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An Investigation into the Effects of Salt Concentration on Surfactant Adsorption Using a Quartz Crystal Microbalance

Shannon Joanne Ray
University of Tennessee, Knoxville

To the Graduate Council:

I am submitting herewith a thesis written by Shannon Joanne Ray entitled "An Investigation into the Effects of Salt Concentration on Surfactant Adsorption Using a Quartz Crystal Microbalance." I have examined the final electronic copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Chemical Engineering.

Robert M. Counce, Major Professor

We have read this thesis and recommend its acceptance:

Paul R. Bienkowski, David J. Keffer, Samuel A. Morton III

Accepted for the Council:
Dixie L. Thompson

Vice Provost and Dean of the Graduate School

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

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Vice Provost and Dean of the
Graduate School

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AN INVESTIGATION INTO THE EFFECTS OF SALT CONCENTRATION ON

SURFACTANT ADSORPTION USING A QUARTZ CRYSTAL

MICROBALANCE

A Thesis

Presented for the

Masters of Science Degree

The University of Tennessee, Knoxville

Shannon Joanne Ray

August 2008

DEDICATION

This thesis is dedicated to my Grandmother,

Sonora Jo Ray

ACKNOWLEDGEMENTS

ABSTRACT

Surfactant adsorption from aqueous electrolyte solutions onto metal surfaces was characterized through the use of a Quartz Crystal Microbalance (QCM). The need for a better understanding of the surfactant adsorption process became apparent in previous studies by Morton *et al*., who used estimated and extrapolated properties in a thermodynamically-based model of oil removal from metal surfaces. These modeling efforts overlap existing data on surfactant adsorption data and require an estimation of surfactant adsorption phenomena, especially the transition between monolayer adsorption and multi-layer adsorption, which corresponds to the critical micelle concentration (CMC). Thus, the purpose of this study was to gain surfactant adsorption data in an effort to increase the efficacy of surfactant degreasing techniques.

A survey of the literature and a summary of the research in this thesis is provided in Chapter 1. Chapter 2 reports the experimental work to establish the mass of surfactant adsorbed from an aqueous electrolyte-surfactant solution onto a vibrating crystal of a quartz crystal microbalance (QCM). Density and viscosity of the aqueous solutions were measured separately so that the change in mass could be observed from the frequency change measurements. Conclusions about the behavior of the surfactant adsorption phenomena taking place at varying salt concentrations were discussed

Chapter 3 presents future direction for the continued study of the cleaning and degreasing studies in this thesis.

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CHAPTER 1

1.1.0 Introduction

The adsorption of surfactants on solid surfaces is a key phenomena in the cleaning and degreasing of metal surfaces. The ability to clean and degrease metal surfaces, and the manner in which this can be accomplished, has been the topic of much environmental and economic debate. Effective cleaning/degreasing is vital to industries where the production process includes fabricating and/or assembling metal parts such as the automotive, aviation, appliance and railroad industries, as well as having applications in other industries [1]. The switch from volatile organic solvents to surfactant solutions can offer enhanced recovery and reuse opportunities which allows for possible savings of both time and money.

Environmental regulations on industrial cleaning and degreasing processes have lead to the consideration of surfactant solutions as a viable substitute for more commonly used volatile organic solvents which are less environmentally desirable [1]. Aqueous surfactant solutions have, in most instances, a distinct environmental advantage over organic solvents. Surfactant solutions also have the added benefit of being safer in the workplace since many volatile organic solvents produce fumes that can be harmful to humans in an enclosed setting [1]. Though progress has been made in optimizing the benefits of substituting aqueous surfactant solutions for organic solvents in cleaning systems, a better understanding of the basic phenomena behind surfactant behavior is needed to improve their cleaning performance in order to fully replace volatile organic solvents in the cleaning and degreasing industry. Research into contact angle and droplet shape of surfactant solutions has shown insight into this issue

of cleaning effectiveness and may be used to help optimize surfactant cleaning processes [2-5].   In general, the prospect for advancement in the area of industrial cleaning solutions remains high and will continue to help reduce the impact of industrial cleaning technology on the environment.

