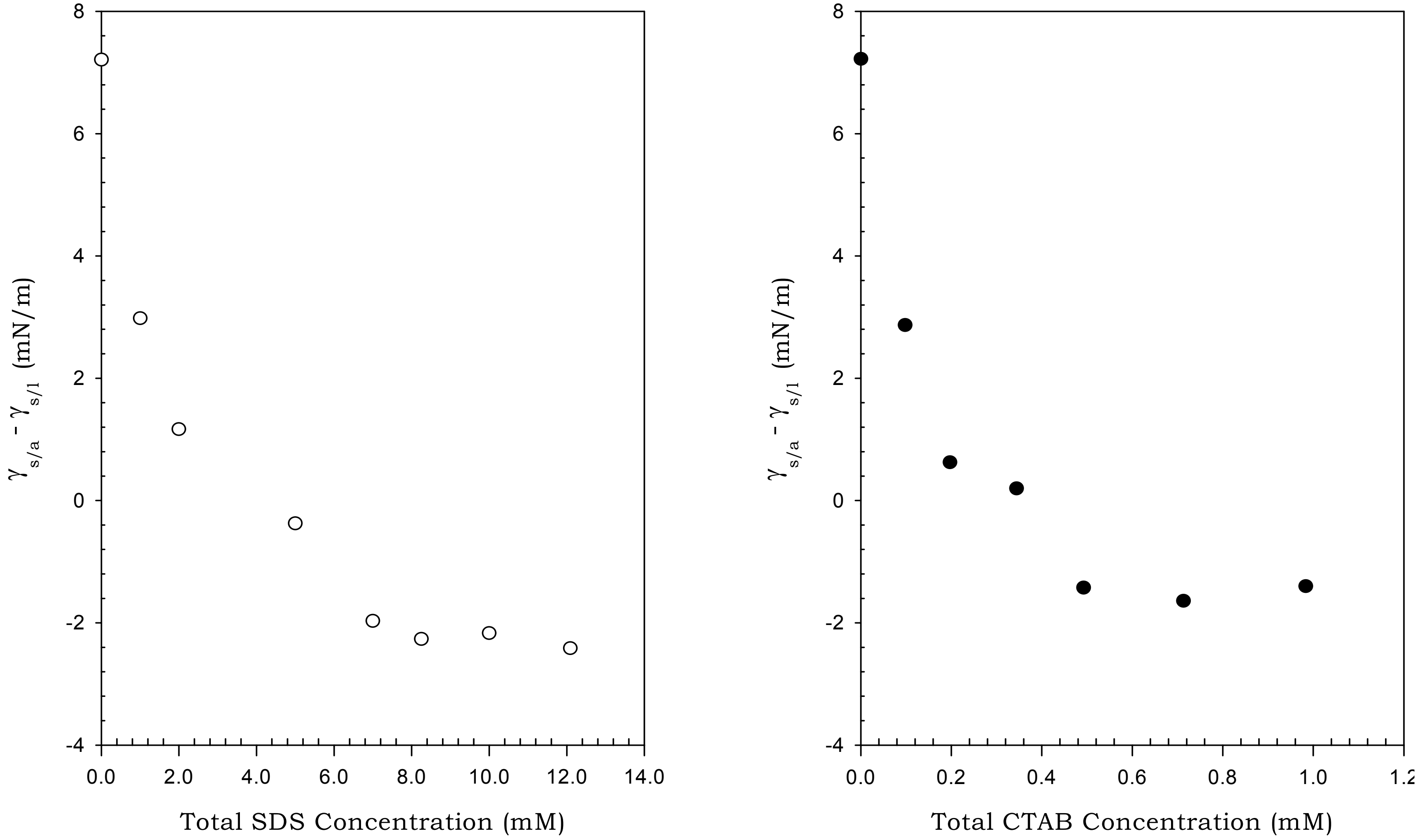

Figure 3. Analysis of Modified Young's Equation for Hexadecane/SDS and Hexadecane/CTAB

toward a bilayer near the onset of Region D. Region D falls above the critical micelle concentration (CMC) for the surfactant where additional surfactant introduced to the system is entrained in the formation of solution aggregates. We will utilize a similar adsorption region concept for the reevaluation of our previous approach to predicting contact angles of oils on metal surfaces in ionic surfactant solutions presented in this article.

3. Theory and Model

In our previous modeling work [10] a system of 5 component balances was developed to describe the redistribution of components in an aqueous/organic/solid system. The balances encompassed the partitioning of surfactant between solution aggregates, the aqueous/organic interface, and the aqueous/solid interface, the partitioning of water between the aqueous/solid interface, and the partitioning of oil between the organic/solid interface. The balances pertaining to component adsorption/desorption to and from the solid surface are of particular interest to this current work. A detailed discussion of the input and output characteristics and requirements for the model is presented in an earlier work [10] and will not be repeated here. In the original work there were two preeminent assumptions: (1) with limited adsorption sites, competition for sites must occur, and (2) surfactant adsorption behavior can be described by the Langmuir isotherm. Using the indication of surfactant phase change, both from the literature and experiment, a revision of this second assumption is due.

A fundamental tenet of the Langmuir type adsorption is that there are no adsorbate-adsorbate interactions. Therefore the Langmuir isotherm excludes increased adsorption due to the lateral interactions that are anticipated between surfactant molecules during self-assembly. There are a number of modifications to the Langmuir isotherm that can account for adsorbate-adsorbate interactions. A discussion of various lateral interaction isotherm models and the selected extension of certain models to competitive adsorption is presented in the work of Quinones and Guichon [19]. Many of these models utilize an averaged lateral interaction factor that fails to account for variations in nearest neighbor effects. This averaged lateral interaction approach is also known as the Bragg-Williams approximation and is of the simplest order of site adsorption techniques. A slightly more robust, yet simple, approach is the quasi-chemical approximation. Kamat and Keffer [20] apply an analytical approach to the quasi-chemical approximation in their study of the adsorption of fluids in nanoporous systems. Kamat and Keffer explain the quasi-chemical approximation in detail and should be referenced for further study. Simply put, the quasi-chemical approximation allows for adsorbate-adsorbate lateral interactions as well as the clustering of like components in a multi-component system. This current work will concentrate on the application of the quasi-chemical approximation as a modification to the solid adsorption balances from our earlier work.

The present application of the quasi-chemical approximation requires the determination of the chemical potentials for the adsorbed components that equals the chemical potentials for the respective components in the bulk phase:

$$\mu_i^{ad} = \mu_i^{bulk} \quad [4]$$

where μ_i^{ad} represents the chemical potential of adsorbed component i and μ_i^{bulk} represents the chemical potential of the same component in the bulk solution. Since the organic component balance is a separate phase from the bulk aqueous solution its distribution will be determined by a different calculation. That leaves the surfactant and water chemical potentials, both of which can be determined for the bulk phase in the manner expressed in the work of Mulqueen and Blankschtein [21-23] for the prediction of surface tension and surface adsorption at the air/aqueous and aqueous/organic interfaces. For water in the bulk phase the following equation is utilized:

$$\mu_w^{bulk} = \mu_w^{bulk,0} + k_b T \ln(x_w) \quad [5]$$

where $\mu_w^{bulk,0}$ is the bulk standard-state chemical potential of water , k_b is the Boltzmann's constant, T is solution temperature, and x_w is the mole fraction of water molecules in the bulk solution. In a similar manner the bulk chemical potential for the surfactant component determined by the following relationship:

$$\mu_s^{bulk} = \mu_s^{bulk,0} + 2k_b T \ln(x_s) \quad [6]$$

with the main difference from Equation 5 being the inclusion the multiplier in the second term which accounts for the ion/counter ion nature of 1:1 ionic surfactants and assures electroneutrality of the bulk [21].

Now the chemical potentials for the adsorbed water and surfactant can be determined using the quasi-chemical approximation. The quasi-chemical approximation is the simplest adsorption approximation that allows for adsorbate clustering and adsorbate-adsorbate lateral interactions. Our model system is composed of a single type of adsorption site, a maximum of one adsorbate molecule per adsorption site, and three types of adsorbate molecules. Additionally, only nearest neighbor interactions are allowed related to the orientation shown in Figure 4.

From the quasi-chemical approximation, the chemical potentials for the adsorbate molecules can be determined from the following relationship:

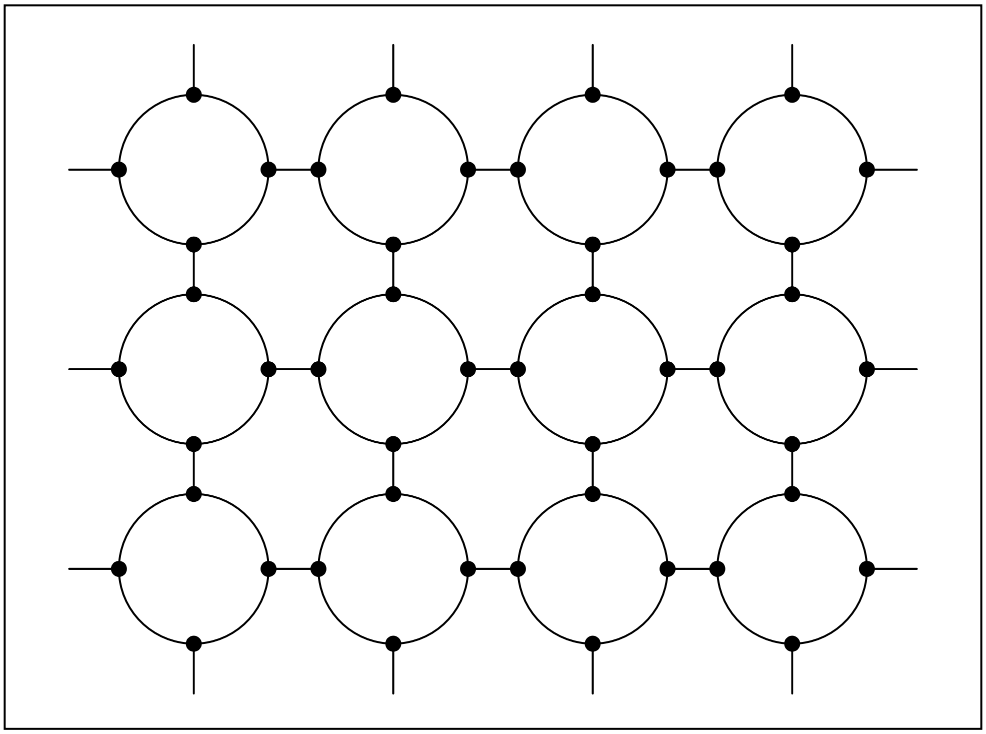

Figure 4. Hypothetical Adsorption Site Lattice Configuration

$$\mu_i^{ad} = -k_b T \left(\frac{\partial \ln Q}{N_i} \right)_{V,T} \qquad [7]$$

where Q represents the total partition function from the canonical ensemble and N_i represents the fraction of sites occupied by a particular component (1 for water, 2 for surfactant, and 3 for organic).

The total partition function for our model system is the product of three terms: (1) the configurational degeneracy, (2) the intra-site partition function, and (3) the energetic interactions due to neighboring atoms. The general form for this relationship is as follows:

$$Q\left(\underline{N},M,T\right) = g\left(\underline{N},M\right) q_S\left(\underline{N},T\right) q_N\left(\underline{\underline{N_{xy}}},T\right) \qquad [8]$$

where $\underline{N}$ is a vector of the number of adsorbates, M is the number of sites, T is the temperature, $g(\underline{N},M)$, is the configurational degeneracy term, $q_S(\underline{N},T)$, is he intra-site partition function term, $q_N(\underline{\underline{N_{xy}}},T)$, is the nearest neighbor interaction contribution.

The configurational degeneracy term, $g(\underline{N},M)$, is discussed by Hill [24] and the reader should refer to his work regarding the formal derivation of this term. For our case with a single type of site, three different adsorbates, and allowed site occupancy of one, the degeneracy term can be written as

$$g(\underline{N},M)=\left(\frac{M!}{N_1!N_2!N_3!}\right)^{(1-c)}\left(\frac{\left(\frac{cM}{2}\right)!}{N_{11}!\left(\frac{N_{12}!}{2}\right)\left(\frac{N_{13}!}{2}\right)N_{22}!\left(\frac{N_{23}!}{2}\right)N_{33}!}\right) \quad [9]$$

where c is the site connectivity value (4 in our case), and N_{11}, N_{12}, N_{13}, N_{22}, N_{23}, and N_{33} are neighbor interaction terms that reflect the interactions between the three adsorbate types. Since one of the assumptions for our current application of the quasi-chemical approximation states that there are no empty adsorption sites, the terms N_0, N_{00}, N_{01}, N_{02}, and N_{03}, which would have described interactions with empty sites, are not required. Through this assumption we know that:

$$M = N_1 + N_2 + N_3 \quad [10]$$

where N_1, N_2, N_3, are the number of adsorbate molecules of water, surfactant, and oil. As the computational model requires an initial guess for the number of component molecules adsorbed to the surface the values of N_1, N_2, and N_3 are known.

In a further simplifying step the symmetric neighbor interactions can be eliminated:

$$N_{xy} = N_{yx} \qquad \text{where } x \neq y \quad [11]$$

In order to obtain the remaining six neighbor-neighbor interactions as well as the occupancy nature of the adsorption sites we require an equivalent number of equations. The like adsorbate neighbor terms can be determined using the following equations:

$$\mathrm{N}_{11} = \frac{\mathrm{cN}_1 - \mathrm{N}_{12} - \mathrm{N}_{13}}{2} \qquad [12]$$

$$\mathrm{N}_{22} = \frac{\mathrm{cN}_2 - \mathrm{N}_{12} - \mathrm{N}_{23}}{2} \qquad [13]$$

$$\mathrm{N}_{33} = \frac{\mathrm{cN}_3 - \mathrm{N}_{13} - \mathrm{N}_{23}}{2} \qquad [14]$$

The remaining adsorbate-adsorbate interactions are determined by minimization of the total partition function with respect to N_{12}, N_{13}, and N_{23}:

$$\left(\frac{\partial \ln Q}{N_{12}}\right) = 4N_{11}N_{22} - N_{12}{}^{2} \exp\left(-\frac{\left(w_{11} - 2w_{12} + w_{22}\right)}{k_b T}\right) = 0 \qquad [15]$$

$$\left(\frac{\partial \ln Q}{N_{13}}\right) = 4N_{11}N_{33} - N_{13}{}^{2} \exp\left(-\frac{\left(w_{11} - 2w_{13} + w_{33}\right)}{k_b T}\right) = 0 \qquad [16]$$

$$\left(\frac{\partial \ln Q}{N_{23}}\right) = 4N_{22}N_{33} - N_{23}{}^{2} \exp\left(-\frac{\left(w_{22} - 2w_{23} + w_{33}\right)}{k_b T}\right) = 0 \qquad [17]$$

where w_{11} is the lateral interaction parameter for water-water interactions, w_{22} is the lateral interaction parameter for surfactant-

surfactant interactions, w_{33} is the lateral interaction parameter for oil-oil interactions, and w_{12}, w_{13}, and w_{23} are determined as follows:

$$\mathrm{w}_{\mathrm{xy}} = \sqrt{\mathrm{w}_{\mathrm{xx}} \mathrm{w}_{\mathrm{yy}}} \qquad [18]$$

The intra-site partition function term, $q_S(\underline{N},T)$, is defined by the following function:

$$q_S\left(\underline{N},T\right) = \prod_{i=1}^{3} q_i^{N_i} = q_1^{N_1} q_2^{N_2} q_3^{N_3} \qquad [19]$$

The intra-site partition functions, q_1, q_2, and q_3 for the adsorbate molecules are determined as follows:

$$\mathrm{q}_{\mathrm{i}} = \frac{\mathrm{V}_{\mathrm{site}}}{\Lambda_{\mathrm{i}}} \mathrm{e}^{\left(\frac{-\mathrm{U}_{\mathrm{i}}}{\mathrm{k}_{\mathrm{b}}\mathrm{T}}\right)} \qquad [20]$$

where V_{site} is the volume of an adsorption site, U_i is the adsorbate-surface interaction parameter, and Λ_i is the thermal de Broglie wavelength.

The remain term from the total partition function, the nearest neighbor interaction, $q_N(\underline{N_{xy}},T)$, is found through the following relationship:

$$q_N\left(\underline{\underline{N_{xy}}},T\right)=\exp\left(-\frac{\sum_{x=1}^{n}\left(N_{xx}w_{xx}+\sum_{y=1}^{n}\frac{N_{xy}w_{xy}}{2}\right)}{k_bT}\right) \qquad [21]$$

where n represents the number of adsorbate types (3 in our case).

With the total partition function defined the chemical potentials for the adsorbate molecules can be generally calculated as follows:

$$\mu_w^{ad} = -k_bT\left((1-c)\ln\left(\frac{N_3}{N_1}\right)+\left(\frac{c}{2}\right)\ln\left(\frac{N_{33}}{N_{11}}\right)+\ln\left(\frac{q_1}{q_3}\right)-\left(\frac{c}{2}\right)\left(\frac{w_{11}-w_{33}}{k_bT}\right)\right) \qquad [21]$$

$$\mu_s^{ad} = -k_bT\left((1-c)\ln\left(\frac{N_3}{N_2}\right)+\left(\frac{c}{2}\right)\ln\left(\frac{N_{33}}{N_{22}}\right)+\ln\left(\frac{q_2}{q_3}\right)-\left(\frac{c}{2}\right)\left(\frac{w_{22}-w_{33}}{k_bT}\right)\right) \qquad [22]$$

The component-wall interaction parameter becomes an adjustable parameter similar to the ε parameters from Morton *et al.* [10]. For the Langmuir approach the adsorbate-surface interaction parameters, would simply be equal to the ε parameters. Reducing the quasi-chemical approximation to the Langmuir Isotherm, where no lateral interactions are present, requires that w_{11}, w_{22}, and w_{33} have a value of zero. The six adjustable parameters utilized above would appear to exceed the capacity of the experimental data shown in Figure 1 and Figure 2. However since the purpose in using the quasi-chemical approximation was to describe the self-assembling nature of the adsorbed surfactants there are in reality only four unknown parameters, U_1, U_2, U_3, and w_{22}, one more than utilized in our previous work [10]. Thus the lateral interaction parameters for water and oil, w_{11} and w_{33}, are set to values of zero. Any alterations in the adsorbate nature of the water and oil components are assumed to be satisfactorily described using their respective component-solid interaction parameters, U_1 and U_3.

4. Results and Discussion

The contact angle predictions for both SDS and CTAB from the Langmuir case utilized in our previous work [10] are shown in Figure 5. While the comparison of prediction and data for the SDS solution data is good, the correlation for droplet contact angles in CTAB solutions is poor in comparison.

Since the Langmuir case neglects lateral adsorbate-adsorbate interactions it is necessary to evaluate the model results when the Langmuir assumption is replaced with the quasi-chemical approximation. As surfactants are known to exhibit self-assembly behavior while hexadecane and water do not, it is a reasonable assumption that only the surfactant molecules will exhibit an affinity for one another. This affinity can be established in the presented model by selecting a new value for the surfactant-solid interaction parameter, U_2, and a value for the surfactant-surfactant interaction parameter, w_{22}. Figure 6 shows the results for this approach for both SDS and CTAB. It