1.2.0 Background Material

1.2.1 Soaps

Any discussion of surface cleaning requires a discussion of the most apparent technology for surface cleaning – soaps. Soaps are salts of higher fatty acids, such as sodium stearate, $C_{17}H_{35}COO^-Na^+$, which are amphiphilic structures comprised of a non-polar organic tail, hydrophobic in nature on one end, and a polar ionic head group with a strong affinity for water on the other end [6]. The cleaning action of soap results mainly from its ability to emulsify foreign objects and lower the surface tension of water. Water, by its very nature, has a very large surface tension due to the cohesive forces between water molecules [6]. Molecules located at the surface of a liquid cohere more strongly to one another because they do not have other like molecules on all sides. This phenomenon is observed as the meniscus on the walls of a glass surface or in the formation of bubbles and water droplets; the spherical shape minimizes the "wall tension" of the surface layer according to LaPlace's law. In solutions containing oils, fats, and other water-insoluble organic materials, the hydrophobic end of the soap will preferentially aggregate with the organic matter, while the polar head group remains in the aqueous phase. This action results in emulsification, or suspension, of the organic material in the water solution as colloidal soap micelles, which can be removed with the bulk water solution [6].

The formation of insoluble salts from the reaction of soap molecules with divalent cations in water solutions (e.g. Ca^{+2}, Mg^{+2}, generally found in hard water) results in ineffective cleaning. These reactions in solution instead lead to unsightly deposits of what is typically referred to as "soap scum" and, as a result, have been replaced as cleaning agents for clothing, dishes, and most other materials. Though the formation of these insoluble salts is problematic, soaps do not, in general, cause environmental problems. As soap is released into sewage or aquatic systems they tend to precipitate and are thus eliminated from the bulk solution, and since they are comprised of fatty acids, are biodegradable and thus are eliminated over time [6].

1.2.2 Synthetic Detergents

The evolution of cleaning technology led to the formation of synthetic detergents, which have many similar qualities to traditional soaps, but are resistant to the formation of insoluble salts with hard water ions. However, while this is an advantage to the cleaning industry, it is a disadvantage due to their high tendency to contaminate water and persist in the environment. Over a billion pounds of detergents are washed into wastewater treatment centers annually from United States households, with even more being consumed in Europe [6].

1.2.3 Organic Solvents and Volatile Organic Compounds (VOCs)

Any liquid that dissolves a solid, liquid, or gaseous solute, resulting in a solution is known as a solvent. The most commonly used solvents are organic chemicals, known as organic solvents. There are many common uses for organic solvents such as dry cleaning (e.g. tetrachloroethylene), paint thinners (e.g. toluene), nail polish removers and glue solvents (e.g. acetone, ethyl acetate), and even perfumes (e.g. ethanol). Organic

solvents are heavily used in chemical syntheses, research chemistry and technological processes [6-7]. Most of these solvents are flammable or highly flammable depending on volatility. Mixtures of organic solvent vapors and air can even explode.

Volatile organic compounds (VOCs) are emitted from solvent-based metal cleaning and degreasing operations and many other industrial cleaning processes as vapors from certain liquids used as solvents. VOCs include a variety of chemicals, some of which may have short- and long-term adverse health effects. Examples of VOCs historically used in metal cleaning and degreasing operations include dichloromethane, tetrachloroethylene, trichloroethylene and trichloroethane [6-7]. Concentrations of many VOCs are consistently higher indoors (up to ten times higher) than outdoors. VOCs are emitted by a wide array of products numbering in the thousands. Examples include: paints and lacquers, paint strippers, cleaning supplies, pesticides, building materials and furnishings, office equipment such as copiers and printers, correction fluids and carbonless copy paper, graphics and craft materials including glues and adhesives, permanent markers, and photographic solutions.

Organic chemicals are widely used as ingredients in household products. Paints, varnishes, and wax all contain organic solvents, as do many cleaning, disinfecting, cosmetics, degreasing, and hobby products. All of these products can release organic compounds while in use, and, to some degree, when they are stored.

EPA's Total Exposure Assessment Methodology (TEAM) studies found levels of about a dozen common organic pollutants to be 2 to 5 times higher inside homes than outside, regardless of whether the homes were located in rural or highly industrial areas [8]. Additional TEAM studies indicate that while people are using products containing

organic chemicals, they can expose themselves and others to very high pollutant levels,

and elevated concentrations can persist in the air long after the activity is completed.

1.2.4 Health Effects from VOCs

Eye, nose, and throat irritation; headaches, loss of coordination, nausea; damage

to liver, kidney, and central nervous system are common effects from exposure to VOCs.

Some organic compounds can cause cancer in animals; some are suspected or known to

cause cancer in humans [6-7]. Key signs or symptoms associated with exposure to VOCs

include conjunctival irritation, nose and throat discomfort, headache, allergic skin

reaction, dyspnea, declines in serum cholinesterase levels, nausea, emesis, epistaxis,

fatigue, dizziness. The ability of organic chemicals to cause health effects varies greatly

from those that are highly toxic, to those with no known health effect. As with other

pollutants, the extent and nature of the health effect will depend on many factors

including level of exposure and length of time exposed. Eye and respiratory tract

irritation, headaches, dizziness, visual disorders, and memory impairment are among the

immediate symptoms that some people have experienced soon after exposure to some

organic compounds [6-7]. At present, not much is known about what health effects occur

from the levels of organic compounds usually found in homes.

1.2.5 Toxic Air Pollutants

Toxic air pollutants, also known as hazardous air pollutants, are those pollutants

that are known or suspected to cause cancer or other serious health effects, such as

reproductive effects or birth defects, or adverse environmental effects. EPA is working

with state, local, and tribal governments to reduce air toxics releases of 188 pollutants to

the environment [7]. Examples of toxic air pollutants include VOCs such as benzene,

which is found in gasoline; tetrachloroethylene (perchlorethlyene), which is emitted from some dry cleaning facilities; and dichloromethane (methylene chloride), which is used as a solvent and paint stripper by a number of industries. Examples of toxic air pollutants historically used in metal cleaning and degreasing operations include dichloromethane, tetrachloroethylene, trichloroethylene and trichloroethane.   Examples of other listed air toxics include dioxin, asbestos, toluene, and metals such as cadmium, mercury, chromium, and lead compounds [6-7].

1.2.6 Health and Environmental Effects of Toxic Air Pollutants

People exposed to toxic air pollutants at sufficient concentrations and durations may have an increased chance of getting cancer or experiencing other serious health effects. These health effects can include damage to the immune system, as well as neurological, reproductive (e.g., reduced fertility), developmental, respiratory and other health problems. In addition to exposure from breathing air toxics, some toxic air pollutants such as mercury can deposit onto soils or surface waters, where they are taken up by plants and ingested by animals and are eventually magnified up through the food chain. Like humans, animals may experience health problems if exposed to sufficient quantities of air toxics over time [6-7].

1.2.7 Origin of Toxic Air Pollutants

Most air toxics originate from human-made sources, including mobile sources (e.g., cars, trucks, buses) and stationary sources (e.g., factories, refineries, power plants), as well as indoor sources (e.g., some building materials and cleaning solvents). Some air toxics are also released from natural sources such as volcanic eruptions and forest fires [7].

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1.2.8 Human Exposure to Air Toxics

People are exposed to toxic air pollutants in many ways that can pose health risks such as by breathing contaminated air or drinking water contaminated by toxic air pollutants. Eating contaminated food products, such as fish from contaminated waters; meat, milk, or eggs from animals that fed on contaminated plants; and fruits and vegetables grown in contaminated soil on which air toxics have been deposited can also cause exposure to toxic air pollutants. One method of exposure, ingesting contaminated soil, is especially dangerous for young children because they often ingest soil from their hands or from objects they place in their mouths. However, any touching of (making skin contact with) contaminated soil, dust, or water (for example, during recreational use of contaminated water bodies) could cause exposure to toxic air pollutants [6-7].

Once toxic air pollutants enter the body, some persistent toxic air pollutants accumulate in body tissues. Predators typically accumulate even greater pollutant concentrations than their contaminated prey. As a result, people and other animals at the top of the food chain that eat contaminated fish or meat are exposed to concentrations that are much higher than the concentrations in the water, air, or soil [7].