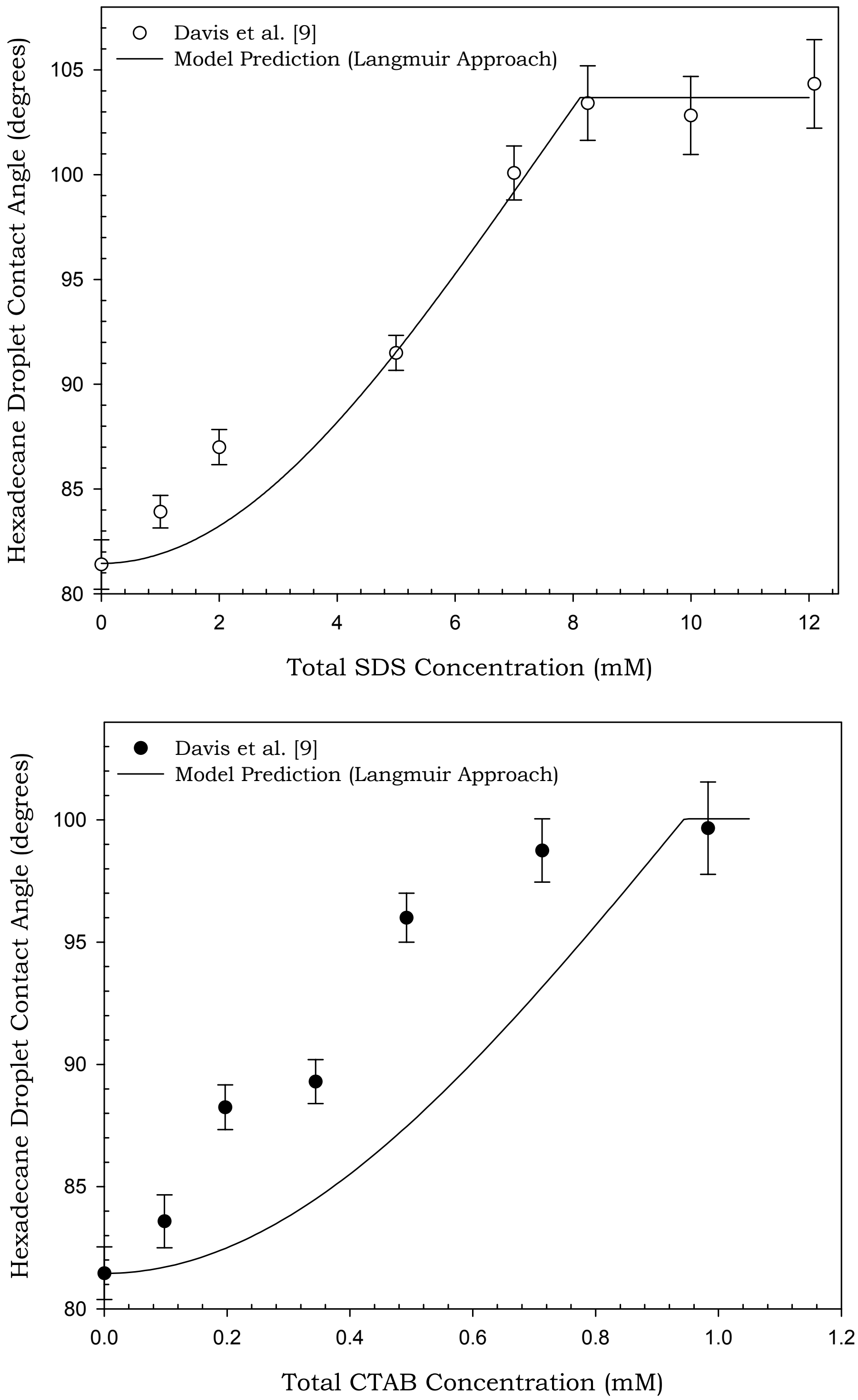

Figure 5. Contact Angle Prediction Based on the Langmuir Adsorption Case

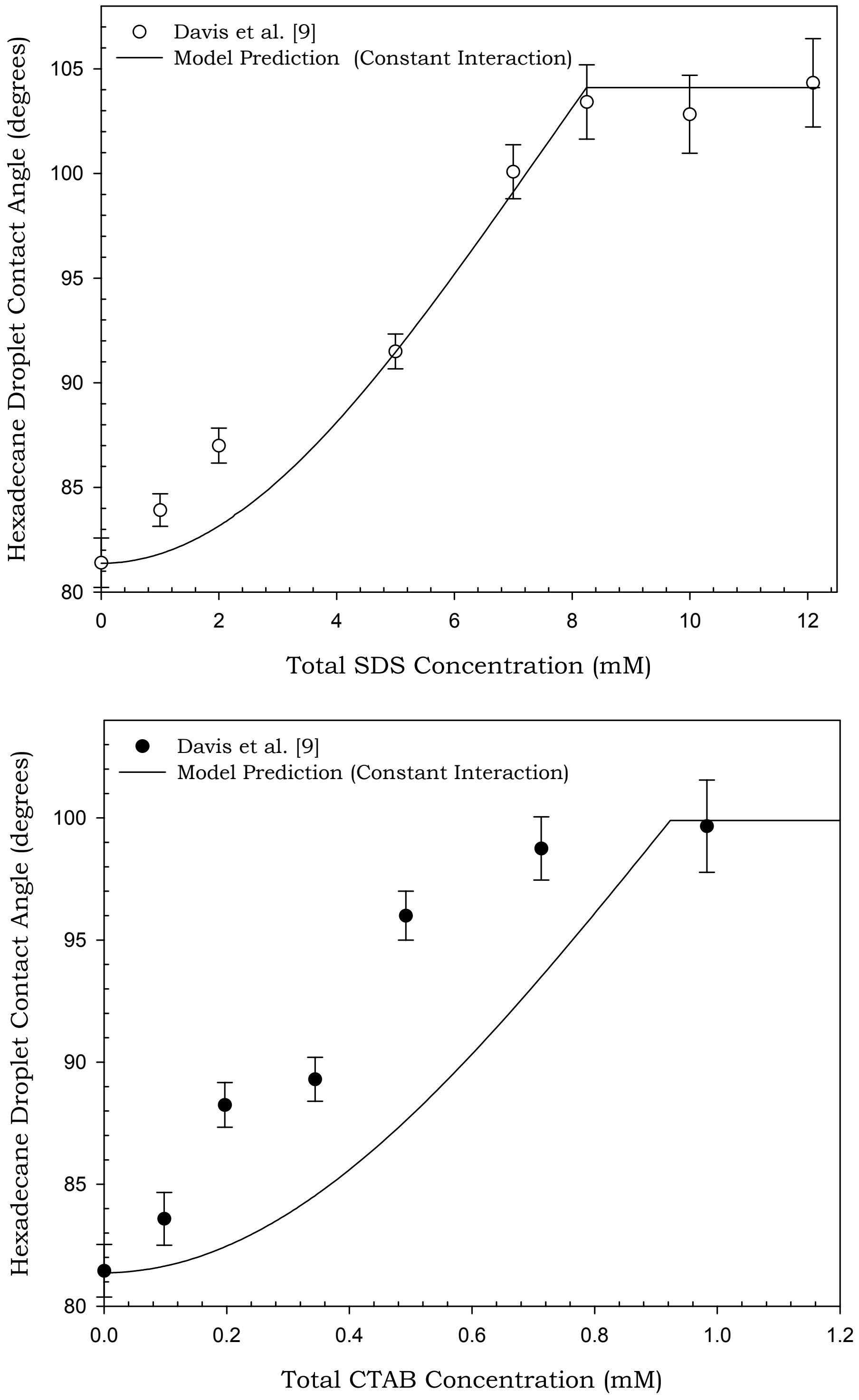

Figure 6. Contact Angle Predictions Based on the Quasi-Chemical Approximation with Constant Lateral Interactions

is evident from this figure that the use of constant lateral interactions for the full range of surfactant concentrations was of little impact when compared to the Langmuir case. This bolsters the case made earlier that the surfactant aggregate phase must change its nature and therefore the lateral interaction parameters would also exhibit a change.

The four regions of the reverse orientation model can be used as a basis for guidance in manipulating the lateral interaction parameters for adsorbed surfactant molecules. First values for w_{22} that begin with a constant value are selected to satisfy the case for initial adsorption found in Region A. Since Region B contains the onset and formation of a monolayer in our approach a linear change in the w_{22} value until the onset of Region C, where a different linear change is utilized to describe the formation of a compressed bilayer. As Region D is above the CMC for each surfactant no additional changes to the lateral interaction parameter is required. Figure 7 shows the predicted contact angle values a variable lateral interaction parameter for the SDS experimental contact angle data as well as a plot of the values of the w_{22} parameter. Figure 8 contains the same information for the CTAB experimental contact angle data. As can be seen from these figures the model has a much greater correlation to the experimental data when lateral interactions are considered and allowed to vary within the adsorption regions. Table 2 provides a listing of the component-solid interaction and surfactant-surfactant lateral interaction parameter for each tested case.

5. Summary

In this work, we first presented an analysis of an experimental procedure, which clearly demonstrates that specific features in the

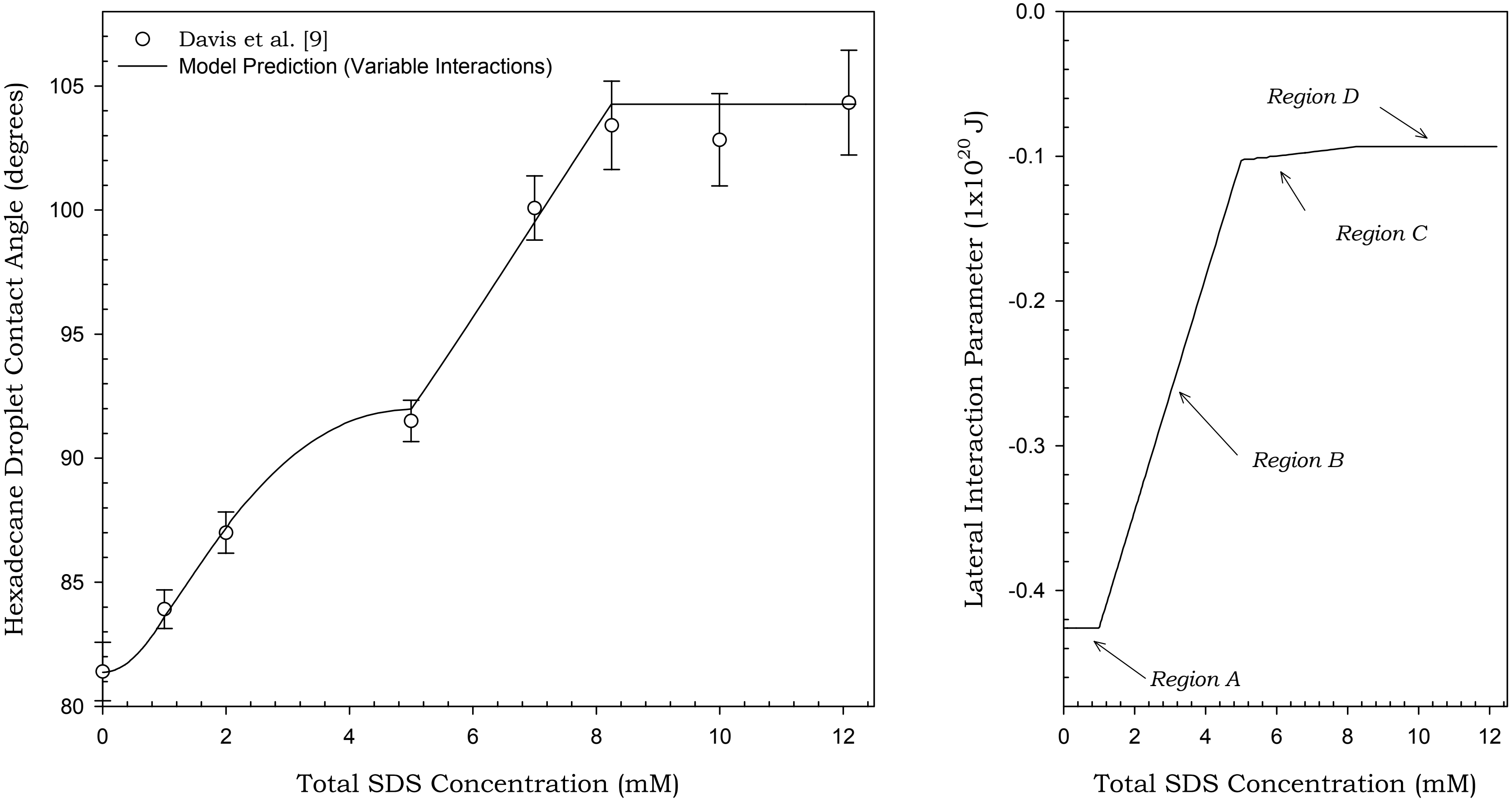

Figure 7. Contact Angle Prediction Based on the Quasi-Chemical Approximation with Variable Lateral Interactions for SDS Solutions

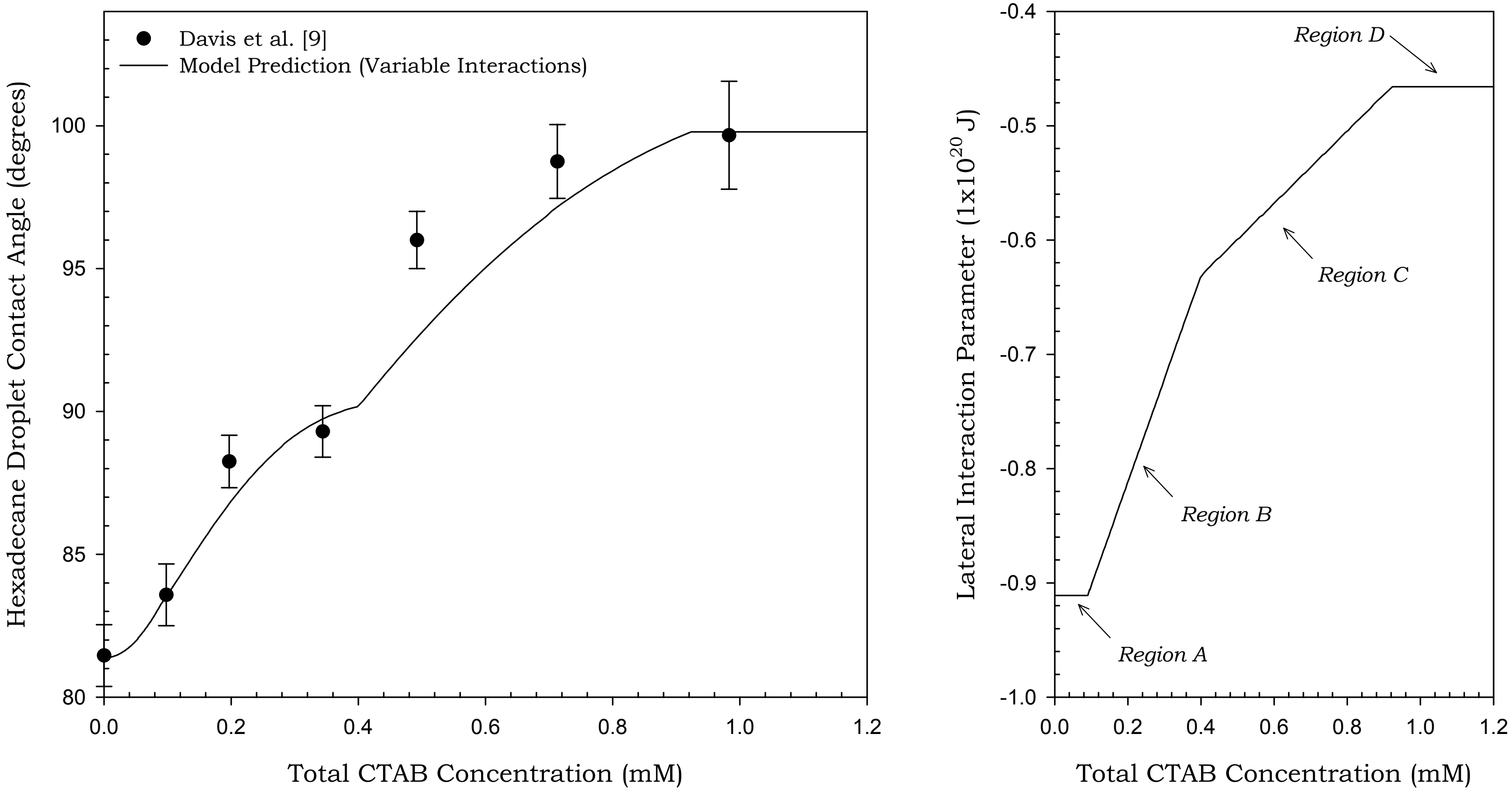

Figure 8. Contact Angle Prediction Based on the Quasi-Chemical Approximation with Variable Lateral Interactions for CTAB Solutions

Table 2. Interaction Parameters for SDS/Hexadecane/Gold and CTAB/Hexadecane/Gold Systems from the Quasi-chemical Approximation

Hexadecane/ SDS / Gold System

	U_1 *(J/ molecule)*	U_2 *(J/ molecule)*	U_3 *(J/ molecule)*		w_{22} *(J/ molecule)*
Langmuir	-1.0087×10^{-20}	-6.8310×10^{-20}	-9.6624×10^{-20}		N/A
Quasi-Chemical *(Constant Interactions)*	-3.1083×10^{-20}	-6.9693×10^{-21}	-8.9012×10^{-21}		-9.7575×10^{-22}
Quasi-Chemical *(Variable Interactions)*	-3.1085×10^{-20}	-7.0970×10^{-21}	-8.9016×10^{-21}	*Region A*	$U_2*(0.60)$
				Region B	$U_2*(0.7138 – 0.1138*C_{SDS})$
				Region C	$U_2*(0.1448– 0.0041*C_{SDS})$
				Region D	$U_2*(0.1111)$

Hexadecane/ CTAB / Gold System

	U_1 *(J/ molecule)*	U_2 *(J/ molecule)*	U_3 *(J/ molecule)*		w_{22} *(J/ molecule)*
Langmuir	-1.0087×10^{-20}	-7.8193×10^{-20}	-9.6624×10^{-20}		N/A
Quasi-Chemical *(Constant Interactions)*	-3.1083×10^{-20}	-1.5201×10^{-21}	-8.9012×10^{-21}		-4.4845×10^{-22}
Quasi-Chemical *(Variable Interactions)*	-3.1085×10^{-20}	-1.4821×10^{-21}	-8.9016×10^{-21}	*Region A*	$U_2*(0.6149)$
				Region B	$U_2*(0.6698 – 0.6098*C_{CTAB})$
				Region C	$U_2*(0.5113– 0.2135*C_{CTAB})$
				Region D	$U_2*(0.3149)$

contact angle of an aqueous/organic/solid system as a function of surfactant concentration can be related to changes in the interfacial tension at the aqueous/solid interface. This interfacial tension reflects, in turn, specific changes in the nanoscale structures formed by surfactant at the aqueous/solid interface.

We have incorporated the 4-region adsorption isotherm of Fan et al. [14], which accounts for change sin surfactant nanoscale structures at the aqueous/solid interface, into our existing thermodynamic model of the aqueous/organic/solid system. With this model we have quantitatively fit experimental data and can predict equilibrium contact angles as a function of surfactant concentration.

At this point, we have arrived at an opportune application for molecular-level simulation, which could be used to confirm that the assumed 4-region adsorption isotherm of Fan et al. is indeed justified. We are also currently applying our thermodynamic model to the case of minute non-surfactant electrolyte addition to the aqueous/organic/solid system.

6. Acknowledgements

The authors would like to acknowledge the financial support of the American Electroplaters and Surface Finishers Society through Grant #110. Additional financial support from the Environmental Management Science Program, U.S. Department of Energy, by a grant to the University of Tennessee through contract DE-AC05-00OR22725 with UT-Batelle, LLC. is greatly appreciated.

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PART V

Effect of Low Concentration Salt on Organic Contact Angle in Ionic Surfactant Solutions: Insight from Theory and Experiment

Part V of this dissertation is a copy of an article by the same name originally submitted for publication in the journal *Langmuir* in 2004 by Samuel Morton III, David Keffer, Alison Davis, Robert Counce,:

> Morton III, S.A., Keffer, D.J., Davis, A.N., Counce, R.M.; E*ffect of low concentration salt on organic contact angle in ionic surfactant Solutions: insight from theory and experiment*, Submitted for Consideration in **2004,** Langmuir

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Abstract

A theoretical approach to predicting equilibirium organic/solid-surface contact angles as affected by the addition of electrolytes to an aqueous surfactant solution has been developed. While the effects of electrolytes on surfactant self-assembly and adsorption are extensively documented, there is a noticable gap in the literature for systems where less than 10 mM of electrolyte is added to the solution. This article presents an improved approach, based on our earlier model, that accounts for the dramatic changes observed for previously published hexadecane droplet contact angles data on gold for such very low concentration additions of sodium chloride (NaCl) in separate aqueous solutions of sodium dodecyl sulfate (SDS) and cetyl trimethyl ammonium bromide (CTAB). In addition to providing insight into changes in interfacial phenomena the model demonstrates that both charge and type of salt ions play a significant role in the extent to which droplet contact angles vary from those of salt-free solutions.

1. Introduction

An understanding of the effect of the addition of electrolytes to aqueous surfactant solutions is of importance to a wide range of applications such as pharmaceuticals, nanomaterials, and aqueous surface cleaning. As a result of this importance the impact of electrolytes on relevant surfactant aggregation and adsorption phenomena has been widely reported in the literature. These phenomena include micellization [1-7], air/solution interfacial adsorption [8-12], organic/solution interfacial adsorption [13-17], and solid/solution interfacial adsorption [18-24]. The study of these phenomena is not always simple since most aqueous surfactant solutions are multicomponent systems, adding compounding degrees of difficulty with increasing system complexity. This complexity is especially relevant to any study of surface cleaning using aqueous surfactant solutions. Commercial cleaning solutions contain a great many compounds designed to treat, modify, and improve the cleaning solution and its subsequent performance. In order to develop an improved understanding of surface cleaning, so that environmental improvements to the industrial scale processes can be attained, a great deal of work has been performed [23-31]. These studies have been undertaken to examine relevant phenomena of the aqueous solution performance and isolate individual effects for important solution additives. Recently an investigation of the impacts from the addition to solution of low concentrations (<5 mM) of a 1:1 electrolyte, sodium chloride (NaCl), on equilibrium organic droplet contact angles and surface cleaning efficiency was reported in the literature [23, 24]. Additionally an effort [30, 31] to develop a theoretical model to predict the evolution of organic contact angles from a thermodynamic viewpoint has occurred in parallel to the aforementioned experimental work.

The work presented in this current article expands the basic model presented in Morton *et al.* [30, 31] to include the effect of very small changes in ionic strength from the addition of NaCl to solution on hexadecane droplet contact angles on a gold surface in both anionic and cationic surfactant solutions. A nearly identical system as modeled in this present article was described in Morton et al. [30] with the main difference being the addition of NaCl molecules and their disassociation products to the bulk solution phase of the system. This modified model is then compared to experimental studies from Davis *et al.* [23, 24].

2. Theory

As indicated earlier the model utilized in this article is based on a previously published version [30] and recent improvements [31]. The modification of the solid surface/solution component balances to account for adsorbate-adsorbate interactions and the allowing of like adsorbate clustering is a significant improvement over the original model that used the Langmuir isotherm. The revised model's lateral interaction parameters, which describe the interactions between adsorbate components, for adsorbed surfactant, demonstrate a series of regions with differing values for the interactions. The four regions are representative of initial surfactant adsorption (Region A), initial self-assembly (Region B), further complex self-assembly (Region C), and the post critical micelle concentration (CMC) adsorption plateau (Region D). A detailed discussion of this most recently revised model is presented in Morton *et al.* [31] to which the reader is directed for greater explanation of the model in total.

It is known that the addition of salts has a dramatic impact on the self-assembly phenomena of surfactants in solution. The bulk of the work to date has concentrated on the addition of simple 1:1 electrolytes such as sodium chloride (NaCl), potassium chloride (KCl), or potassium bromide (KBr) in concentrations of greater than 10 mM in solution. As the self-assembly processes of surfactants are known to be impacted by such salt addition, it is necessary to discuss the related surfactant component balances utilized in the current model:

$$\text{surfactant}_{\text{solution}} \rightleftarrows \text{surfactant}_{\text{micelles}}$$

$$\text{surfactant}_{\text{solution}} \rightleftarrows \text{surfactant}_{\text{organic/solution interface}}$$

$$\text{surfactant}_{\text{solution}} \rightleftarrows \text{surfactant}_{\text{solid/solution interface}}$$

The first balance accounts for the formation of micelles in solution, the second balance accounts for the adsorption of surfactant monomers at the organic/solution interface, while the third balance accounts for the adsorption and self-assembly of surfactant monomers at the solid/solution interface. The theoretical relationship between these various phenomena and the concentration of surfactant in solution is well investigated in the literature [18, 29-45], however the impact of salt addition in low concentrations is not as well studied in the referenced works.

The most detailed work relating to low-concentration salt addition exists for the formation of micelles. A number of researchers [4, 5, 9] have shown the effect of NaCl and KCl on the critical micelle concentration (CMC) or air/solution interfacial tension of the anionic surfactant sodium dodecyl sulfate (SDS). Others [8, 12] have shown the effect of KCl and KBr on the air/solution interfacial tensions of the cationic surfactant cetyl trimethyl ammonium bromide (CTAB), which can be utilized to determine the CMC for such systems. From this work it is evident that the CMC decreases with increasing salt concentration to a point of diminishing effect as the concentration approaches 1.0 M, however the point of greatest change from a salt-free solution is present at very low concentrations. It is these very low concentrations that have been the focus of our recent work [23, 24]. Because self-assembly processes are hydrophobically driven and restricted by interaction, it seems reasonable to expect that similar effects will be present for the remaining two balances. However, this is an assumption, and as such, requires theoretical investigation to determine its validity. It is to this end that the model for the prediction of contact angles on solid surfaces presented in Morton *et al.* [31] will be used to analyze the experimental contact angle information presented by Davis *et al.* [23]

The work of Davis focused on the effects of the addition of NaCl to solutions of CTAB and solutions of SDS on the contact angles formed at the edges of submerged droplets on a solid surface. It is evident from the experimental data presented by Davis that equilibrium contact angles exhibit a complex relationship to ionic strength and the concentration of surfactant in aqueous solution. Utilizing the minimum and maximum experimental cases from Davis' work, 0.0 mM NaCl and 2.5 mM NaCl respectively, the unmodified model presented in Morton *et al.* [31] was tested. As can be seen in Figure 1, the model was unable to satisfactorily account for the effect of salt addition on contact angle formation. It is therefore necessary to analyze the model and determine if it can be modified to incorporate the effects of salt on the previously mentioned balances and therefore contact angles.

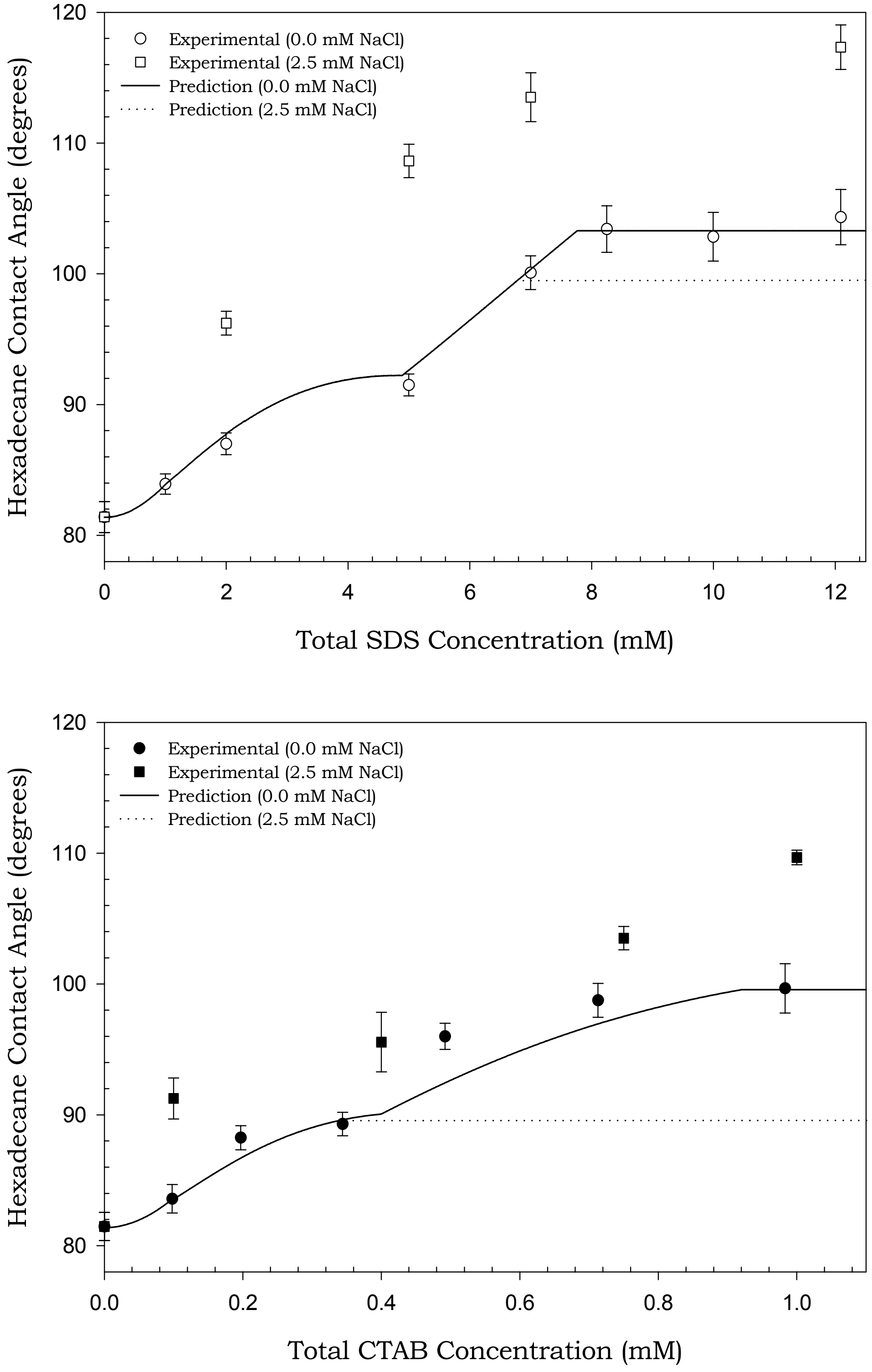

Figure 1. Model Performance Prior to Modification to Account for Effects of Salt on Self-Assembly Processes

2.1. Micellization

The model bases its calculations related to the formation of micelles on a previously published model by Nagarajan and Ruckenstein [34] for the self-assembly of solution aggregates. This model uses a contribution approach to determining the value of the change in Gibbs free energy and consequently the equilibrium constants and distribution of monomers between micelles and the free-state. Its primary purpose was to provide a broad theoretical approach to surfactant self-assembly and is well referenced due to it success in this regard. However, upon review of the original model, it is evident that scince it was developed for salt-free conditions it does not provide direct guidance as to a method for incorporating the observed effects. A possible empirical solution to the problem becomes evident following the deformational free-energy contribution (ΔG_{def}) relationship of Nagarajan and Ruckenstein.. This empirical relationship for predicting the CMC is:

$$\Delta G_{def} = k_b T(-0.50 + 0.24 n_c) \tag{1}$$

where k_b is the Boltzmann's constant, T is the system temperature, n_c is the number of carbons in the tail chain, has been utilized in the previous models and can be modified as follows:

$$\Delta G_{def} = k_b T(-0.50 + 0.24 n_c)(\Phi_{CMC}) \tag{2}$$

where Φ_{CMC} becomes an adjustable parameter with a dependence on salt concentration. It is not entirely obvious as to the reason for using this empirical relationship since the tail chains in the hydrophobic core are essentially shielded from the solution and therefore would have little or no interaction with the ions in solution. However, as the electrostatic free energy contribution (ΔG_{elec}) already accounted for ionic strength and the steric free energy contribution (ΔG_{str}) is only a function of head group area compared to micelle/solution interfacial area [30], the remaining choice is the tail-chain deformation term. The tail-chain term is dependent on the volume of the micelle core, which in turn is dependent on the separation distance between surfactant head groups at the core/solution interface due to the well known effect of ionic strength on the Debye screening length for charged species and the subsequent compression of the electric double layer (EDL) [46]. Therefore the logic in utilizing the tail chain conformation free energy term to account for electrolyte effects on CMC becomes apparent.

2.2. Organic/Solution Interfacial Surfactant Aggregation

The second balance relates the distribution of surfactant monomers between the bulk and the organic/solution interface.. It is important to remember that droplet shape changes are manifested through two distinct mechanisms, roll-up and elongation/emulsification [29, 47]. Droplets that detach due to the roll-up mechanism are typically controlled by the solid surface interaction, while droplets that elongate are controlled by the organic/solution interfacial tension [29] and bouyancy. The droplets studied in this article exhibited the roll-up mechanism. Also, it is safe to assume that the low concentration of salt utilized in the Davis's work was below the concentrations where dramatic organic/solution interfacial tension effects are observed. This does not mean that the model ignores the impact of salt addition on organic/solution interfacial adsorption; rather, the effects should be adequately included in the electrostatic free energy contribution term built into the portion of the model concerned with this balance [30]. The effect of salt on this balance is expected to increase the adsorption of surfactants moderately due to the reduction of repulsive electrostatic interactions resulting from the compression of the EDL.

2.3. Solid/Solution Interfacial Surfactant Aggregation

The remaining balance is concerned with the distribution of surfactants between the bulk and the aggregates formed at the solid/solution interface. It follows from Figure 1 that the changes in droplet contact angle, keeping in mind that the droplets in question exhibit the roll-up mechanism, are likely a result of changes in the solid/solution interfacial surfactant aggregate. As indicated earlier, the model presented in Morton *et al.* [30] has been modified as shown in Morton *et al.* [31] to allow for interactions between adsorbate species at the solid/solution interface. Since the lateral-interaction-enabled model accounts for the multiregional interaction between surfactants, the effect of salt addition and its subsequent incorporation into the model will be most extensive for this balance. It is known that the addition of salt to aqueous surfactant solution affects the adsorption of surfactants to solid surfaces[18, 21, 38, 39, 45]. This effect will most likely manifest itself in the interactions between surfactant monomers and the solid surface and the interactions between aggregated surfactant monomers. The previous model [31] provides a potential empirical solution similar to the one proposed for the micellization balance. This can be accomplished by allowing the solid-surfactant interaction parameter (U_2 [30]) and the lateral surfactant–surfactant interaction parameter (w_{22} [31]) to become functions of bulk salt concentration. The salt-dependent surfactant-surface interaction parameter (U_2^{Salt}) becomes:

$$U_2^{Salt} = U_2^{Salt-Free}\Phi_{U2} \tag{3}$$

where Φ_{U2} becomes an adjustable parameter incorporating the dependence of U_2 on salt concentration. This should account for salt-related changes in solid surface potential as discussed by other investigators [18, 19, 39]. The lateral interaction parameters for surfactant for the four regions (A-D) are potentially more complex. As explained in our previous modeling work, the surfactant-surfactant lateral interaction parameter is based on the surfactant-solid interaction parameter; therefore a certain degree of salt effect will be incorporated through this dependence. However, as with the shift in CMC, a potential shift in the initiation concentration for Region C interactions (CRC) could likely be observed. A potential method for determining this point and any potential shifts would be if a maximum was reached in the contact angle predicted in Region B due to the salt dependence of the U_2^{Salt} parameter. The dependence on surfactant concentration for the lateral interaction adjustment parameters in Region B and C was taken to be a linear function in Morton *et al.* [31] If, as expected, the Region B interactions are sufficiently salt-sensitive due to the change in the surfactant-surface interaction parameter then any changes in CRC and CMC will dictate the required changes for the Region C lateral interaction parameter, w_{22-RC}. The original form for this relationship:

$$w_{22-RC} = U_2(A_{RC} - B_{RC}C_{surfactant}) \tag{4}$$

where A_{RC} and B_{RC} are empirical constants for the Region C adsorption, and $C_{surfactant}$ is the concentration of surfactant. This relationship can be modified as follows:

$$w_{22-RC}^{salt} = U_2^{salt}(A_{RC}^{salt} - B_{RC}^{salt} C_{surfactant}) \quad (5)$$

which will result in salt dependence for the A_{RC} and B_{RC} constants reflected in A_{RC}^{salt} and B_{RC}^{salt} respectively. Any potential changes in the constants contained in the linear approximation will require an analysis of the experimental data and are developed later in this article.

3. Analysis and Discussion

As stated earlier, the two surfactants of interest in this work are SDS and CTAB. The experimental work being analyzed investigated the effects of NaCl of concentrations less than 5 mM in homogenous aqueous solutions of a particular surfactant on the contact angle of hexadecane droplets on an immersed gold surface. The experimental methods and procedures utilized to acquire the data are detailed in our previous works [23, 24].

Figure 1 demonstrates that the model in its unmodified state does not satisfactorily account for the effects of salt addition on the CMC of a particular surfactant solution. It is surprising that, considering the impact such an addition has on surfactant self assembly processes, the body of published literature appears lacking regarding the impact of very low salt addition on CMC. Fortunately there are a few articles [4, 5, 8, 12] that deal with salt effects on micelle formation, air/solution interfacial tension, or other self-assembly-related behaviors that examine salt concentrations across a sufficiently broad range for the generation of correlations and trends in the low-salt concentration ranges relevant to

Davis's work. Figures 2 and 3 show data relating to CMC changes due to salt addition for SDS and CTAB respectively. It is evident from these figures that in addition to the concentration of salt in solution, the nature of the salt anions and cations play a considerable role in the magnitude of the changes observed for the CMC. The observation relating to the salt ion effect on SDS CMCs is explored in detail in the work of Dutkiewicz & Jakubowska [5] where it is shown that the salt cation is of greatest impact. The order of impact for the salt cation on decreasing the CMC of SDS, from least to greatest, is $Na^+ < NH_4^+ < K^+ < Mg^{+2}$. Additionally, they show that the salt anion plays a very limited part on micellization. The order of effect for the anion is $Cl^- < ClO_4^- < F^-$. Sudholter and Engberts [2] suggest another salt anion hierarchy for solutions of 1-methyl-4-dodecylpyridinium iodide, a long tail chain cationic surfactant, where the order as given is: $Cl^- < Br^- < NO_3^- < I^-$. In addition to these direct statements the effect of Cl^- and Br^- on CTAB can be extracted from the surface tension study of Para *et al.* [12]. With these studies in mind the following observations regarding the effect of salt ions on SDS and CTAB CMC can be made: (1) the ionic species of opposite charge to the surfactant will have the greatest effect on the CMC, (2) the effect of the common charged ion on the CMC for a particular surfactant will be much less but still important, (3) the relative effect for monotonic ions of the same magnitude and polarity of charge increases with increasing atomic size.

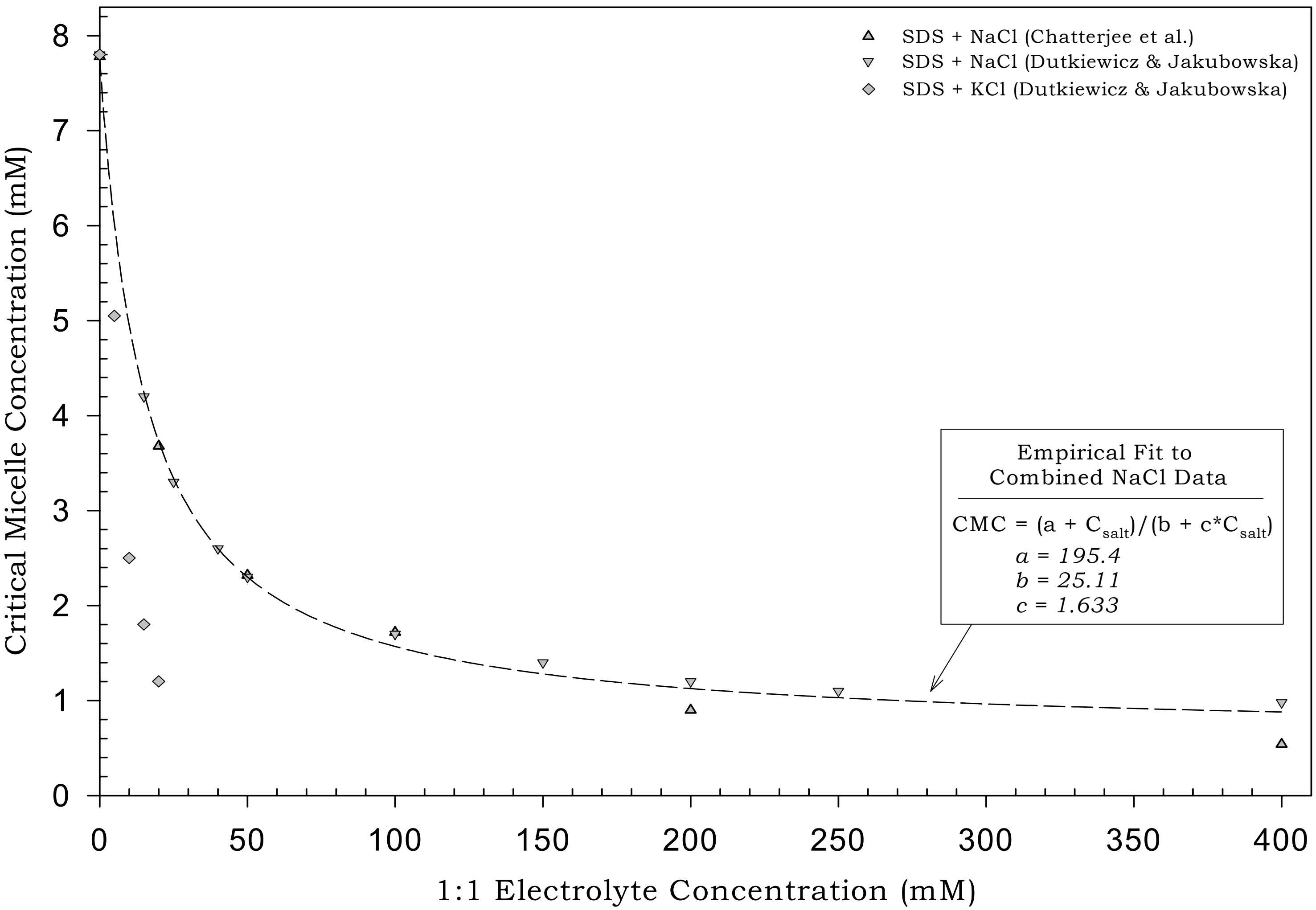

Figure 2. Effect of 1:1 Electrolytes on the CMC of SDS

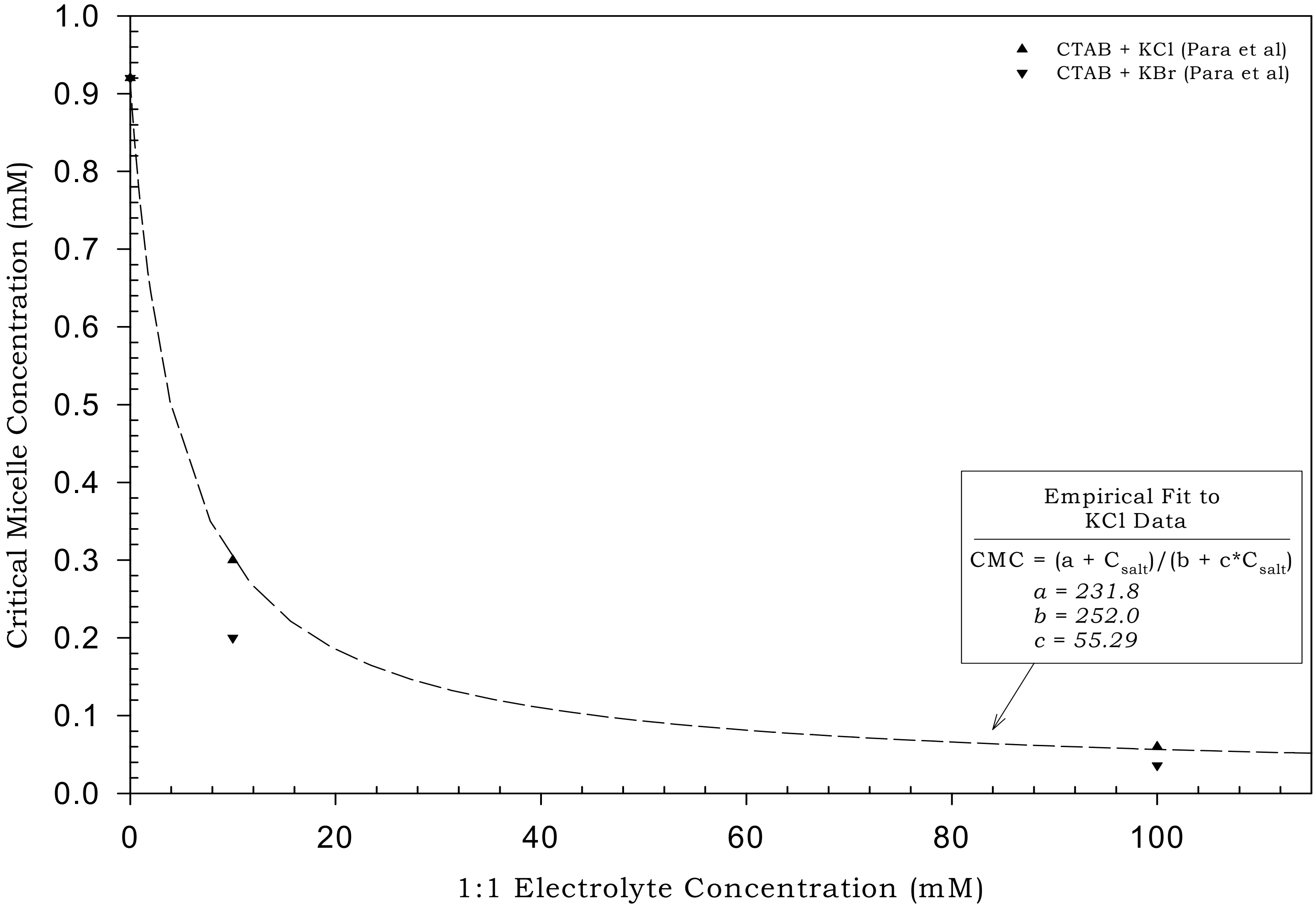

Figure 3. Effect of 1:1 Electrolytes on the CMC of CTAB

3.1. SDS & NaCl Solutions

We analyzed the impact of NaCl on the CMC of SDS. For the case of SDS, sufficient experimental information exists to determine the values of the Φ_{CMC} parameter used in Equation 2. Figure 4 shows the model predicted CMC for SDS where the Φ_{CMC} parameter is held constant at the salt-free value and where it is allowed to vary with the addition of NaCl. Optimum values of Φ_{CMC} for a range of salt concentrations were determined using the empirical relationship shown in Figure 2. This was necessary since no CMC data was available for the very low salt concentrations reported by Davis *et al.* [23]. Using these optimized values, an empirical relationship for Φ_{CMC} as a function of NaCl concentration was fit and is shown in Figure 5.

With the model correctly accounting for changes in CMC we may now analyze the other balance where the impact of salt addition was expected to have a substantial impact, the aggregation of surfactant at the solid/solution interface. Since the addition of salt affects the surfactant-solid interaction parameter, as shown in Equation 3, we need to determine Φ_{U2} as a function of salt concentration. Optimized values for Φ_{U2}^{salt} were generated for various salt concentrations using the experimental contact angle data from Davis for SDS concentrations above the CMC (C_{SDS} = 12 mM) where the CMC related contact angle plateau was reached. An empirical relationship for was fit to the optimized values of Φ_{U2} and is shown in Figure 6. From this we can that as the salt concentration increases, the effective surfactant-solid interaction increases.