1.2.9 Previous Research Work by Green Engineering Group

Our Green Engineering Group at UT began their activities in surface cleaning with the research of Starkweather *et al*. [9-11] which, in agreement with previous research by Carroll [12], established a strong relationship between the interfacial tension, contact angle and the oil removal from a surface. The work of Starkweather *et al.* focused on the effects of varying surfactant concentration and pH on the removal of oil from a metal surface. These studies found that oil removal increased as the concentration

of surfactant at a constant pH was increased. In a similar manner, when surfactant

concentration was held constant and the pH was increased, oil removal was again

increased.   This research also showed that increases in either of these two factors,

surfactant concentration or pH, reduced the oil/surfactant interfacial tension, increasing

the contact angle of the oil on the surface [9-11]. Thus, a relationship is established

suggesting that reduction in interfacial tension and increased contact angle correlate to

increased oil removal from a solid surface.

Rowe *et al.* [2-3] extended Starkweather's research incorporating results from

various surfactant types in the study of the effect of pH and applied potential on oil

removal from a stainless steel surface. This research directed more attention to the

solution/solid interface rather than the oil/solution interface that was the primary focus of

Starkweather *et al* [9-11]. In investigating whether an applied potential could cause the

same effects as pH alterations, Rowe *et al.* discovered a difference between surfactant

solutions at high and low pH solutions. It was found that oil removal increased at high

pH solutions with surfactant solutions that exhibited negatively charged oil/aqueous

interfaces. However, when dealing with oil/water interfaces that are positively charged,

the surfactant solutions showed an increase in oil removal in low pH solutions. It was

then concluded oil removal from a solid surface was greatly influenced by surfactant

adsorption from the same surface [2-3]. The findings of Rowe *et al*. involving electrified

interfaces were confirmed and extended by Morton *et al.* [1, 13-17] and again

emphasized the relationship between oil contact angle and extent of cleaning.

To better understand the surface science phenomena and its relationship to

surface cleaning, Davis *et al.* [4-5] focused more on the ability to modify oil contact

angles in aqueous surfactant solutions by addition of electrolytes. Through the addition

of low concentrations of salt (<3mM), Davis manipulated changes in ionic strength that

resulted in dramatic changes in oil droplet contact angle. Davis theorized that these

changes were due to changes in surface charge and adsorption behavior of surfactants at

the solid/solution interface rather than any organic/solution interfacial tension changes

[4-5]. This work was a direct predecessor for the current study and led to the desire to

better understand surfactant adsorption behavior.

Morton *et al*. [1, 13-17] developed a thermodynamically-based model for the

prediction of equilibrium oil droplet contact angles on solid surfaces immersed in

aqueous surfactant solutions. This model assumes competition between oil and

surfactant on the metal surface as a basis for predictions. By applying classical

thermodynamics, relevant surfactant self-assembly modeling theory, and an estimation

of the impact of ionic strength and other systemic parameters on the prediction of oil

droplet contact angle, this model provides a foundation upon which to further

understand and subsequently enhance industrial aqueous cleaning processes [1, 13-17].

With the established relationship between surface cleaning and contact angle, a sound

model relating the extent of surface cleaning and system parameters was thus

established. These modeling efforts overlap existing data on surfactant adsorption data

and require an estimation of surfactant adsorption phenomena, especially the transition

between monolayer adsorption and multi-layer adsorption, which corresponds to the

critical micelle concentration (CMC). The CMC is reached when the concentration of

surfactants in free solution is in equilibrium with surfactants in aggregate form. A

monolayer is formed when amphiphilic molecules orient themselves at the interface of

aqueous solutions [1]. The model developed by Morton was able to predict the early changes in contact angle at surfactant concentrations below the CMC. However, the experimental evidence to validate the necessary assumptions made by the model did not exist at the time.

The adsorption phenomena were characterized in this work through the use of a Quartz Crystal Microbalance (QCM). A QCM is capable of measuring changes of surface mass in the nanogram range and thus measure the adsorption of surfactants on the crystal surface. Experimental work using a QCM was proposed to validate the assumption inherent in the model presented by Morton *et al* [1, 13-17]. An example schematic of the experimental setup is shown in Figure 1.1. This system consists of a frequency counter, oscillator, power supply and quartz crystal, the electrode and the QCM sample cell. The use of the QCM here is similar to that of Caruso *et al* [18]. who also studied detergency.