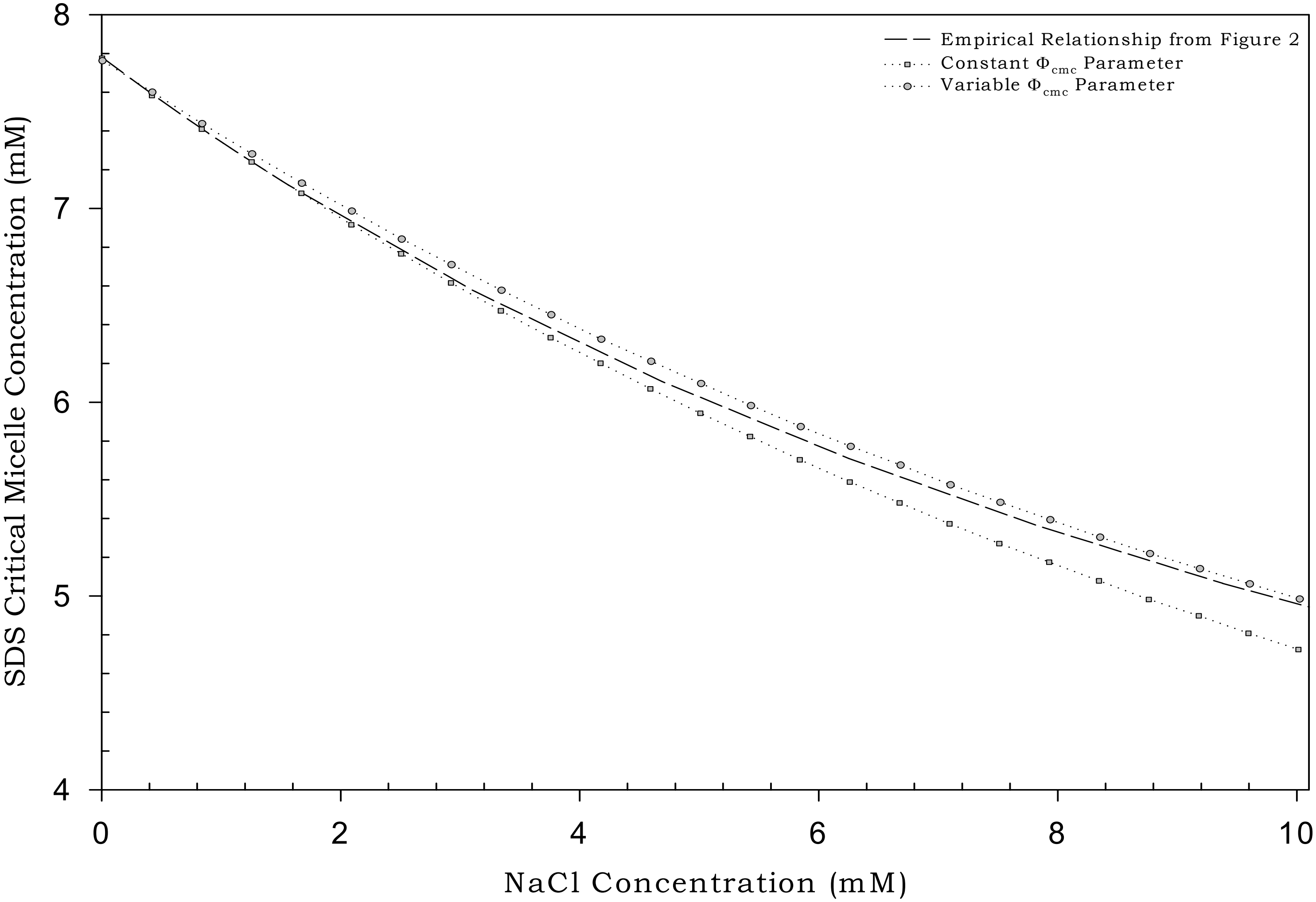

Figure 4. Model Prediction for the Impact of NaCl on SDS CMC

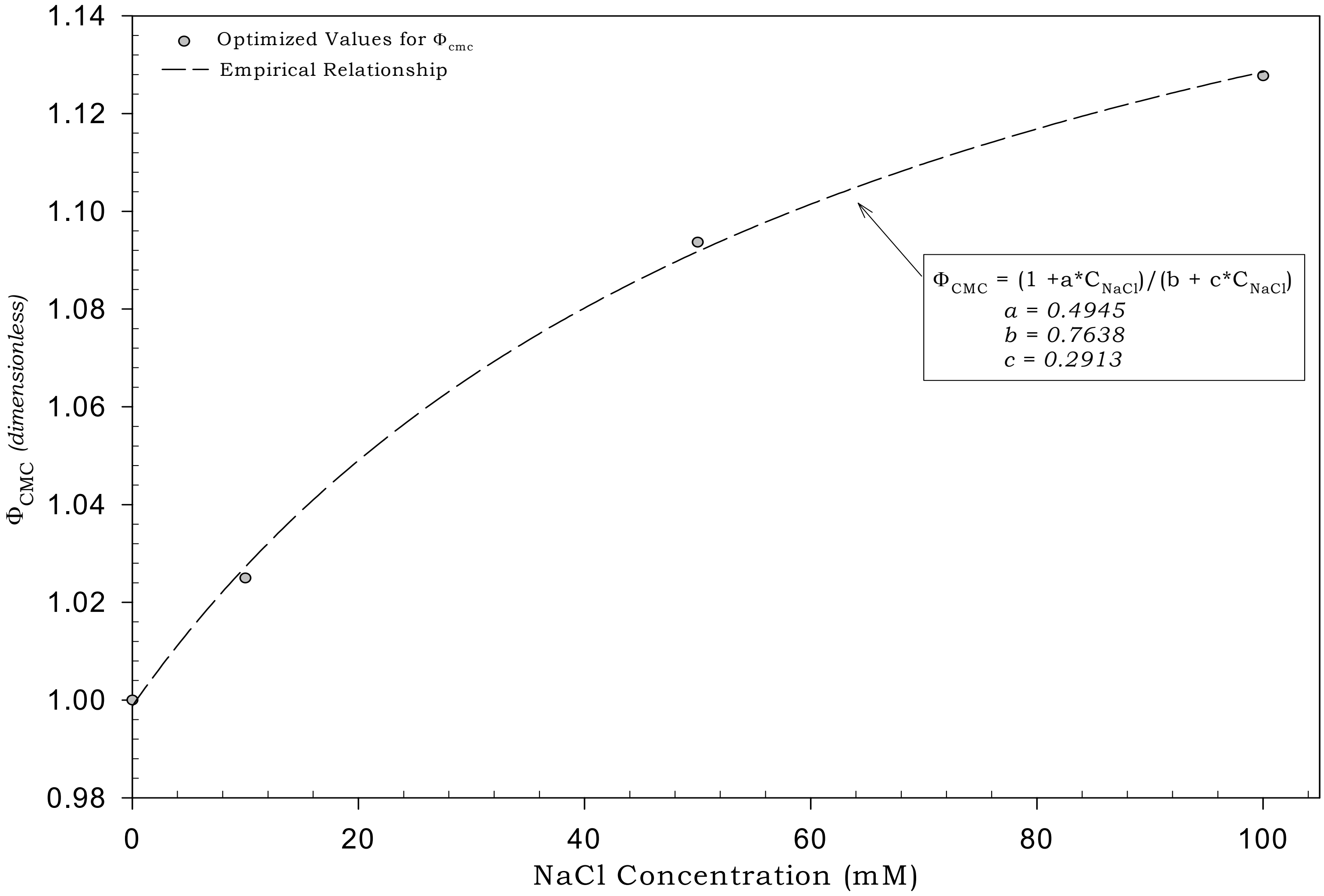

Figure 5. Analysis of NaCl Concentration Effects on the Salt Dependent CMC Parameter

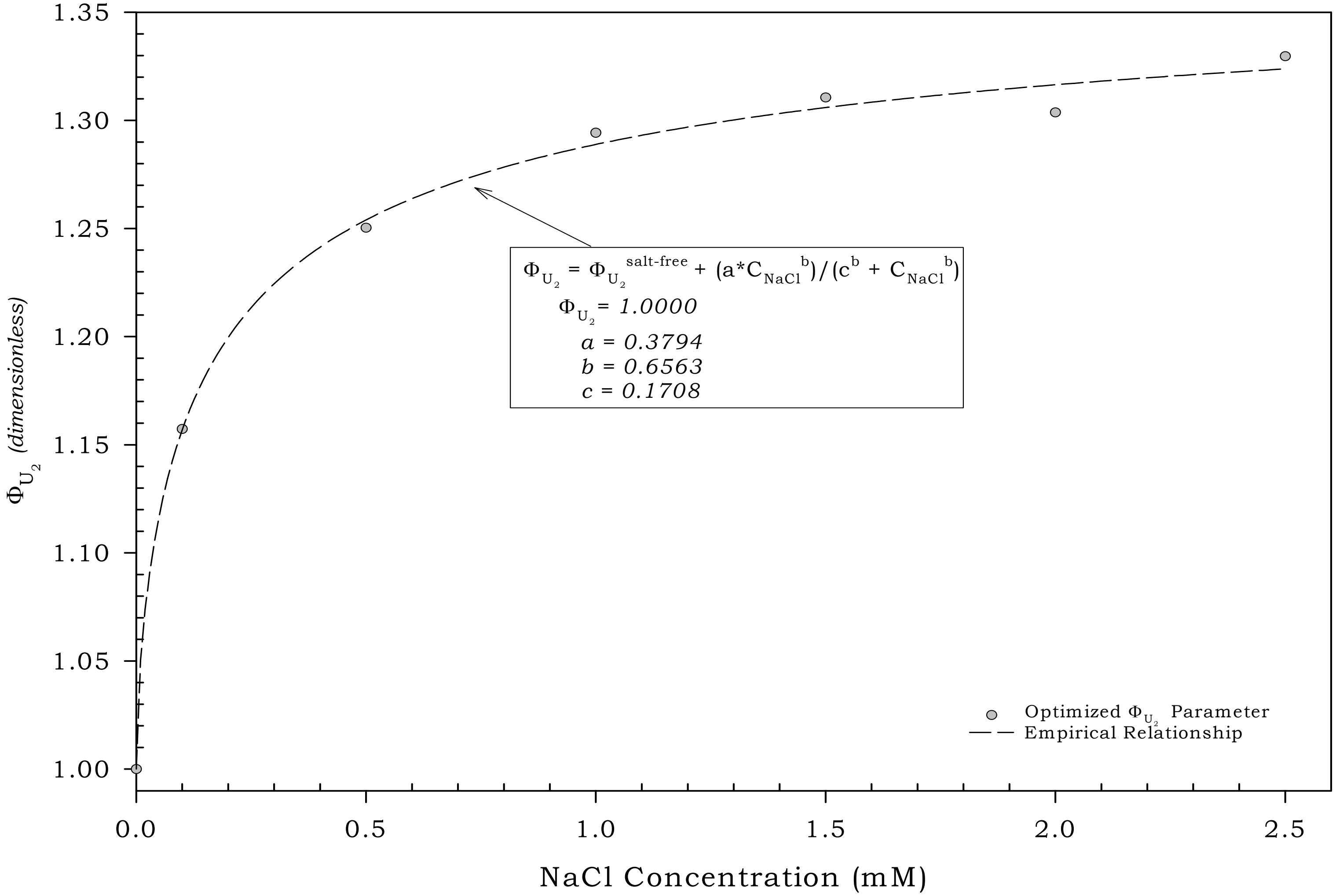

Figure 6. Impact of NaCl on the Salt Dependent Surfactant/Solid Interaction Parameter for a SDS/Gold System

We turn our attention to the effect of salt on the lateral interactions of surfactants adsorbed at the solid interface. Since the lateral interaction parameter, w_{22}, was defined as a function of the value of the surfactant-solid interaction, U_2, the model provides us with the ability to determine if there are any additional salt effects, such as a shift in the adsorption initiation concentration for Region C (CRC). From an analysis of the data and model prediction it is apparent that a change in the CRC is occurring for the SDS relative contact angle data shown in Figure 1. The method for determining the values of the CRC using the model relies on the w_{22} relationship for Region B remaining unchanged. This can be assumed to be valid in that for the formation of simple monolayer type aggregates, the impact of salt on self-assembly should be accounted with the previously developed relationship for the effect of such salt on the U_2 parameter. Since the w_{22} parameter has a different relationship in Region C than in Region B and this relationship is sensitive to the CRC an iterative process must be utilized to determine any impact on the lateral interaction parameters used in the model. The first requirement was the determination of the CRC. This was simple in that the model reached a local maximum in its prediction of Region B contact angles at the CRC. With an estimate for the CRC determined, the linear relationship used to describe the surfactant concentration dependence of the w_{22} parameter for Region C could be estimated for the addition of salt. This resulted in an empirical relationship for the A and B constants from Equation 4, which is shown in Figure 7.

Once these relationships have been developed so that the respective component balances account for changes due to salt addition the model may be used to predict contact angle data for the specified system and compared to actual experimental data. The model prediction is compared

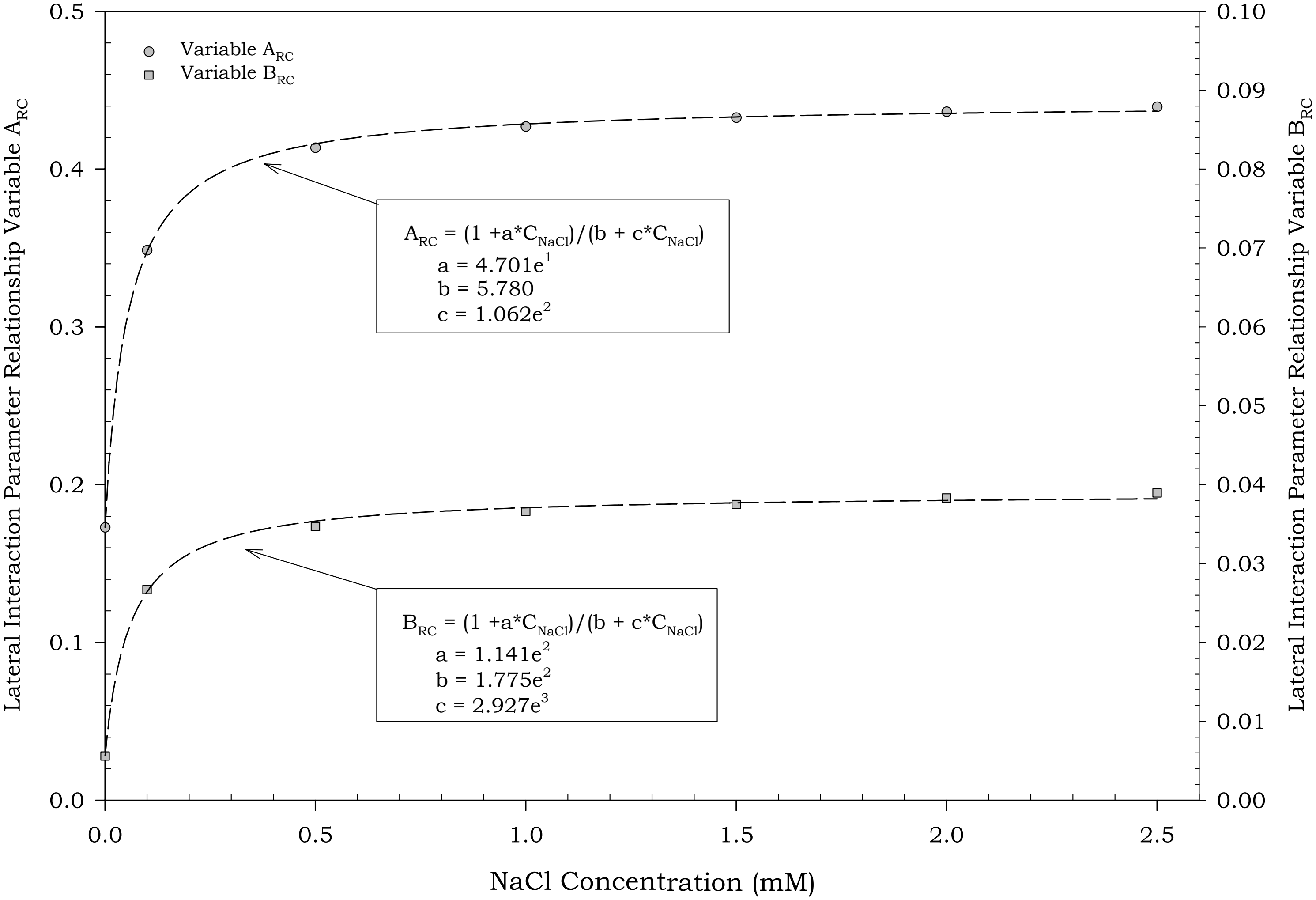

Figure 7. Impact of NaCl on the Surfactant Concentration Dependent Relationship for w_{22} in Region C

to the SDS solution experimental data from Davis *et al.* [23] in Figures 8 and 9. Not only do these figures demonstrate that the model's prediction is greatly improved from Figure 1, but that the greatest change to contact angle for the NaCl concentration range studied here occurs between 0.0 mM and 1.0 mM.

3.2. CTAB & NaCl Solutions

A similar process to that employed for the SDS data analysis can be used to analyze the effects of NaCl on CTAB. A major limitation to this analysis is that the literature has a lack of CTAB/NaCl solution CMC data for the same conditions as utilized by Davis. From the salt ion effect observations developed earlier it would appear that the ion of greatest import for the CTAB system is the anion. Since there is CMC information for a CTAB/KCl system, shown in Figure 3, it becomes possible to determine the degree of impact the common anion, Cl^-, between this data and our system. Additionally, it will allow for the determination of the relative impact of the cation in the CTAB/NaCl system and a prediction for the CMC of the solution over our NaCl concentration range.

The same computation procedure as employed in the previous analysis of the SDS/NaCl system was utilized for the CTAB system. Optimum values for Φ_{CMC} and Φ_{U2}^{salt} were determined, based on the assumption that the KCl CMC relationship will satisfy a NaCl system since they share a common anion. It is readily apparent from Figures 10 that the contact angle plateau related to micelle formation in solution occurs at too low of an overall surfactant concentration. This indicates that the use of the KCl approximation still dramatically over-predicts the change in CMC for

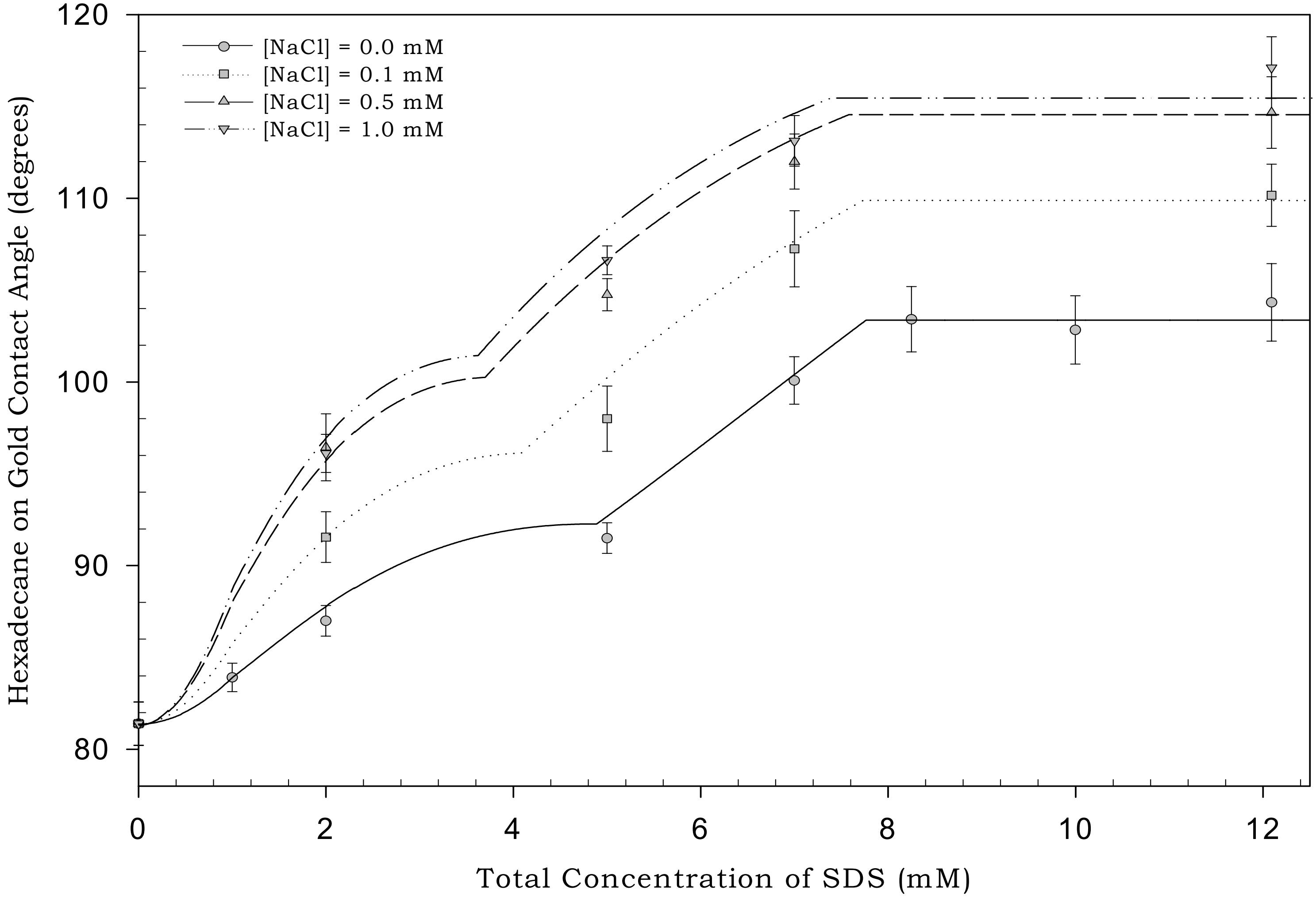

Figure 8. Experimental and Predicted Hexadecane Contact Angles in SDS/NaCl Solutions: 0.0 mM to 1.0 mM NaCl

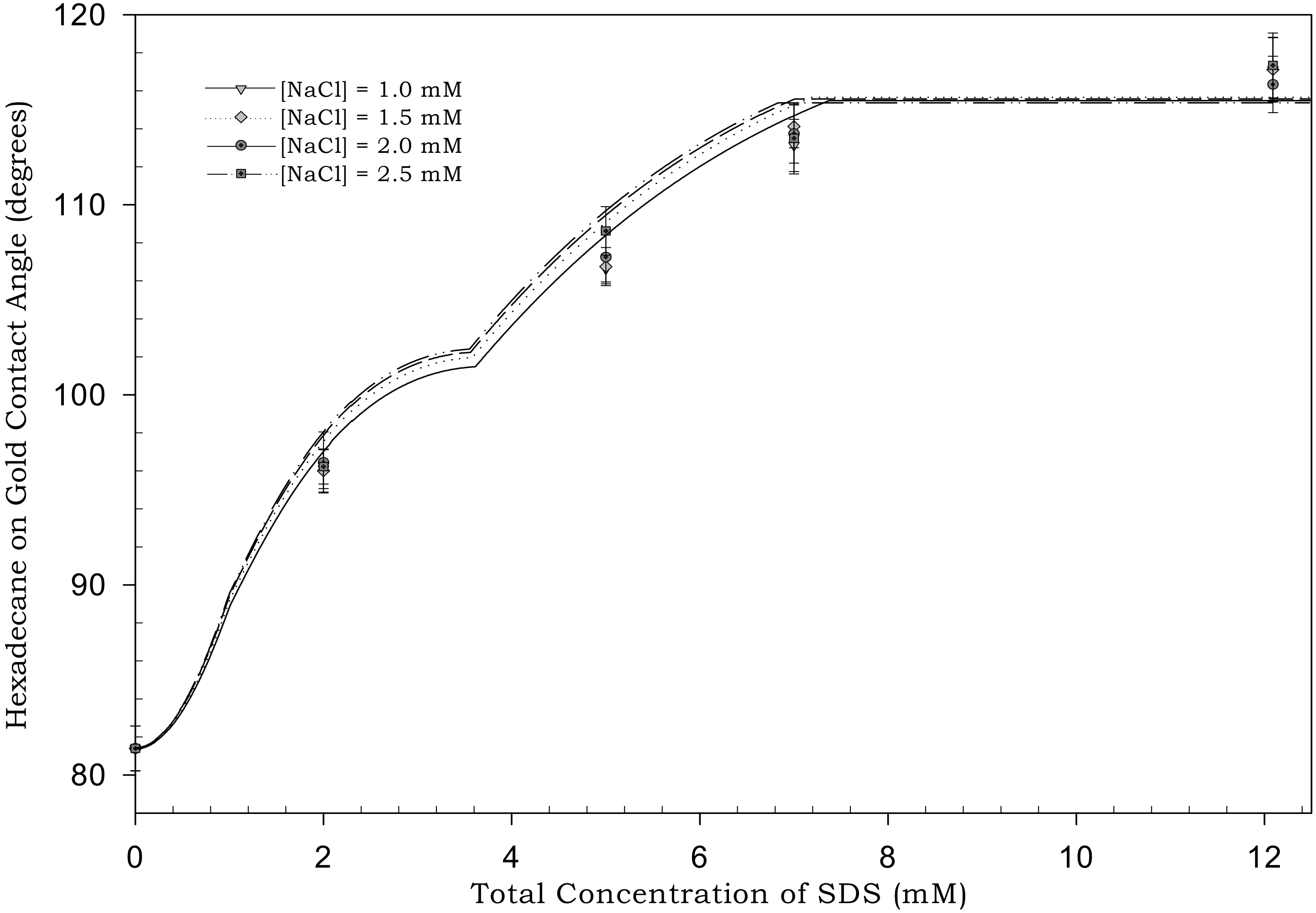

Figure 9. Experimental and Predicted Hexadecane Contact Angles in SDS/NaCl Solutions: 1.0 mM to 2.5 mM NaCl

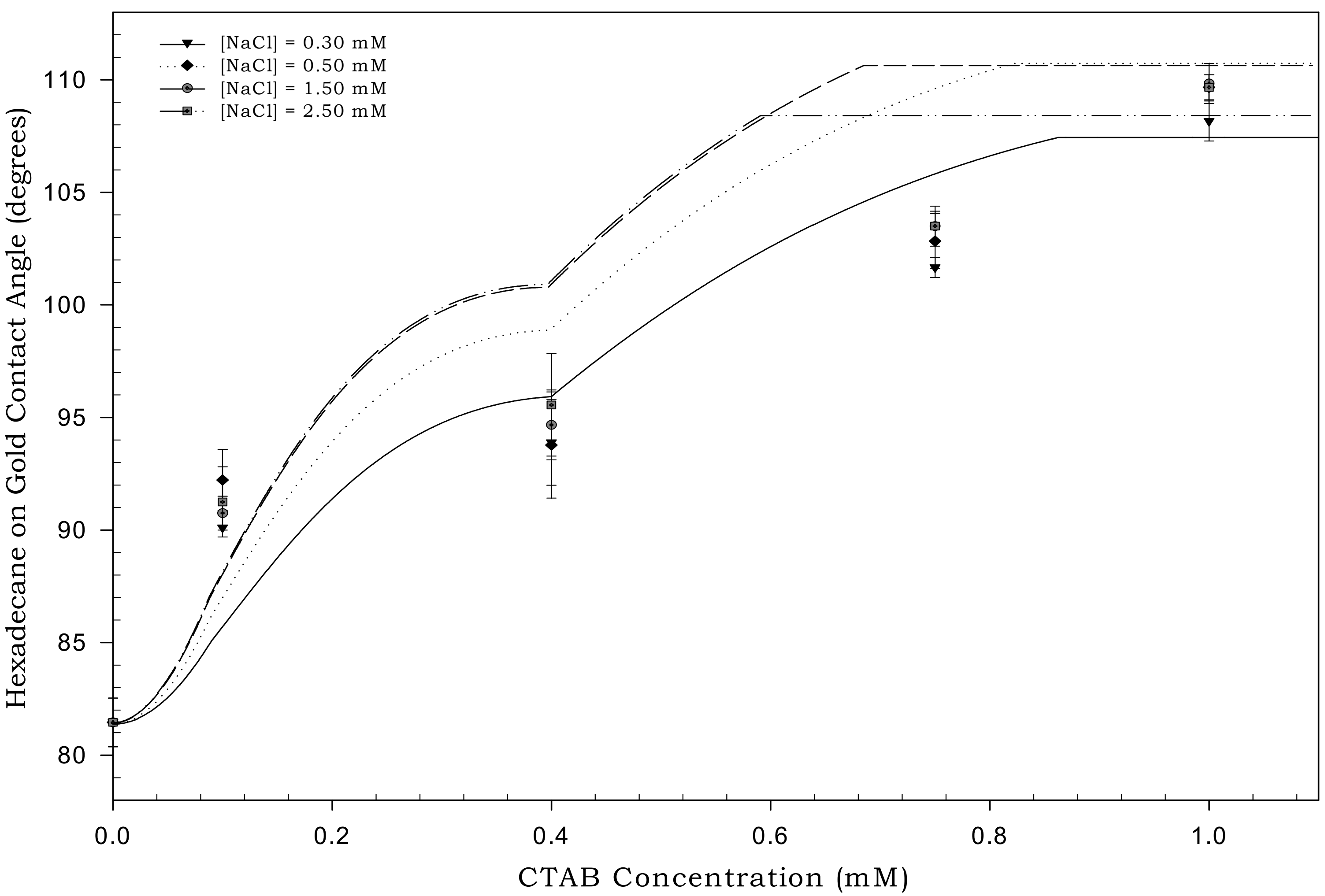

Figure 10. Experimental and Predicted Hexadecane Contact Angles in CTAB/NaCl Solutions: 0.3 mM to 2.5 mM NaCl *(Based on KCl CMC Empirical Relationship)*

the salt range reviewed and therefore can not be used to accurately predict contact angles for a CTAB/NaCl system. This over-prediction gives insight into the magnitude of the impact on the system of the cations, Na^+ and K^+. This figure demonstrates that both the salt cation and anion have a significant impact on self-assembly processes for cationic surfactants and thus neither of the ions can be ignored.

As a result of the failure of the KCl approximation, we must develop a realistic relationship for the effect of NaCl on CMC. Lacking any direct experimental information other than the contact angle data presented by Davis we must make an estimate for the effect of NaCl. At the maximum salt concentration present in the contact angle data, 2.5 mM NaCl, the CMC for SDS changes by roughly 12 percent. Making the assumption that the CMC change for the CTAB/NaCl system is of a similar degree to the SDS/NaCl system, approximate values for the Φ_{CMC}, Figure 11, and the Φ_{U2}, Figure 12, were determined. Figure 13 demonstrates the effects of these approximations on the calculated CMC for CTAB solutions. This figure also demonstrates the extensive impact on CMC that the type of salt and subsequent anions and cations manifest. Utilizing these optimized relationships, the model predicted contact angles for hexadecane on gold in CTAB/NaCl solutions are shown in Figures 14 and 15. From these figures it becomes apparent that the change in CMC of CTAB solutions with NaCl is much less than KCl and that the model, when given a better estimate for the CMC change, is able to predict the change in contact angles much more accurately. Unfortunately there is insufficient experimental data in the required concentration range to determine if addition of NaCl to these solutions resulted in a change in the CRC. Additionally it appears that the linear function used to describe the change in w_{22} for Region B does not

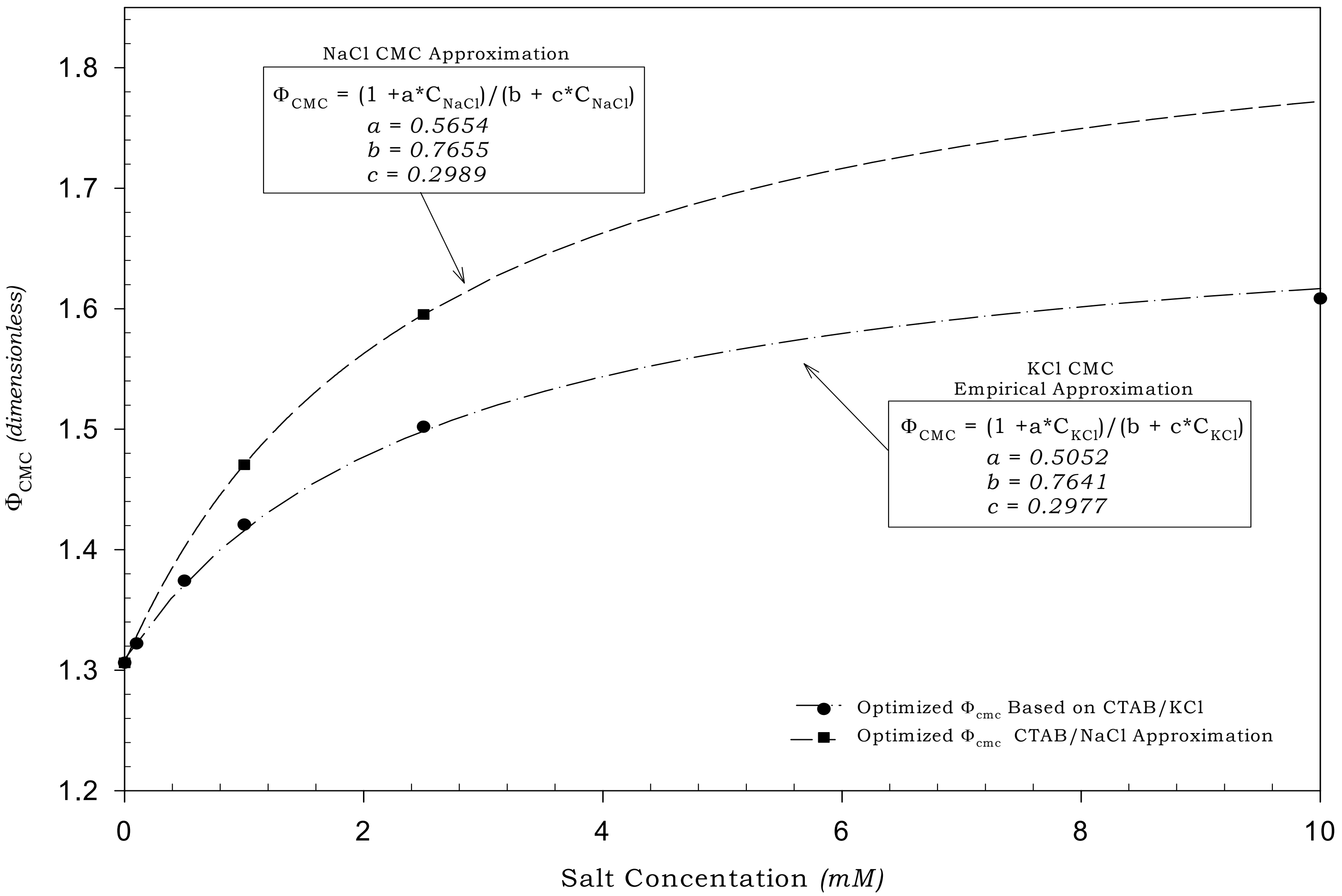

Figure 11. Estimation of Improved Φ_{CMC} for CTAB/NaCl Solutions

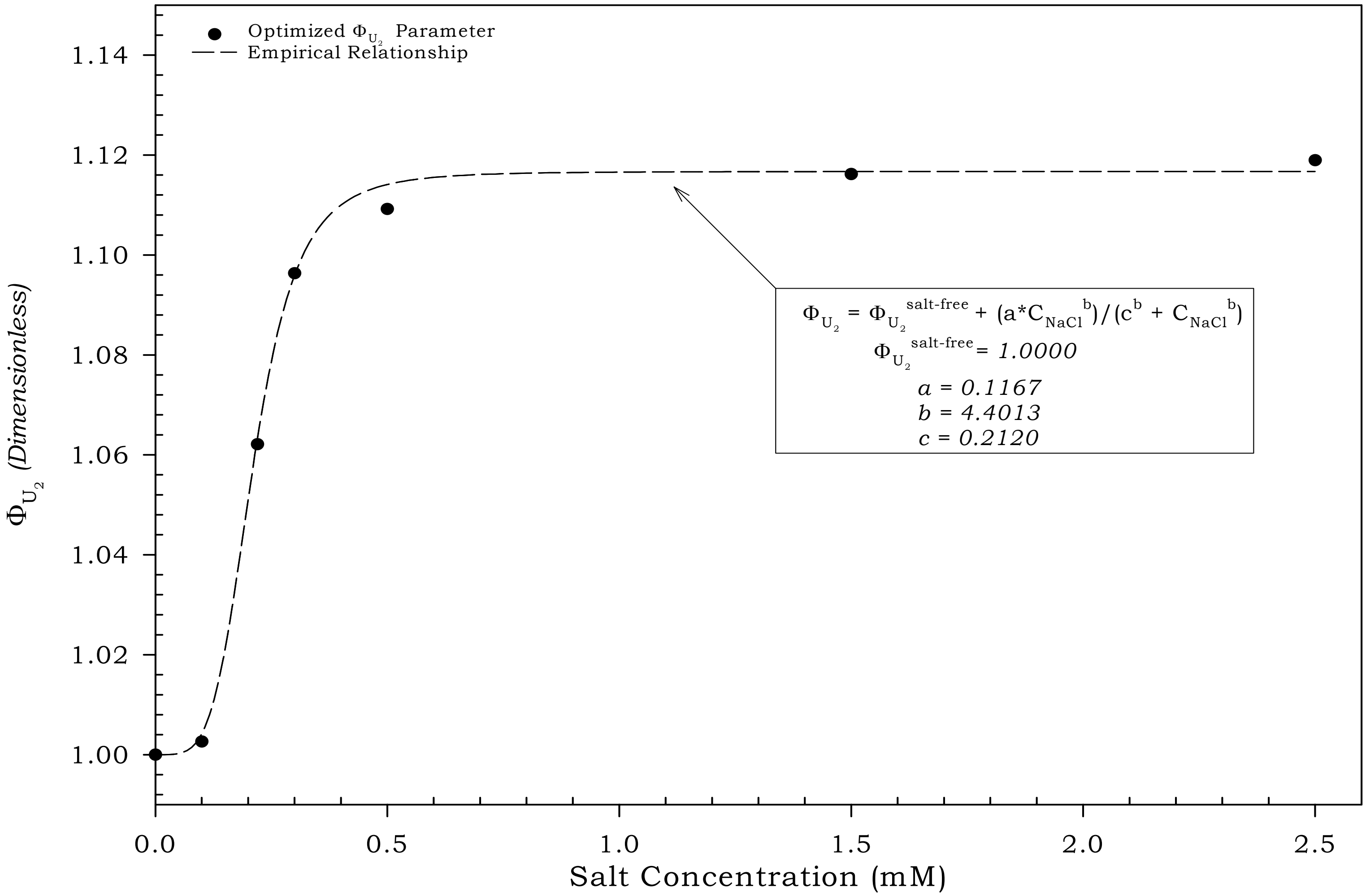

Figure 12. Estimation of Surfactant/Solid Interaction Parameter Using the Improved CMC Approximation

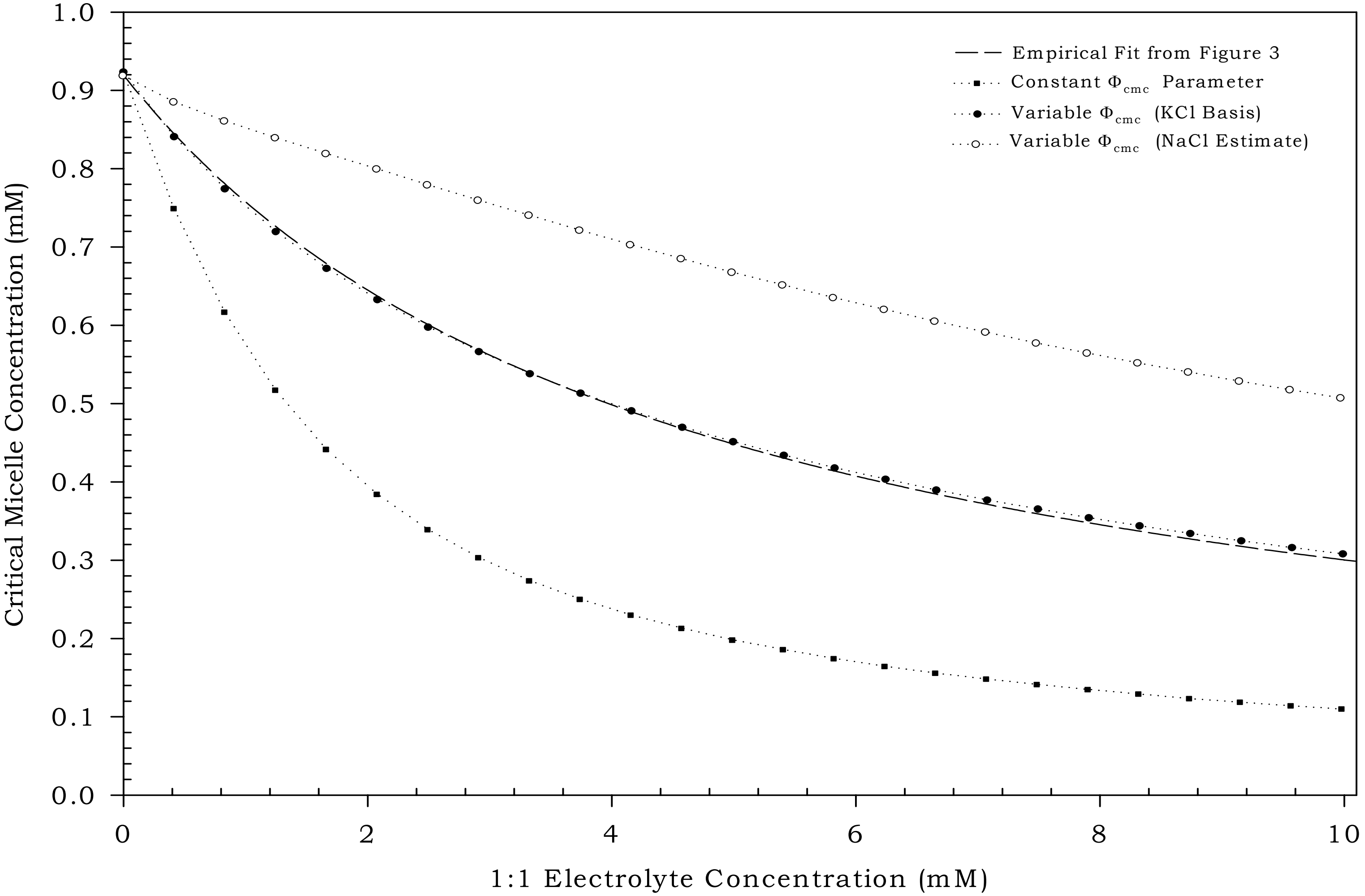

Figure 13. Model Predicted Values for the CMC of CTAB Solutions as Affected by Salt in Low Concentrations

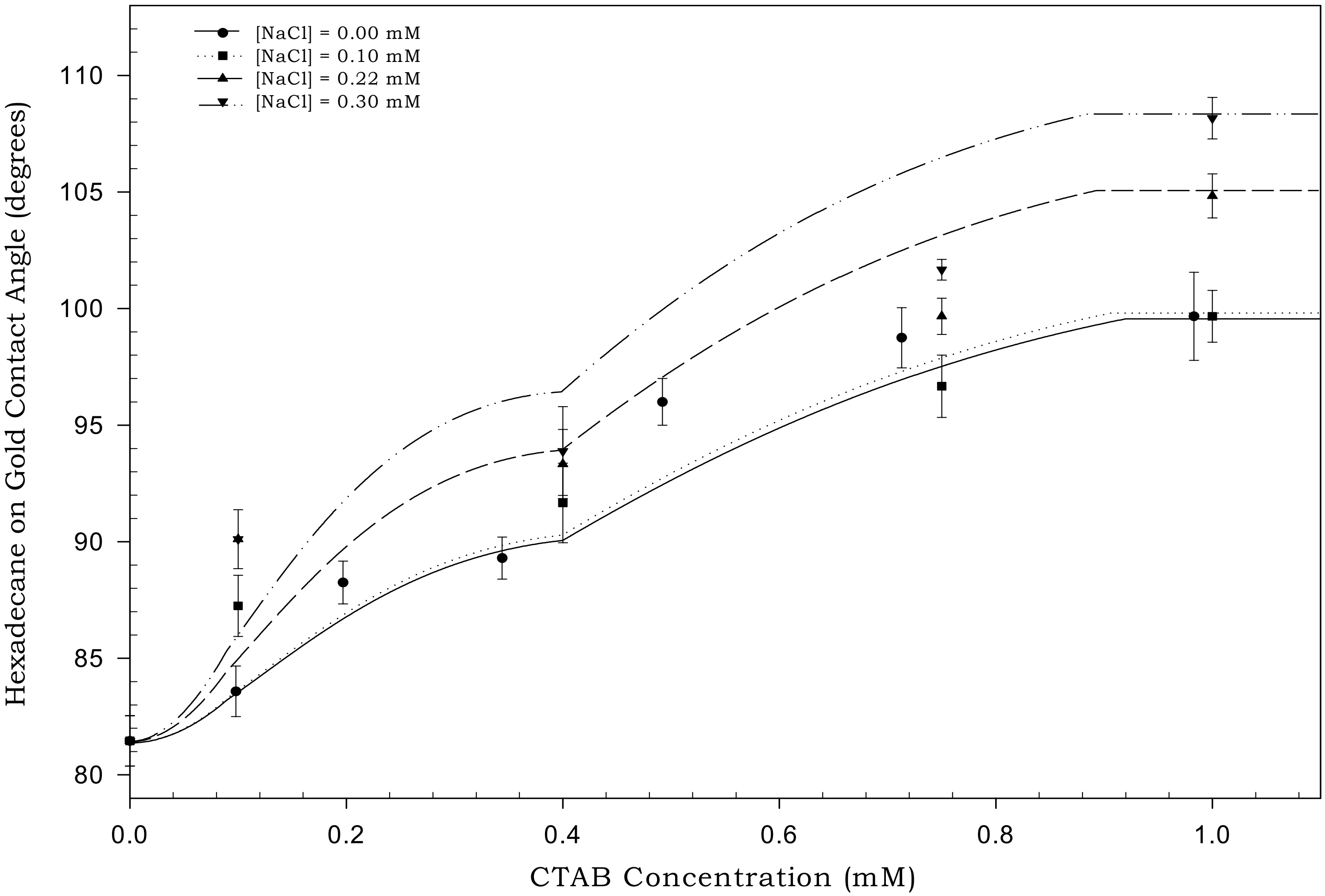

Figure 14. Experimental and Predicted Hexadecane Contact Angles in CTAB/NaCl Solutions: 0.0 mM to 0.3 mM NaCl *(Based on Improved Empirical Relationship)*

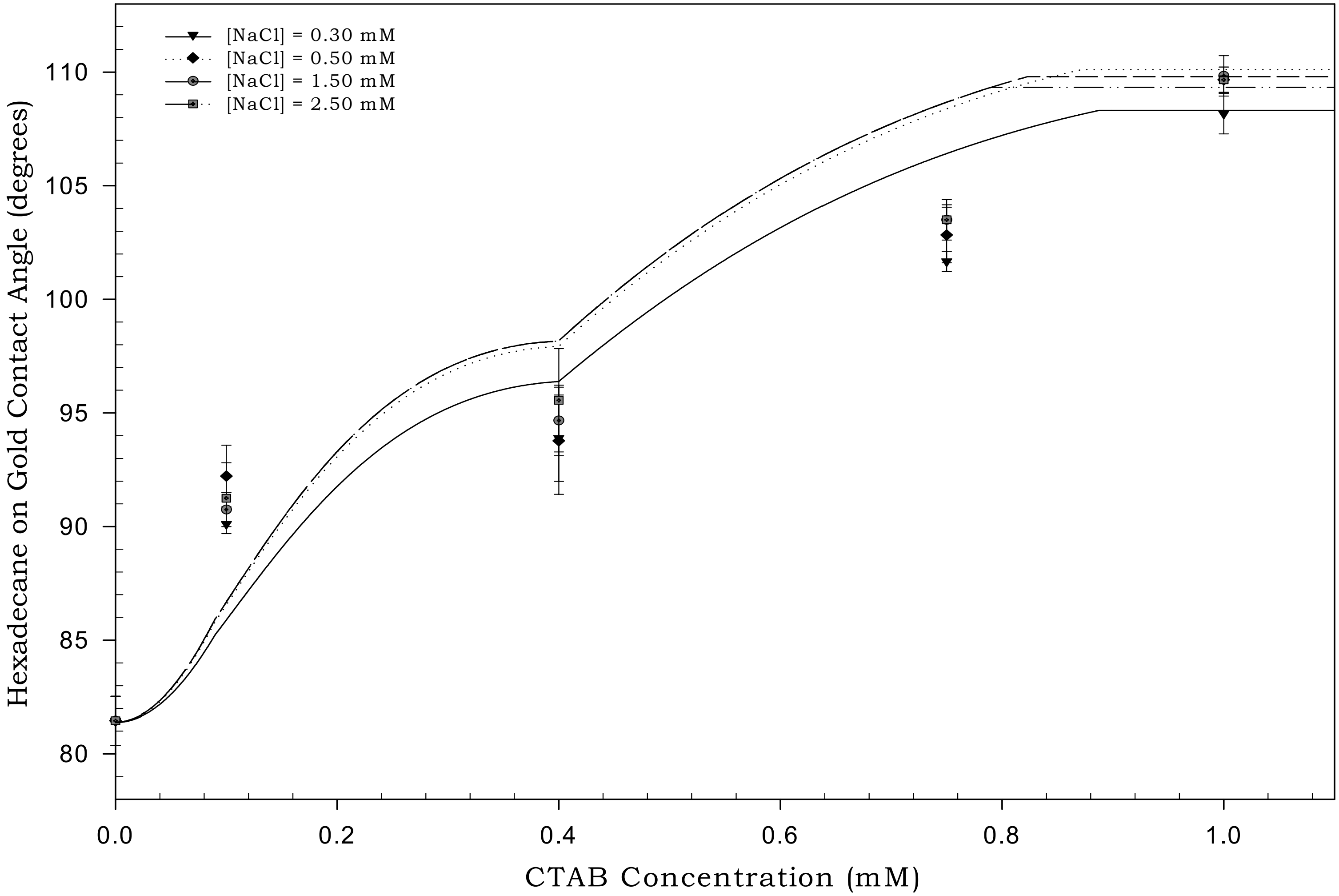

Figure 15. Experimental and Predicted Hexadecane Contact Angles in CTAB/NaCl Solutions: 0.3 mM to 2.5 mM NaCl *(Based on Improved Empirical Relationship)*

capture the perceived curvature of the contact angle data trend. However, there is again insufficient experimental data available to generate an alternative approximation for this change with any additional rigor.