A. Control/Data Acquisition Computer
B. Frequency Counter
C. Oscillator
D. Power Supply
E. Quartz Crystal and Electrodes
F. QCM Sample Cell
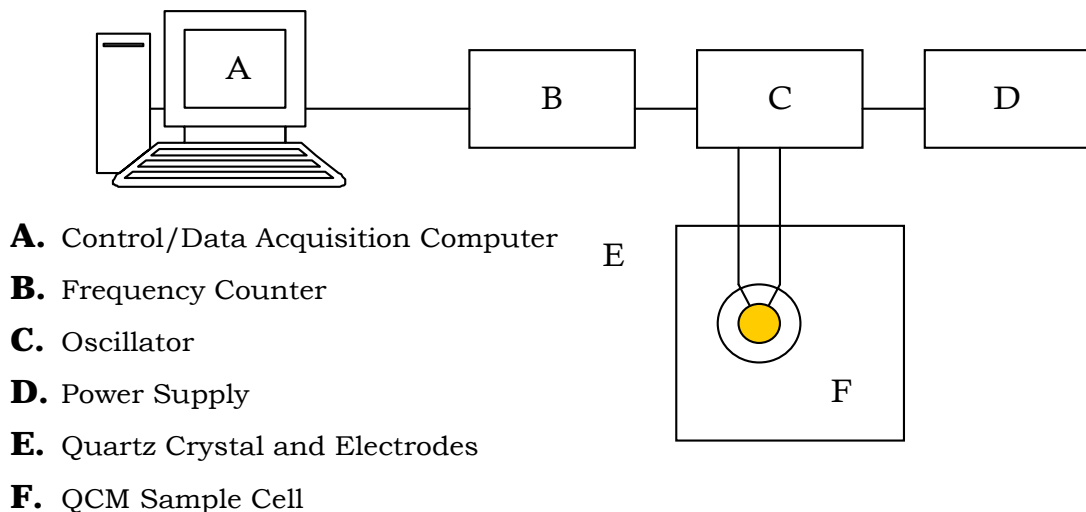
Figure 1.1   Quartz Crystal Microbalance Experimental Setup.

A QCM measures mass by measuring the change in frequency of a piezoelectric

quartz crystal when it is disturbed by the addition of a small mass [19]. QCMs were, for

many years, regarded as solely gas-phase mass detectors. However, recent applications

have proven that QCMs can be operated in contact with liquids and viscoelastic deposits

[20-34]. Working with a QCM in a vacuum or liquid environment is useful in

determining the properties of polymers and adhesion of proteins [24]. Frequency

measurements are known to be highly accurate making the measurement of small masses

easy and precise [28-29]. Other common uses of the quartz crystal microbalance are as a

thickness monitor in thin film technology, as chemical and biological sensors to obtain

information about processes such as protein adsorption/desorption and drug analysis, and

microrheology [30].

1.3.0 Quartz Crystal Microbalance Theory

The fundamental understanding of the relationship between a film of mass, m,

deposited on an oscillating crystal surface and the change of the frequency (period) of

oscillation is credited to Sauerbrey and verified first in vacuum [19]. This relationship is

shown as:

$$\Delta F = -\frac{2F_o^2}{A\sqrt{\mu_q \rho_q}}\Delta m \qquad (1)$$

where ΔF is the change in frequency, F_o is the fundamental resonance frequency of

the crystal, A is the area of the electrode surface, μ_q is the shear modulus of the

crystal, ρ_q is the density of the crystal and Δm is the change in mass [19]. This

equation is often simplified through the application of a linear sensitivity factor, C_f, as

shown in the following equation:

$$\Delta F = -C_f \Delta m \tag{2}$$

where ΔF is the observed frequency change, Δm is the change in mass per unit area,

and C_f is the sensitivity factor for the crystal used. This sensitivity factor is a

fundamental property of the QCM crystal, $C_f = 56.6$ Hz $\mu g^{-1} cm^2$, and can be solved

for by the following equation:

$$C_f = \frac{2F_o^2}{\sqrt{\mu_q \rho_q}} \tag{3}$$

Given that the sensitivity factor, C_f, is a fundamental property of QCM crystal, the

QCM mass sensor, in theory, would not require calibration [19]. However, the

Sauerbrey equation is only strictly applicable to uniform, rigid, thin-film deposits.

Therefore, another useful form of the Sauerbrey equation was developed as seen below:

$$\frac{\Delta f}{f_o} = -\frac{\Delta m}{m} \tag{4}$$

where Δf is the change in frequency, f_o is the initial resonant frequency of the crystal,

Δm is the change in mass, and m is the measured mass [20]. From this relationship it

can be seen that the change in frequency is proportional to the change in mass on the

crystal surface. As mass accumulated on the crystal surface exceeds that

accommodated in a thin layer (monolayer), the Sauerbrey equation looses it validity.

Kanazawa and Gordon apply this technology to applied films in liquid solutions and

point out the importance of the liquid viscosity and density on the frequency change in liquid applications in the following equation,

$$\Delta f = -f_o^{3/2} \left[\frac{\rho_l \eta_l}{\pi \rho_q u_q} \right] \tag{5}$$

where ρ_1 is the density of the liquid, η_1 is the viscosity of liquid, ρ_q is the density of quartz and μ_q is the shear modulus of quartz [20]. Kanazawa and Gordon also point out that the above relationships are limited to thin films and when a thick film is present on the oscillating crystal, the relationship between deposited mass and frequency change will become more complicated. Thin film thickness is governed by the amount of material deposited on the crystal during experimentation [20].

Experimentation involving the use of a QCM requires that these effects due to outside forces be taken in to account. The frequency change measured by the QCM, Δf, is actually the sum of frequencies due to different factors as shown by the expression below:

$$\Delta f = \Delta f_m + \Delta f_p + \Delta f_\eta + \Delta f_r \tag{6}$$

where Δf_m is the frequency due to the mass effect discussed by Sauerbrey, Δf_p is the compression effect due to changes in pressure, Δf_η is an effect due to the interaction of the smooth surface of a vibrating crystal with a viscous medium, and Δf_r is the roughness effect due to the interaction of the rough surface with the fluid [33]. For the study of surfactant adsorption, the mass effect, Δf_m, is the most important factor and the

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desired result. This data must be separated from the other influencing factors which could cause large shifts in the measured frequencies and thus affect the accuracy of the effect of the adsorbed mass.

1.4.0 Experimental Setup and Operation

The central experimental tool for these studies is the Stanford Research System (SRS) QCM200 instrument. The crystal was a 5 MHz quartz crystal with a resonance frequency of 5 MHz.   Technical grade sodium chloride (NaCl) [CAS 7647-14-5] and an ionic surfactant, sodium dodecyl sulfate (SDS), [CAS 151-21-3] were both obtained from Fisher Scientific. Aqueous solutions of SDS and NaCl were prepared in deionized water and mixed in varying ratios to create stock solutions. Experiments were conducted at room temperature and required approximately 30 minutes per observation. All chemicals were used as received. Density measurements were done using an analytical balance and a 1000 μL pipette. Viscosity measurements were done using a Cannon-Finske viscometer and a stopwatch. For both the density and viscosity data, each measurement was replicated ten times and the results were averaged. The standard deviation of the data sets were also calculated using Microsoft Excel and retained for use in analysis.

For adsorption experiments, the QCM crystal was mounted vertically and immersed in each stock solution for approximately 30 minutes. Between each solution set, the crystal face was rinsed by immersing the crystal in deionized water. Frequency measurements were obtained using the SRS software.

1.5.0 Results and Discussion

Experiments were initially performed using the equilibrium method as previously described. The QCM was immersed in each stock solution, allowed to come to equilibrium, and the data was then gathered using the SRS software. The results of these experiments are shown in Figure 1.2. The trends observed on this plot demonstrate that even minute amounts of salt can significantly affect surfactant adsorption.

Experimental results are also presented for aqueous solutions of SDS only (Figure 1.3), and NaCl only (Figure 1.4). A data table of individual measurements for all experiments is presented in the Appendix. Figure 1.2 indicates that for each data set, the system reaches a minimum frequency indicating the maximum level of surfactant adsorption at approximately 2.0 mM SDS, and then proceeds to increase asymptotically, though for increasing amounts of NaCl, the effect on surfactant adsorption is lessened. Including the trends observed from Figures 1.3 and 1.4, taking each agent separately, this behavior would indicate an adsorption followed by desorption, which is contrary to accepted theory. In addition, this data pointed out that there was more activity between the 0.0 mM and 4.0 mM concentrations of SDS than was initially expected. Another surprising aspect of the measured data shown in Figure 1.2 was that the maximum amount of surfactant adsorption would normally occur at or near the established CMC for that particular surfactant, in this case at approximately 7.0 mM SDS. This change could indicate the formation of a monolayer at the minimum, which could also be tied to reaching the CMC at lower concentrations of SDS due to increased micelle formation affected by NaCl concentration. This explanation would account for the apparent lack of additional surfactant adsorption at increasing SDS concentrations where the relationship