4. Summary

The work presented in this article demonstrates a significant improvement to our model for the prediction of organic contact angles in aqueous surfactant solutions. The impact of low concentration salt can be very beneficial to processes removing organics and/or other contaminants from solid surfaces by enhancing the performance of the surfactant solution while reducing the overall cleaning solution complexity. This reduction in complexity should result in better contaminant removal, increased solution life span, and simplified surfactant solution recycle activities.

From the evidence and analysis present in this work it is obvious that a significant impact on contact angles is manifested at low salt concentrations. It is also apparent that the greatest change in contact angle per change in salt concentration occurs between 0.5 and 1.0 mM NaCl for both the anionic and cationic surfactants studied. The effect of salt on contact angles is due in part to the compression of the EDL and its subsequent impact on surfactant self-assembly and in part to changes in the interactions between surfactant monomers and the charged solid surface. The model assists in analyzing organic droplet contact angles acquired via the method of Davis and coworkers. Information regarding the various surface aggregation phenomena and the CMC of the surfactant solution can be extracted from the model's theoretical analysis.

It is also apparent from the analysis presented in this article that there are still areas of uncertainty regarding the impact of salts on aqueous surfactant phenomena. From the experimental analysis of CMCs, presented in this and other works the addition of salt appears to have a continuous impact until reaching a point of diminishing effect at salt concentrations approaching 1M. This contrasts dramatically with the apparent maximum impact of salt on contact angle evolution, through surfactant aggregation at the solid interface, which appears to have a maximum in the vicinity of 1.0 mM. Additionally, the determination of the primary contact angle plateau and the concentrations for the various region transitions requires significantly more experimental work before the model can be fully refined to predict it. Lastly there is a great deal of uncertainty regarding the precise reason that different cations and anions have such a varied effect on the surfactant related system phenomena. Further experimental studies should be undertaken to illuminate these areas and a proper analysis using the model can determine the most efficient direction for these studies to follow.

5. Acknowledgments

The authors would like to acknowledge the financial support of the American Electroplaters and Surface Finishers Society through Grant #110. Additional financial support from the Environmental Management Science Program, U.S. Department of Energy, by a grant to the University of Tennessee through contract DE-AC05-00OR22725 with UT-Batelle, LLC. is greatly appreciated.

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PART VI

Behavior of Oil Droplets on an Electrified Solid Metal Surface Immersed in Ionic Surfactant Solutions

Part VI of this dissertation an article by the same name originally submitted for publication in the journal *Langmuir* in 2004 by Samuel Morton III, David Keffer, Robert Counce, and David DePaoli:

> Morton III, S.A., Keffer, D.J., Counce, R.M., DePaoli, D.W.; Behavior of Oil Droplets on an Electrified Solid Metal Surface Immersed in Ionic Surfactant Solutions, Submitted for Consideration in **2004,** *Langmuir*

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Abstract

The present study investigates the change in the shape of oil droplets immersed in an ionic surfactant solution which are in contact with metal surfaces to which an electrical potential is applied. The three-phase system of aqueous solution-oil-steel was subjected to low-voltage electric potentials, which resulted in sometimes dramatic changes in droplet shape and wetting. This electric potential was applied to the conductive steel surface directly and the counter electrode was immersed in the solution. Changes in both the shape and wetting extent of hexadecane and phenylmenthyl polysiloxane were observed for voltages between ±3.0 volts in both sodium dodecyl sulfate and cetyl trimethyl ammonium bromide solutions. The droplets' behavior was opposite to that observed in electrowetting; however, the addition of surface-active agents resulted in an amplification of these changes. In one instance, hexadecane droplets in sodium dodecyl sulfate solutions with a voltage of -3.0 volts, a rapid and repeating droplet elongation and detachment was observed. The observations lead to the possibility of employing simple electrowetting techniques in the removal of oil from metal surfaces in a manner that could greatly improve the environmental and economic performance of aqueous cleaning techniques.

1. Introduction

The influence of electric charge on the shape and behavior of a liquid droplet contacting a solid surface is a well known phenomenon. Since the seminal work of Lippman on the nature of the aqueous electrolyte solution-mercury electrode interface [1], electrocapillarity and electrowetting have been investigated and exploited in a variety of ways. Electrocapillarity is typically defined as the reduction of the interfacial tension of a liquid in the presence of an electric field. Electrowetting on the other hand is defined as the manipulation of the wetting behavior of a liquid on a surface. These phenomna are currently undergoing an rise in interest due to their potential application in a number of newly developing technologies [2], such as microfluidics [3-5] and electronic paper [6].

In tandem with the increased use of electrowetting in novel technologies, a number of researchers [7-20] are working to further the understanding of the fundamental phenomena that cause the changes in the behavior of the liquid droplet. It is evident from these works that there is much that remains undefined since several competing explanations for observed phenomena are presented and discussed. Of this body of work, particular attention should be paid to the explanation of the relationship between surface charge and wetting phenomena as present by Kang *et al.* [7]. Kang discusses three droplet/surface system configurations in his work on charge-related wetting. These systems are defined to be (1) droplet on electrode, (2) droplet on charged surface, and (3) droplet on a dielectric. The bulk of recent electrowetting research has been focused toward the third system, where the wetting liquid is separated from the conducting solid by a dielectric or insulating material. The goal of much of this work is to better define and demonstrate the effect of applied potential on the equilibrium and dynamic spreading of liquids on these dielectric materials. This is best exemplified by Janocha *et al.* [20] in their study of the competitive wetting of various dielectric polymer materials by water and decane.

While those studies are beneficial to a better understanding of electrowetting in general, it is the works of Ivosevic *et al.* [17-19] and Tsekov et al. [16] that are of particular interest to our work in improving aqueous surface cleaning in the metal finishing/electroplating industry [21-24]. Unlike the bulk of the recent electrowetting work, these studies were interested in a modified version of the first of Kang's systems, droplet on an electrode. Both Ivosevic and Tsekov study the wetting behavior and surface charge phenomena for an organic droplet in contact with a mercury-electrode immersed in an aqueous electrolyte solution. This differs from Kang's observations in that the droplet is no longer in direct contact with the counter electrode. They theorized that organic droplets are manipulated by potential through alteration of the organic/solution interfacial tension. The lessening of interfacial tension results in a decrease in surface free energy, which allows the droplet to elongate due to buoyancy forces. This elongation could result in the droplet shearing, in which a portion of the droplet floats to the air/solution interface while a much smaller amount of oil remains to wet the surface. This is important to the present study, in that Rowe et al. [22] observed a similar elongation and detachment for droplets of a quench oil, Mar-TEMP 355, in aqueous surfactant solutions with application of an electric potential to the metal substrate between -4.0 and +4.0 volts. A significant difference between this work and that of Ivosevic et al. and Tsekov et al. is that instead of a simple electrolytic solution we are focused on ionic surfactant solutions. Additionally ,the experimental work of Davis et al. [21] and the theoretical work of Morton et al. [23, 24] provide us with resources that assist in developing an improved understanding of the behavior of oil droplets on a solid metal surface in ionic surfactant solution when an electric potential is applied to the metal surface.

Thus we present a study of the effect of an applied electric field on the wetting and shape phenomena of oil droplets on a steel surface. Additionally the effect of an applied potential on a prototypic industrial cleaning process will be demonstrated so that any impacts on industrial cleaning systems can be compared to the observed equilibrium phenomena. This allows for the development of a mechanistic understanding of the controlling phenomena which in turn should enhance the environmental and economic performance of industrial metal cleaning processes.

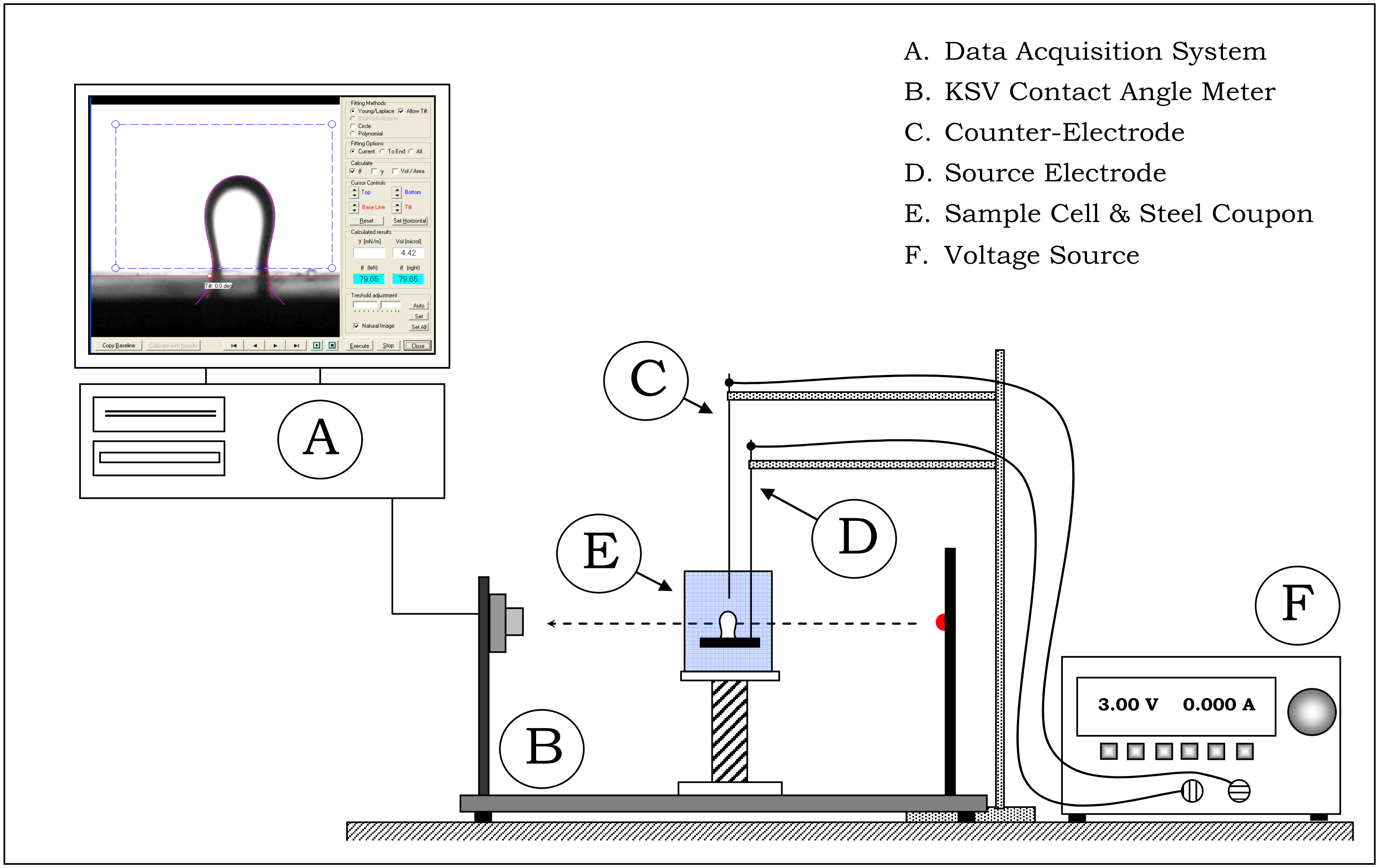
2. Experimental Section

2.1. Materials

The oils used for the experiments presented in this article were hexadecane and phenylmethyl polysiloxane (PMPS) (Fisher Scientific). The surfactant solutions were prepared using deionized water and either sodium dodecyl sulfate (SDS), an anionic surfactant, or cetyl trimethyl ammonium bromide (CTAB), a cationic surfactant (Fisher Scientific). The coupons used in this study were press cut from a single piece of 304 stainless steel flat stock, and measured approximately 45 mm × 25 mm × 3 mm. The counter-electrode was a 304 stainless steel rod approximately 3 mm in diameter. The coupons and counter-electrode were cleaned upon receipt by soaking in petroleum ether (Fisher Scientific), repetitively rinsing with deionized water, and drying with a lint-free cloth. The coupons were then stored in petroleum ether for a 12-24 hour period prior to use.

2.2. Droplet Shape Analysis

The experimental scheme for these measurements is shown in Figure 1. The effect of applied potential on droplet shape was analyzed using a digital contact angle meter (CAM 200, KSV International). The contact angle meter utilized a CCD camera to acquire a snapshot image of the droplet profile. The profile was then fit using either a circle fit or the Young-Laplace equation. For spherical droplets, the profile fitting software provided essentially the same contact angle for either method. Droplets with an elongated profile were only satisfactorily fit using the Young-Laplace method. The contact angle was determined at the point of incidence of the droplet with the solid surface. This analysis method allowed for the determination of apparent contact angle, base-width, and droplet height for both spherical and elongated droplets. The image capture software was configured to record the droplet profile every 10 seconds. The voltages were applied to the coupon surface using a HP E3632A DC power supply (Hewlett Packard) with a measurement precision of 10^{-3} volts/amps. A separation distance of 18 mm was maintained between the coupon surface and the tip of the counter electrode. This separation distance was selected to be the point at which the current reading fluctuated between a reading of 0.000 A and 0.001 A for the maximum current to be applied, ± 3.000 V, when the coupon and electrode were immersed in the aqueous SDS solution.



Fitting Methods: ● Young/Laplace ☑ Allow Tilt ○ Bashforth/Adams ○ Circle ○ Polynomial

Fitting Options: ● Current ○ To End ○ All

Calculate: ☑ θ ☐ γ ☐ Vol / Area

Cursor Controls: Top, Bottom, Base Line, Tilt, Reset, Set Horizontal

Calculated results: γ [mN/m]: Vol [microl]: 4.42 θ (left): 79.65 θ (right): 79.65

Treshold adjustment: Auto, Set, ☑ Natural Image, Set All

Figure 1. Experimental Setup for the Analysis of Droplet Shape in the Presence of Applied Voltage

The coupons were stored between trials in a glass container with sufficient petroleum ether to cover the coupon surface. Each coupon was removed and exposed to air for 15 minutes, which allowed any residual petroleum ether to evaporate. A 5-µL droplet of the selected oil was placed on the coupon surface and allowed to wet the surface until all apparent spreading had ceased. The coupon was then immersed in the particular surfactant solution to be studied. The surfactant solutions were prepared so that the concentration was very near the critical micelle concentration (CMC). The selected concentration was 8 mM for SDS and 1 mM for CTAB. The coupon was initially immersed in the solution for 15 minutes, allowing the droplet to reach equilibrium with the surfactant solution in the absence of the applied potential. After this initial period elapsed the selected voltage was applied for 15 minutes. During this 30-minute period the contact angle meter acquired droplet images every 10 seconds, which were then stored for later analysis. The coupon was then removed from the surfactant solution, rinsed with deionized water, dried using a lint-free tissue, and returned to the petroleum ether filled storage container. This procedure was repeated for each coupon for all tests.

2.3. Oil Removal Efficiency Analysis

The effect of applied potential on the removal efficiency of oil from a metal surface submerged in an ultrasonic bath was measured using a bench-top ultrasonic bath (Genesis, Crest Ultrasonics). The ultrasonic bath had an effective capacity of 15 L. To limit the waste of surfactant solution, a 2000-mL glass beaker was placed in the bath and filled with the particular solution being analyzed. The remaining volume of the bath was then filled using distilled water. The coupon electrode and counter electrode were held in place with a nonconductive acrylic block, which prevented unwanted movement of the coupon and maintained the desired electrode separation distance of 18 mm. This experimental series used the same coupons, voltage source, and surfactant concentrations that were employed in the drop shape analysis tests.

The storage and cleaning procedure used in this phase was the same as the one used in the drop shape analysis tests. The clean dry coupon was weighed to ascertain the basis coupon weight, W_B. Next the coupon was contaminated with sufficient oil as to cover roughly 75 percent of the surface. The coupon was then inverted 90 degrees for 5 minutes, which allowed any excess oil to drain from the surface that would be directly facing the counter electrode. The coupon was then returned to a horizontal orientation for an additional 15 minutes. The weight was recorded prior to immersion to determine the oily coupon weight, W_O. The coupon was then secured to the acrylic holder, immersed in the selected surfactant solution, and allowed to equilibrate for 10 minutes. The ultrasonic generator was then turned on at the same time the voltage was applied and the coupon was held in the bath for 10 more minutes. The bath and voltage source where then powered down and the coupon removed. The coupon was then stored in a locked cabinet overnight which allowed the residual water to evaporate. The coupon was again weighed and the weight recorded as the cleaned coupon weight, W_C. The oil removal efficiency, η_{OR}, was determined using the following equation:

$$\eta_{OR} = \frac{W_O - W_C}{W_O - W_B} \tag{1}$$

The coupon was then rinsed with deionized water, dried using a lint-free tissue, and returned to the petroleum ether filled storage container. This procedure was repeated for each coupon for all tests.

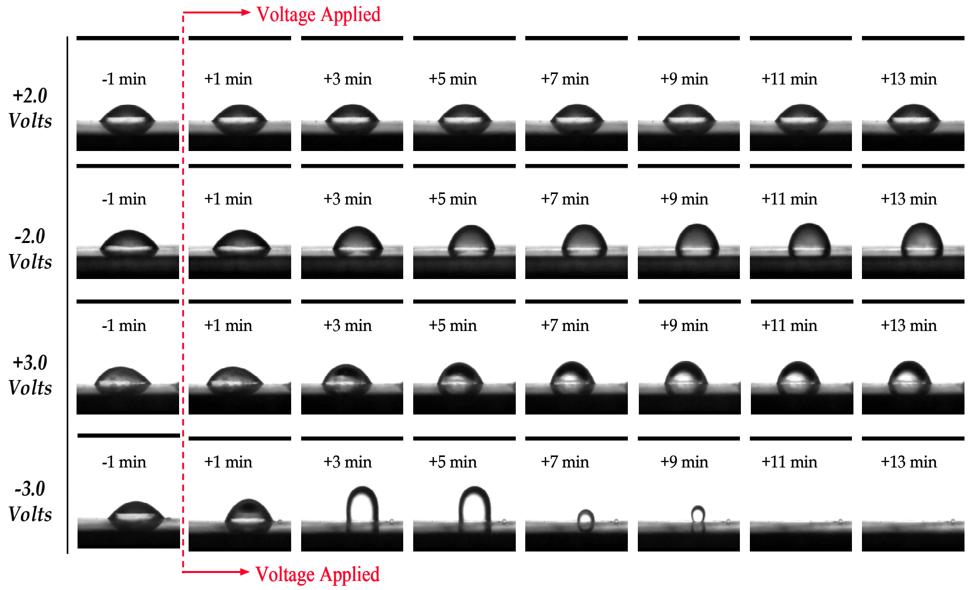
3. Results

Two different oils were investigated during the course of this work. First, hexadecane was selected for this study because it is the largest straight-chain n-alkane that is a liquid at room temperature, and a large body of information is available regarding physical properties, interfacial behavior, and surface wetting phenomena. Unfortunately, straight chain alkanes like hexadecane are not typically utilized as lubricants or coating oils in the metal finishing/electroplating industry, to which this study was originally directed. Silicone oils are favored due to their thermally stable physical properties and their ability to be tailored to a particular application by altering the attached hydrocarbon groups. The second oil, PMPS, used in this study has both phenyl and methyl groups which are known to impart thermal stability, water repellency, noncombustibility, and compatibility with a range of materials.

The range of voltages to be explored, -3.0 to +3.0 volts, was selected to avoid the electrolysis of water. Through a process of trial and error we found that voltages outside the select range would result in bubble formation at either the surface or the counter electrode during potential application, a sign of the formation of hydrogen or oxygen for the electrode-surface configuration previously discussed. The presence of hydrogen at either electrified surface could result in hydrogen embrittlement, rendering the metal surface undesirable for future use. Likewise the presence of oxygen has the potential to result in surface oxidation, again rendering the surface undesirable for future use. The ±3.0 volt bound was further verified by the observation that, for higher voltage magnitudes, some of the metal surfaces exhibited scoring in the vicinity of the counter electrode. These surface damaging conditions are undesirable from a metal finishing/electroplating industrial standpoint and we have sought to avoid them in our experimental studies.