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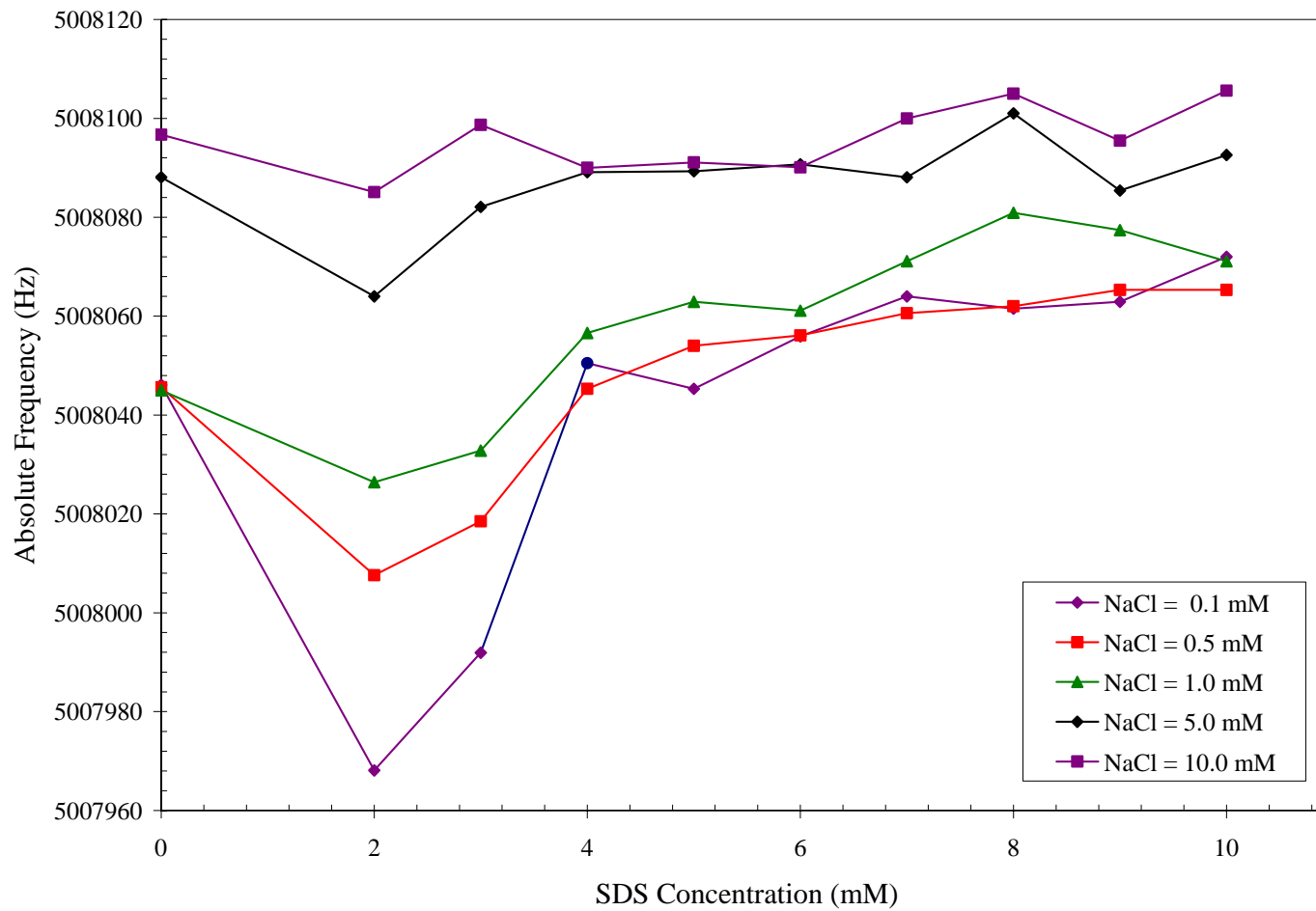
Figure 1.2   SDS Concentration Vs. Absolute Frequency With Respect To NaCl Concentration.