The application of voltage to an immersed metal surface can have a dramatic effect on droplet shape. This impact can be seen in Figure 2 for hexadecane droplets and Figure 3 for PMPS droplets in both SDS and CTAB solutions. It is evident from these figures that voltage application has a significant impact. However, the manifestation of this impact takes two distinct forms. In our earlier work, hexadecane was shown to produce spherical droplets in ionic surfactant solutions [21]. However, Figure 2 shows that when sufficient voltage is applied, -3.0 volts for SDS and +3 volts for CTAB, the droplets take on an elongated shape. Unlike hexadecane, PMPS retains the spherical shape regardless of voltage magnitude or polarity for both SDS and CTAB solutions, as can be seen in Figure 3. The spherical nature of the PMPS droplets were confirmed by the software used to analyze the oil droplets. This difference in droplet shape, between hexadecane and PMPS, makes analysis and comparison using contact angles problematic, since an elongating droplet will have an initially increasing contact angle followed by a decreasing one as the droplet approaches detachment. Fortunately, there are other droplet characteristic measurements that could be used to alleviate this problem. Figure 4 shows a comparison of contact angle, droplet height, and droplet base-width for hexadecane and PMPS in SDS solutions with an applied voltage of -3.0 volts. As can be seen from this figure, droplet base-width appears to be the ideal characteristic for comparing the

8 mM SDS Solutions



1 mM CTAB Solutions

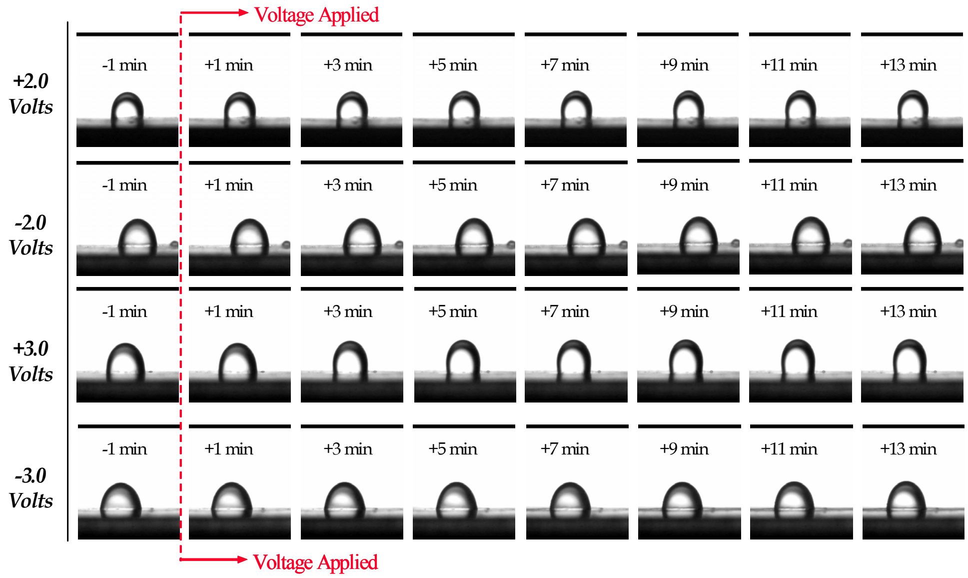


Figure 2. Selected Droplet Images for Hexadecane in SDS and CTAB Solutions

Figure 3. Selected Droplet Images for PMPS in SDS and CTAB Solutions

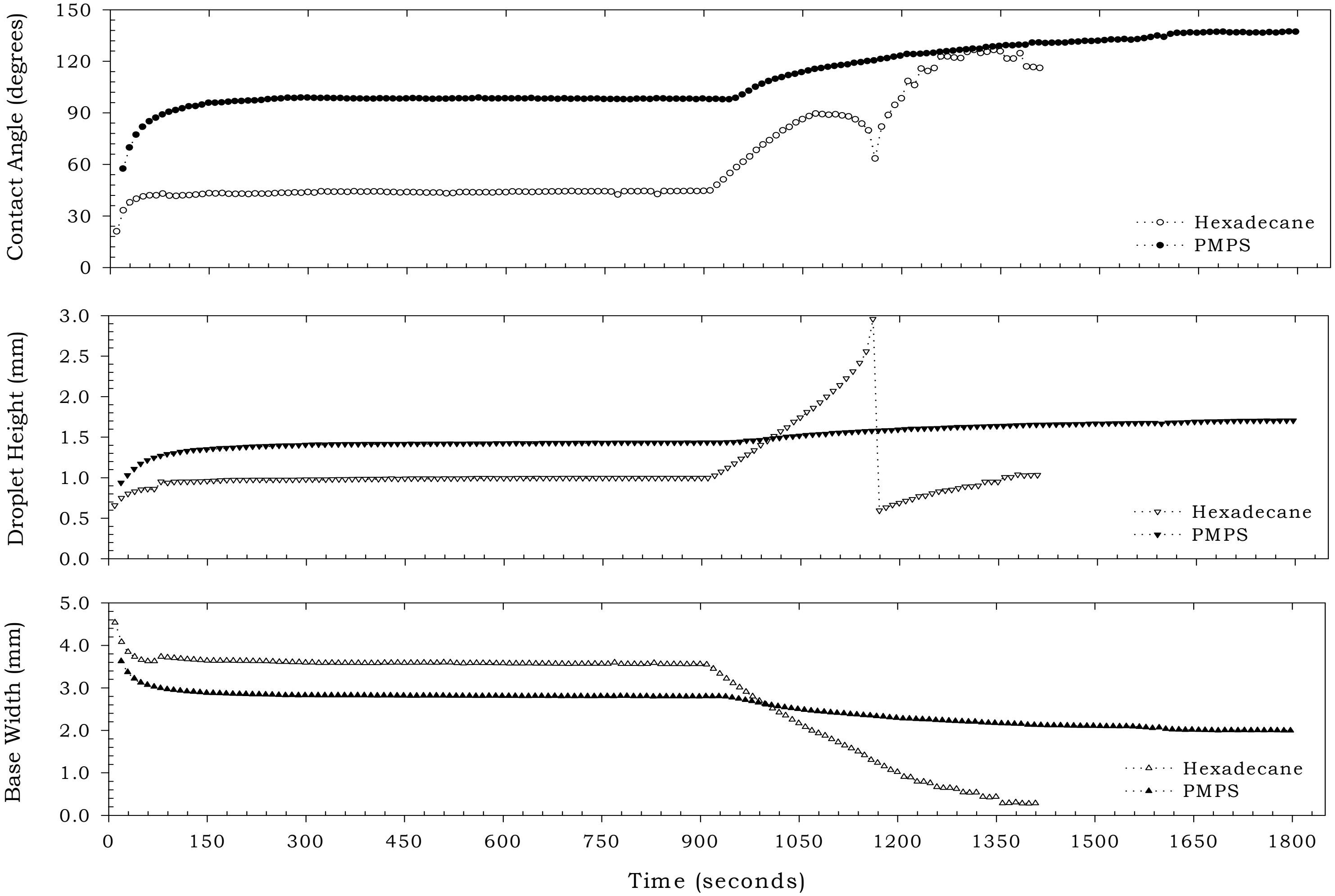


Figure 4. Comparison of Characteristic Measurements for Hexadecane and PMPS Droplets

relative impact of applied voltage between such dissimilar droplet shapes. The justification for this is that the base-width reflects the area of contact between the droplet and the surface and as a result provides information relating to wetting, spreading, and eventual droplet detachment. While not as effective a comparator, the changes in droplet height indicate the dynamic effects of applied voltage on droplet shape such as perturbations in the droplet due to detachment or the retraction of the droplet across the metal surface caused by surface roughness variations.

Since hexadecane and PMPS droplets have been observed to exhibit variations in the type of detachment mechanism, the fractional change in the width of the droplet at the solid/oil interface was selected for comparison. Figure 5 shows the effect of applied voltages between of -3.0 and +3.0 volts on hexadecane and PMPS droplets in SDS and CTAB solutions. It is apparent from this figure that both oils are affected most dramatically in SDS solutions when a voltage of -3.0 volts is applied. Additionally it is evident that both oils show a greater change in droplet shape and surface wetting in SDS solutions than for CTAB solutions, regardless of surface polarity.

In addition to the equilibrium effects of voltage we have observed the dynamic changes in droplet shape and attachment. Returning to Figure 4 we can see that the relative rate of change for these droplets is dramatically different. PMPS droplets exhibit a gradual retraction from the surface following the roll-up mechanism, while the hexadecane droplets quickly elongate until conditions favorable for detachment are achieved. This could be due in part to the difference in specific gravities of the two materials. Hexadecane has a specific gravity of 0.773, making

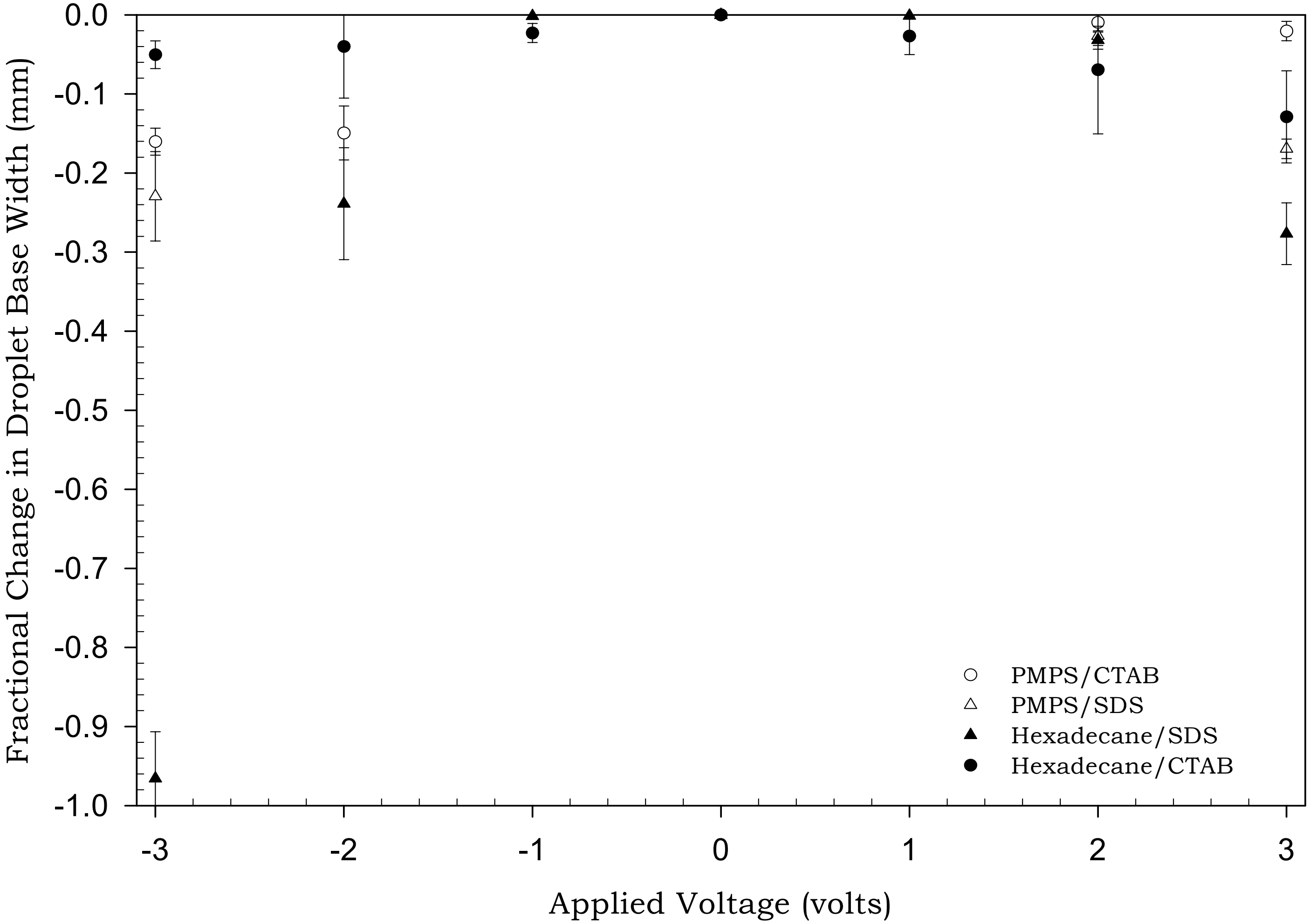


Figure 5. Effect of Voltage Application on the Fractional Change in Hexadecane and PMPS Droplet Base Width

it buoyant in aqueous solutions, while PMPS has a specific gravity of 1.11, thereby eliminating buoyancy-induced detachment.

In our earlier work [22] we have shown that single droplet shape changes have been directly related to the efficiency of removing oil from a surface when immersed in an ultrasonic bath. Bench-top ultrasonic experiments were performed to determine if this relationship holds true for the application of voltage to a metal surface contaminated with an oily film. Figure 6 shows the results for the removal of PMPS via ultrasonication while immersed in SDS and CTAB solutions. Figure 7 shows the comparison of the applied voltage induced change in droplet base width to the corresponding ultrasonic oil removal fficiency. The trend in the cleaning efficiency with respect to applied voltage mirrors the trend found for the fractional change in base width for the PMPS droplets, with the greatest oil removal occurring for -3.0 volts for SDS. Additionally the relative effectiveness of SDS compared to CTAB trends with the base width change results. This provides further evidence that changes in the equilibrium shape for a single droplet are good predictors of overall oil removal efficiency.

Tests concerning the removal efficiency of hexadecane in these solutions were also performed, however they were inconclusive since nearly all, >99%, of the hexadecane was removed during the ultrasonication process irrespective of surfactant solution or the magnitude and polarity of the voltage applied. As with the dynamic studies the relative specific gravities of the oils could be a cause. Another possible explanation for the behavior of hexadecane is that its viscosity (3.0 centistokes) being much lower than PMPS (500 centistokes) might result in a greater susceptibility to removal via ultrasonication

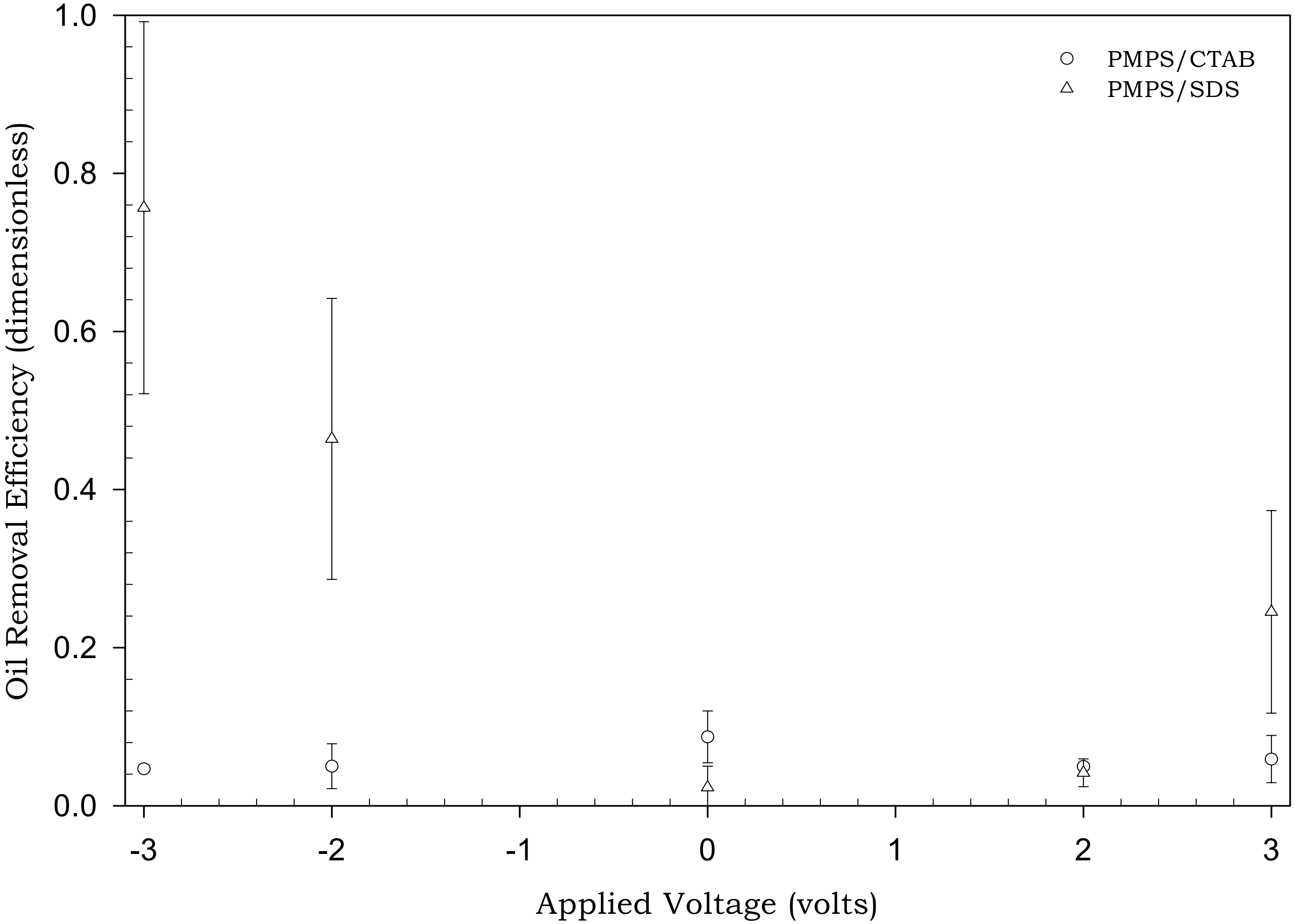


Figure 6. Effect of Voltage on the Removal Efficiency of PMPS via Ultrasonication

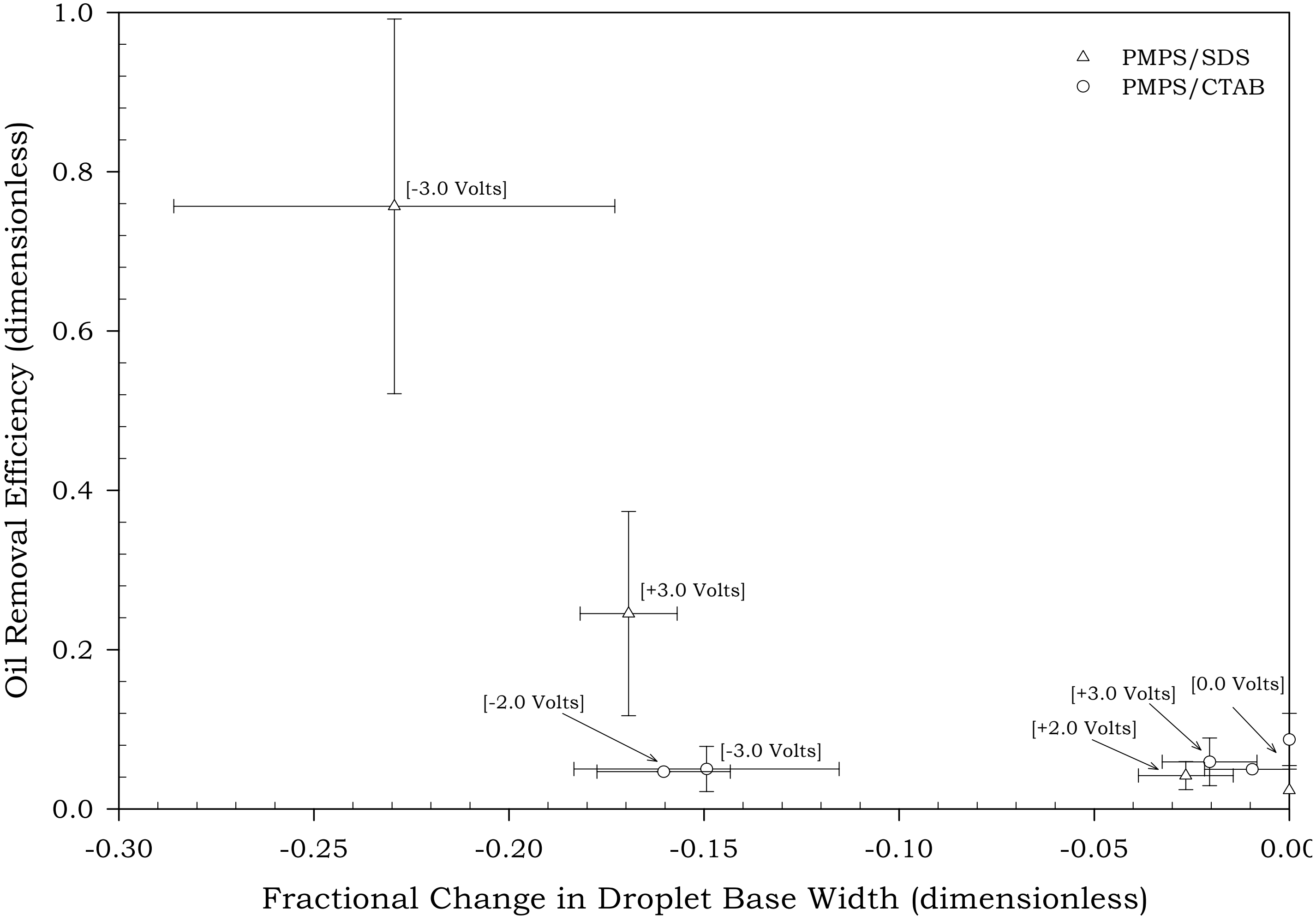


Figure 7. Correlation of Fractional Base Width Change with Ultrasonic Oil Removal Efficiency

4. Discussion

Our results related to the effect of an applied voltage on oil droplet behavior are in qualitative agreement with previous research [22]. Our work shows that the droplets are dramatically altered in shape in the presence of low applied voltages, ± 3.0 volts for this study reported in this article. A voltage of -3.0 volts was found to have the greatest impact for hexadecane droplets in SDS solutions. A voltage of +3.0 volts was more effective for hexadecane droplets in CTAB solutions. A very different voltage/shape change relationship was seen for PMPS, with -3.0 volts having the greatest effect for both CTAB and SDS solutions.

In order to develop a mechanistic interpretation for the observed phenomena we must analyze the potential changes in interfacial phenomena that could result in the observed changes. From previous theoretical work we can postulate that there are three possible mechanisms that are being affected by the applied potential: (1) solution/solid interfacial surfactant adsorption, (2) oil/solution interfacial surfactant adsorption, and (3) oil/solid interfacial adsorption.

The first mechanism pertains to the changes in the adsorption of surfactant molecules at the solution/solid interfacial region. Since the work undertaken in this article utilized ionic surfactants, it would seem reasonable for the droplet to wet the surface where the surfactant and solid were of opposite polarity with the solid surface and be repulsed for a like charge situation

The second mechanism pertains to changes in the adsorption of surfactant molecules at the oil/solution interfacial region. In some of the literature mentioned earlier [2, 14, 16-20] one of the reasons given for droplet wetting changes is an alteration of the solution/oil interfacial tension. This is attributed, in electrolyte solutions, to changes in the interactions with water molecules in the vicinity of the oil/solution interface. Our system is complicated by the presence of surfactant adsorption at the oil/solution interface. If the same reduction in the water molecule/surface interaction were to happen for the surfactant solutions as for simple electrolyte solutions, we would expect, from our earlier theoretical work [24], a reduction of the resistive forces and therefore increased surfactant adsorption. These changes would therefore result in a decreased interfacial tension, which, owing to changes in the buoyancy and balance of forces on the droplet, could increase the potential for the droplet to exhibit roll-up or elongational detachment from the solid.

The third mechanism pertains to changes in the adsorption nature of the oil phase at the oil/solid interfacial region. Little evidence for this mechanism is presented in the literature, as the bulk of the systems utilized a dielectric material and as such there is no direct oil/charged-surface contact. This would eliminate this mechanism in most electrowetting situations, however our system does have direct droplet/electrode contact and as such there must be some alteration of the surface interaction when moving from a neutral to a charged surface. The electrowetting phenomena observed for the mercury electrode in the work of Ivosevic et al. [18, 19] would seem to bolster this observation, since the organics observed in their studies exhibited a critical range of potentials for which wetting would occur. Complicating this mechanism is the observation that hexadecane [25] and silicone oils [26, 27] have been shown to have an inherent negative charge in aqueous solutions which is either increased or decreased dependent on the ionic nature of the surfactant present. This could result in either an increase or decrease in this mechanism's impact as the droplet is either repelled or attracted to the surface.

In order to determine which mechanism(s) could be dominant we must return to Figure 5. From this figure it becomes obvious that hexadecane and PMPS do not exhibit the same wetting behavior relative to the magnitude and polarity of the voltage applied, therefore they must be discussed separately. It was shown in Figure 2 that hexadecane exhibited the elongational method of detachment. This occurred for -3.0 volts in SDS solutions and +3.0 volts in CTAB solutions. From this it appears that, for hexadecane droplets on steel, changes in the oil/solution surfactant interfacial region combined with changes in the repulsion/attraction of the droplet due to interfacial surface charge are the most probable controlling phenomena. Thus changes in the balance of forces on the droplet could explain the detachment observed in Figure 2.

The phenomena for PMPS are decidedly different from hexadecane, where the greatest observed changes occur for both SDS and CTAB at a voltage of -3.0 volts. Since PMPS droplets retained a spherical shape it is possible to analyze the change in contact angle in addition to changes in base width. This becomes necessary since PMPS droplets are heavier than water and will not exhibit the previously observed buoyancy phenomena. Figure 8 shows the change in contact angle for PMPS in solutions of SDS and CTAB. From this figure it is obvious that no single mechanism is sufficient to explain the observed droplet shape phenomena. These shape change phenomena are shown to correspond

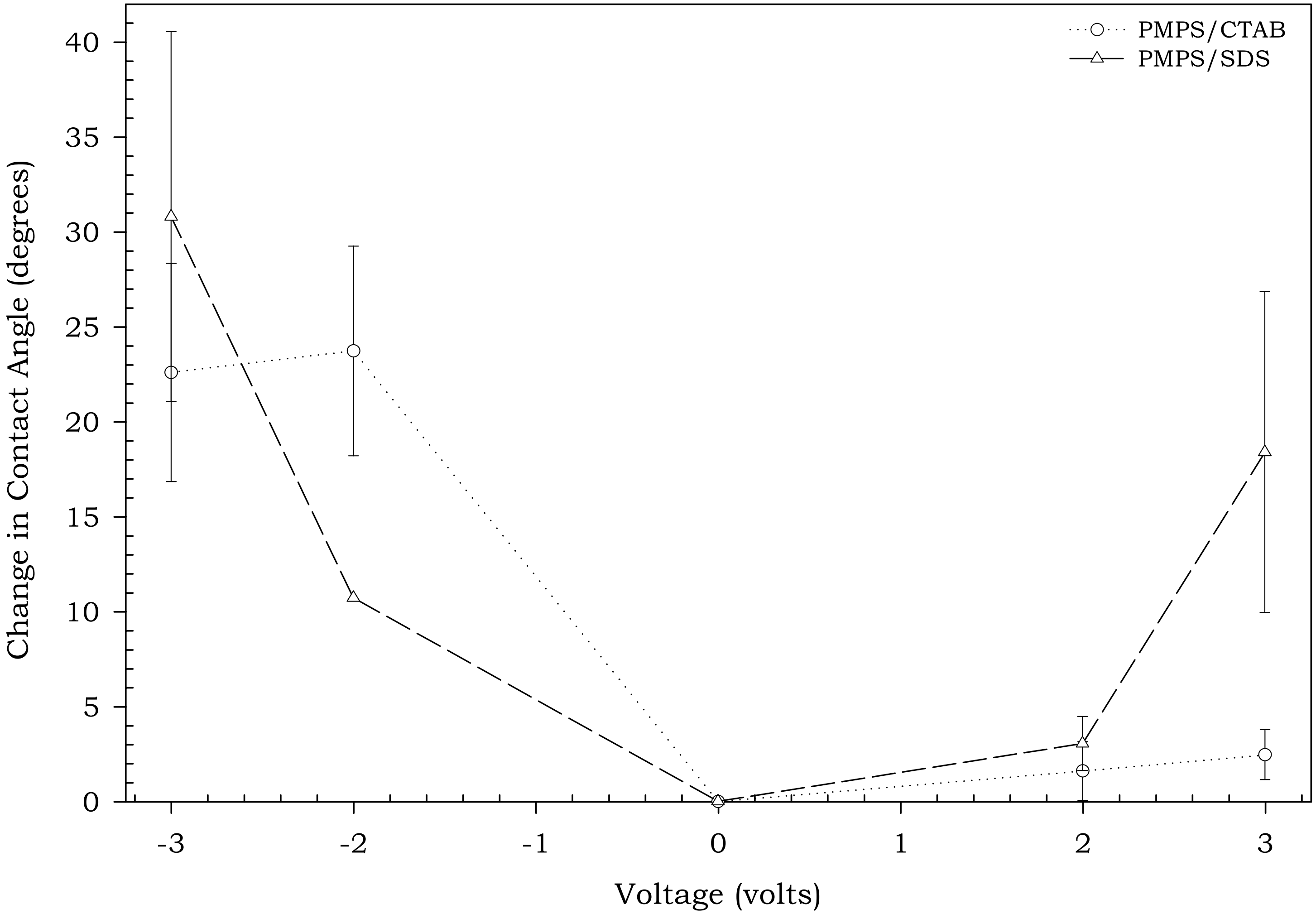


Figure 8. Changes in PMPS Droplet Contact Angle by the Application of Voltage

to four different surfactant/solid-surface charge cases: (1) surface and surfactant are negatively charged, (2) surface is negative and surfactant is positively charged, (3) surface is positively charged and surfactant is negative, and (4) surface and surfactant are both positively charged.

For case 1, where the surface is negatively charged and the surfactant is anionic, the PMPS droplets behave in a manner similar to hexadecane. In this situation the solid/solution interface would be repulsive to the surfactant molecules. For the oil/solution interface the surface charge of the PMPS droplets should also be repulsive to the surfactant molecules. Both of these phenomena should result in increased droplet wetting, however since this is not occurring the controlling phenomena must be repulsion of the negatively charged droplet from the negatively charged surface. Since the adsorption of surfactant molecules is driven by the hydrophobic effect there is still most likely a certain degree of surfactant molecules adsorbed at the oil/solution interface. This would result in a greater negative droplet surface charge and increased repulsion. As a result, it seems most probable that the controlling phenomenon is the third mechanism, where the droplet is less attracted to the surface due to repulsive surface charges.

Applying the logic used in case 1 to case 2, where the surface is negatively charged and the surfactant is cationic, we would expect that the droplet should be attracted to the surface as the negative oil surface charge is mitigated by the adsorption of CTAB. As can be seen from the figure the droplet behavior is not that of wetting instead the base-width decreased as the droplet was repelled. A possible explanation for this, based on our earlier theoretical work, is that the negative solid-surface charge results in improved cationic surfactant adsorption to the solid/solution interface, thereby increasing the competition for solid adsorption and decreasing the oil/solid interfacial area. Therefore a situation where mechanism one is controlling appears to satisfy the observed contact angle changes for this case.

In case 3, where the surface is positively charged and the surfactant is anionic, both the droplet and the surfactant should be attracted to the surface of the electrode. Were this the controlling feature we would have expected increased wetting, however the droplet exhibited the opposite behavior. A plausible explanation for the observed effect, is that increased surfactant adsorption at the solid/solution interface results in a decrease in the area of the oil/solid interface. This is a very similar mechanism to that observed in case two with the exception, in this case, of attractive forces acting on the droplet due to surface charge. Thus the droplet being attracted to the surface rather than repulsed could account for the fact that the droplet changes in case three are less than those in case two. Therefore a situation where mechanism one is controlling but is mitigated by mechanism three would appear to satisfy the observed contact angle changes for this case.

Case 4, where the both the surface and surfactant are positively charged, is where the smallest droplet changes where observed. For this case the surfactant should be repelled from the surface as well as the oil, however if the surface charge imparted to the oil by the CTAB is not significantly positive the loss of surfactant at the solid/solution interface could result in an increase in the surface area available for the oil/solid interface that could counterbalance the repulsion forces. Therefore this case contains the same mechanisms as case two and three, with mechanism three controlling and being mitigated by mechanism one.

From the analysis of the PMPS cases, it becomes evident that changes in oil/solution interfacial tensions are at most a minor factor, unlike the observations for hexadecane, and in fact play little more than a supporting role in PMPS droplet shape change. This analysis is supported by similar observations made by Kang et al. [8] and Digilov [12].

Therefore, we can postulate that for oils that are less dense than the aqueous solution, like hexadecane, the dominant controlling mechanism will be changes in the oil/solution interfacial energies resulting in droplet alterations that favor buoyancy detachment. This is dramatically demonstrated in the -3.0 volts test where the droplet actually elongated and detached. Conversely for oils that are denser than the aqueous solution, like PMPS, a combination of oil/solid changes and surfactant/solid changes will dominate droplet shape behavior. Regardless of the controlling mechanism, the remarkable impact of voltage on both droplet shape and oil removal efficiency presents a potentially useful technique for improvements in the cleaning of metal surfaces.

5. Conclusions

Our results demonstrate that the application of a low voltage to a metal surface produces significant changes in droplet shape and wetting. In this study we have shown that the choice of surfactant when combined with the polarity of the voltage to be applied has a dramatic impact on droplet phenomena. We have proposed three distinct mechanisms to account for the changes in droplet shape and wetting. Through a process of logical evaluation the controlling mechanisms for hexadecane and PMPS droplet behavior were established. For hexadecane, and other light oils, alterations in the adsorption of surfactant at the oil/solution interface will dominate droplet shape change and detachment. For PMPS, and other heavy oils, a combination of change at the solid/solution interface and the oil/solid interface will dominate droplet shape change. The dominant mechanism for these changes was observed to be related to the polarity of the voltage applied. In addition to alterations to droplet shape, the observed changes in oil removal efficiency with respect to voltage provide direct validation of the benefits of low voltage application.

Our studies provide insight into a potential avenue for improving the performance of industrial metal cleaning using aqueous surfactant solutions. The ability to employ low voltages so as to minimize negative impacts on the surfaces being cleaned can result in the development of environmentally benign aqueous cleaning technologies for an area that has been traditionally resistant to them.

6. Acknowledgements

The authors would like to acknowledge the financial support of the American Electroplaters and Surface Finishers Society through Grant #110. Additionally, the authors would like to thank Bob Stone from Federal Mogul and Anne Wells from the University of Tennessee for their assistance and collaboration in this work.

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PART VII

Conclusions

1. Future Work

As with any study concerning an area of research as broad as droplet phenomena on solid surface in aqueous solutions, there are numerous avenues for future investigation. These avenues, experimental and theoretical, can be divided into three main categories: (1) studies relating to various surfactant solution phenomena, (2) studies relating to changes in the ionic strength of aqueous solutions, and (3) studies relating to the application of voltage to surface immersed in solution. While not exhaustive, the following should detail a few directions in which derivative work could proceed.

1.1. Surfactant Solution Studies

The current work has primarily utilized two surfactants, sodium dodecyl sulfate (SDS) and cetyl trimethyl ammonium bromide (CTAB). A logical first step would be to investigate through experiment the behavior of hexadecane droplets on gold in solutions composed of other various-length surfactants from the same surfactant family as the two currently employed. This would explore an unutilized capacity of the model that should account for the impact of physical variations of surfactants on surfactant solution phenomena. In addition to simple contact angle measurements, the determination of surface tension isotherms using the Szyzkowski equation, for these surfactants and hexadecane would allow for the improvement of the theory relating to oil/solution interfacial phenomena. With a better understanding of the effects of varied surfactant chain length, the model could be further refined to account for variations in surfactant counterions. As was seen in the section related to ionic strength manipulation the counterion has a significant effect on micellization and surface tension, it would be interesting to examine if various counterions have a similar effect on differences in micellization and surface tension for surfactant with the same length tail chains. An additional area of exploration relating to aqueous surfactant solutions would be to examine surfactants from the remaining two charge categories, nonionic and zwitterionic. The presented work has dealt primarily with surfactants of the anionic and cationic categories. The model as developed and presented was designed with these surfactants in mind. However, a lack of experimental data has prevented the evaluation of such systems using the current model.

In addition to changes in the composition and type of surfactants selected for experiment, alternative oils and surface materials should be employed. Hexadecane is a well defined organic compound in the literature; unfortunately the industrial applications for hexadecane are limited in the area of metal finishing and electroplating. As a result oils, like the phenyl methyl polysiloxane (PMPS) employed in the applied potential work should be evaluated. There are numerous alternative organics, silicone oil, and natural extract oils that could be utilized. Variations in oil properties such as density and viscosity would be ideal variables for such initial work. Additionally the introduction of particulates into the organic droplets is of industrial relevance and interest to the studies of surface cleaning.

1.2. Ionic Strength Studies

In the reported analysis of the effect of low concentration salt addition on droplet contact angle for hexadecane on a gold surface immersed in a surfactant solution, a number of instances where experimental data were lacking. This lead to the formation of estimates to reconcile the model results with the available data. In order to eliminate the need for such estimates experiments should be performed that evaluate the actual effect of the addition of sodium chloride (NaCl) on both the critical micelle concentration (CMC) of the solution and the interfacial tension of the oil/solution interface. Additionally, since there is a lack of a satisfactory explanation for the actual cause of the change in CMC for salt compound of various composition that have the same valence, tests should be performed to provide the necessary experimental evidence for developing such a theory. These experiments could involve the use of a quartz crystal microbalance (QCM), atomic force microscopy (AFM), x-ray diffraction, or neutron scattering studies. These experimental techniques are quite effective for studying colloidal and interfacial phenomena and would provide an opportunity to collaborate with external groups. A simpler method exists to determine the actual CMC of the solution, drop shape analysis. This would allow for the determination of air/solution interfacial tensions which can be used to deduce solution CMCs. Another interesting direction would be to analysis the impact of salt on the oil/solution interfacial tension of various oils other than hexadecane. Yet another direction to follow would be to analyze systems that are modified by salts of other anion to cation ratios, 2:1, 1:2, and 2:2, or mixtures of such salts.

1.3. Applied Potential Studies

As with the ionic strength studies there are numerous avenues for further investigation relating to droplet shape behavior on electrified metal surfaces. It would be advantageous to future studies to determine experimental approaches that would elucidate the interfacial phenomena occurring in the presence of the applied voltage. Many techniques have been developed to study interfacial phenomena. Of these techniques, neutron scattering, atomic force microscopy or sum-frequency spectroscopy may provide insight into the effects of voltage on the oil/solution interface. To eliminate the effect of surfactant adsorption on the interface and to determine if the interfacial tension is modified by the applied potential the replacement of the surfactant by an electrolyte of similar anion to cation ratio should be a reasonable first step. In addition to replacing the surfactant with another electrolyte, changing the total concentration of surfactant would help identify the minimum amount of surfactant required to affect the droplet shape in solution. Both sets of tests, replacement with electrolytes and variations of surfactant concentration, should be performed for a wide range of surfactants and oils as discussed previously. The remaining observable interfacial region, the solution/solid interface, would also benefit from the experimental techniques mentioned above. These techniques would aid in the identification of the nature of the adsorbed surfactant aggregating at the electrode interface. Another interesting variable indicated in the applied voltage work was the position and separation distance of the electrode and counter-electrode. If the separation distance had little or no effect on the droplet phenomenon, when the separation is close enough to allow current flow, the influence of the electric field may assumed to be limited and therefore the observed droplet behavior is more likely related to the charge at the surface. Another avenue for investigation is to return to using a gold surface to minimize the effects of surface roughness.

The suggested avenues for future work listed above should be considered prior to any further experimental or theoretical tests. With the foundations provided in this work, improvements to experimental methods and procedures and further refinements to the model can be more effectively performed.

2. Summary and Conclusions

A model for the prediction of equilibrium oil droplet contact angles on solid surfaces immersed in aqueous surfactant solutions has been developed. This model applies classical thermodynamics, relevant surfactant self-assembly modeling theory, the impact of ionic strength and other systemic parameters in an analysis of oil droplet contact angle changes. The model and related theory provide a foundation upon which to further enhance and understand industrial aqueous cleaning processes. Additionally, an analysis of various system parameters and their impact on droplet shape and subsequent prototypic cleaning has been performed. The following discussions provide a summary of each part of this dissertation as well as significant accomplishments. The reader should refer to the relevant part of the dissertation should a more detailed assessment be desired than present in this summary.

Part I provided a quick introduction to the dissertation. Additionally, a review of previous research work was included. This should assist future researchers by providing a starting point for developing an enhanced understanding of industrial aqueous cleaning.

Part II showed the earliest development phase of the modeling effort. A significant literature review and discussion of droplet shape phenomena was provided to facilitate an understanding of the related theory. The cleaning system was simplified and five component equilibrium balances were developed. These balances related the equilibrium distribution of molecules in the cleaning system as affected by various cleaning system parameter changes. This was accomplished by calculating equilibrium constants for each balances and using numerical techniques to determine a solution that satisfied these balances. As aqueous surfactant solutions are known to foster certain self-assembly process, such as the formation of surfactant micelles in solution, a method of summed contributions to free energy changes was employed for micelle formation and extended to aqueous/organic interfacial surfactant adsorption. This change in free energy was then used to determine two of the equilibrium constants. The remaining three equilibrium constants were developed using a competitive Langmuir isotherm that described the adsorption of components to the solid interface. The model was then compared to preliminary experimental data and shown to provide a satisfactory level of agreement. The major accomplishments described in this section are (1) the development of a preliminary thermodynamic model to predict droplet contact angles in aqueous surfactant solutions, (2) the description of the aqueous/organic/solid system in terms of component distribution balances, (3) the use of modern self-assembly theory for the determination of surfactant distribution, (4) the application of a competitive Langmuir isotherm for the determination of surfactant, water, and organic adsorption to the solid surface, and (5) the comparison to experimental data acquired via a consistent and robust experimental methodology.

Part III provided a significantly more detailed and through development of the model for contact angle prediction than was presented in Part II. Various improvements to the calculation approach for various balance equilibrium constants were addressed. The model was tested against several sets of published contact angle data, for hexadecane droplets on gold and steel in sodium dodecyl sulfate (SDS) solutions and cetyl trimethyl ammonium bromide (CTAB) solutions. Through this more detailed investigation several areas for improving the model were identified. Among these were the empirical relationship required in the oil/solution interfacial surfactant balance, the apparent curvature of contact angle data relative to surfactant concentration, and the limitations related to self-assembly posed by the use of the Langmuir isotherm. Overall the model was found to effectively predict equilibrium contact angles as a function of surfactant concentration for these systems, with average errors less than five percent. The major accomplishments presented in this section are (1) the presentation of a refined thermodynamic model for the prediction of organic droplet contact angles on solid surfaces, (2) the replacement of the "Dressed Micelle Model" with a more robust theory for surfactant self-assembly which utilized the contributional approach to the calculation of changes in Gibbs free energy, and (3) the presentation of an extensive comparison of the model results to experimental data for contact angles in ionic surfactant solutions for a broad range of concentrations at or below the critical micelle concentrations.

Part IV addresses the effects of aqueous/solid interactions on oil contact angles in aqueous surfactant solutions. This part addresses several of the previously identified areas for improvement. The model was significantly improved through the replacement of the competitive Langmuir isotherm approach by the quasi-chemical approximation. An obvious weakness of the Langmuir approach was that it failed to account for lateral interactions at the aqueous/solid interface. These lateral interactions were reasonably expected to exist since self-assembly processes for surfactants rely on such interactions. Since self-assembly related adsorption was anticipated at the solid interface this incorporation of lateral interactions dramatically improved the model's predictive capabilities. Additionally, the apparent curvature of the experimental contact angle data was addressed through an improvement to the methods used to determine the lateral interactions. These lateral interactions were allowed to vary with respect to surfactant concentration, which simulated changes in the nature of the adsorbed phase. The model was again compared to the experimental data utilized in Part III and found to have greatly improved as a result of the indicated changes. The major accomplishments found in this section are (1) the demonstration that, for certain aqueous/organic/solid systems, a significant impact on contact angle can be primarily related to changes in aqueous/solid surfactant aggregate nanoscale structure, (2) the replacement of the competitive Langmuir approach, utilized earlier, with the more robust quasi-chemical approximation approach which allowed for a refined description of adsorbed surfactant interactions, (3) the integration of a multi-region aqueous/solid surfactant adsorbate structure concept that allow changes in the adsorbed phase to impact surfactant adsorbate lateral interactions, and (4) the comparison of the improved model to experimental contact angle data.

Part V detailed the processes by which the model was enhanced to account for the effect of very low concentration sodium chloride (NaCl) added to the previous systems. During the process of this work, significant gaps in the published literature concerning the relative effects of the type of 1:1: salt added to the solution were identified. Utilizing the information that was available the model was improved and several empirical relationships accounting for the effect of low concentration salt on various portions of the model were developed. Additionally, this work drew attention to the evidence that individual salt ions have varied effects on the value of the CMC and other self-assembly dependent processes. The improved model was again compared to experimental data for hexadecane on gold in SDS and CTAB solutions for the addition of less than 2.5 mM NaCl. The model compared favorably to the experimental data and provided insight into the reasons for the observed phenomena. The major accomplishments presented in this section are (1) the extension of the improved thermodynamic model presented in Part IV to account for the effects of the addition of very low concentration salt (<2.5 mM) on organic droplet contact angle in aqueous surfactant solutions, (2) the demonstration that the extent of the effects of salt on contact angles in aqueous/organic/solid system is greatly dependent on the concentration and type of salt anion and cation present, (3) the development of salt ion relevant empirical relationships to account for the effects of salt on contact angle, (4) the identification of a significant void in the published literature regarding the effects of salt concentration on organic contact angles, and (5) the comparison of model derived contact angle predictions to experimental contact angle data sets.

Part VI was primarily concerned with an experimental investigation into the effects of low magnitude electric potentials applied to the metal surface in systems similar to those discussed previously. These studies evaluated changes in droplet shape and wetting for hexadecane and phenylmethyl polysiloxane (PMPS), a silicone oil, on a steel surface immersed in ionic surfactant solutions of SDS or CTAB. This study found significant changes in droplet shape in the presence of a ±3.0 volt applied potential. The phenomena observed in this study, when analyzed using the theoretical insight developed for the contact angle model, were found to exhibit three main controlling mechanisms. The significance for each mechanism was found to be dependent upon not only voltage magnitude and polarity, but upon the density and related detachment styles of the oils being studied. In addition to the equilibrium measurements related to droplet shape, a series of prototypic industrial cleaning test using ultrasonication were performed. These tests validate the premise that equilibrium droplet analysis provides a predictive insight into the cleaning performance for a particular set of aqueous system parameters. This work should have direct impact on efforts to improve the performance of cleaning processes specific to the electroplating and surface finishing industry. The major accomplishments presented in this section are (1) the experimental investigation of the impact on oil droplet contact angles in aqueous/oil/solid systems when a low voltage is applied to the solid surface, (2) the experimental evaluation of the effects of low voltage surface electrification on ultrasonic oil removal from solid surfaces, (3) the evaluation of the controlling mechanisms related to the observed changes in droplet shape during surface electrification, and (4) the comparison of equilibrium bench-scale contact angle measurements to the efficiency of oil removed via ultrasonication of contaminated metal coupons in ionic surfactant solutions.

VITA

Samuel Albert Morton III was born in Bristol, Tennessee on January 1, 1974. He attended high school at Sullivan East High School in Bluff City, Tennessee, graduating in 1992. He attended Tennessee Technological University in Cookeville, Tennessee, earning a Bachelor of Science degree in Chemical Engineering in 1996. He continued his education at the University of Tennessee Space Institute in Tullahoma, Tennessee, graduating in 1998 with a Master of Science degree in Chemical Engineering. He was employed by Bechtel Savannah River, Inc. as a Senior Process & Control Engineer at the Department of Energy Savannah River Site from 1998 to 2000. In 2000 he returned to graduate school at the University of Tennessee, Knoxville. While at the University of Tennessee he was elected by the graduate student body to the position of President of the Graduate Student Association. He was awarded a Doctor of Philosophy with a major in Chemical Engineering in 2004. He is currently a professor in the Chemical Engineering Department at Lafayette College in Easton, Pennsylvania.