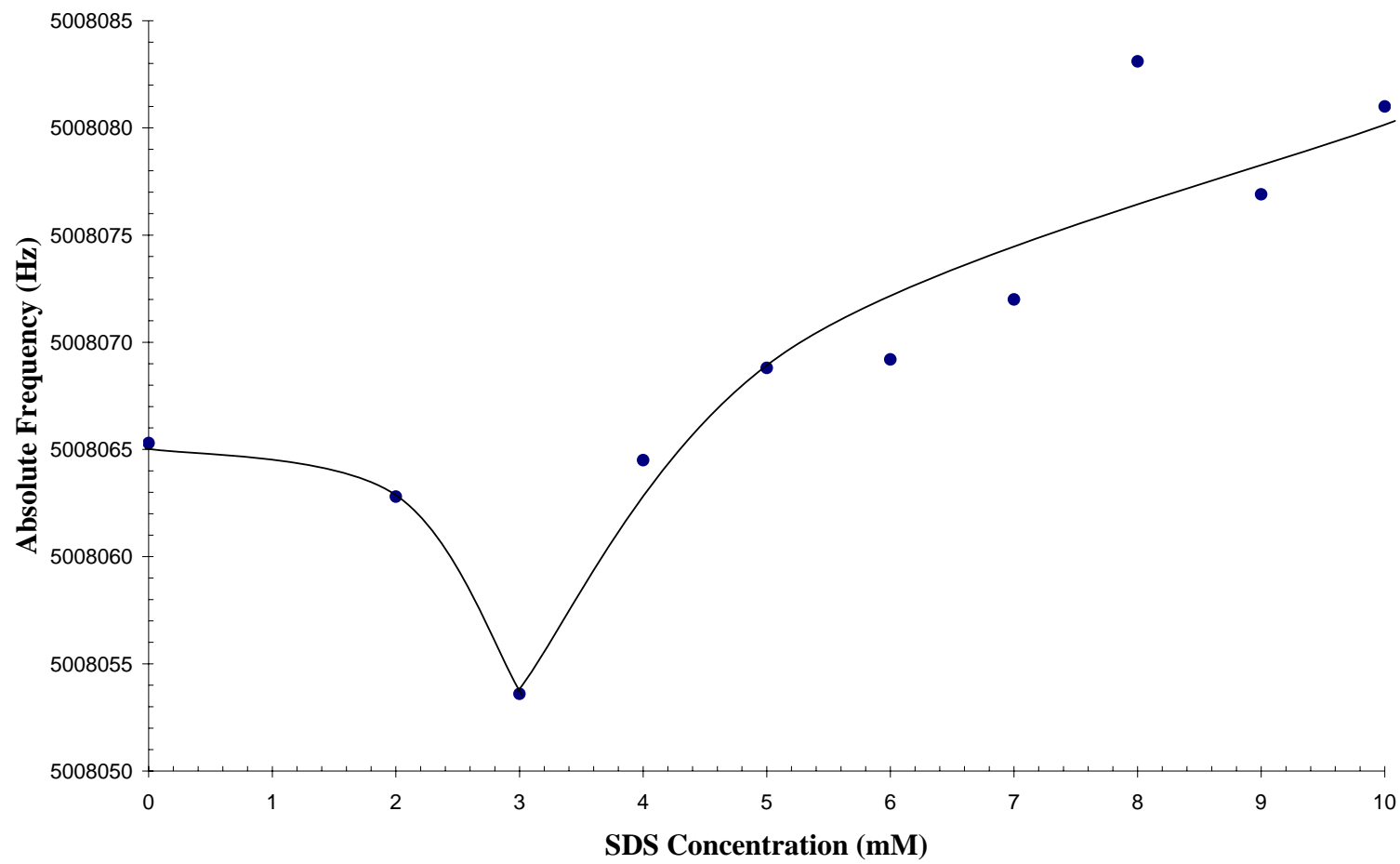
Figure 1.3   Effects of SDS Concentration on QCM Frequency.

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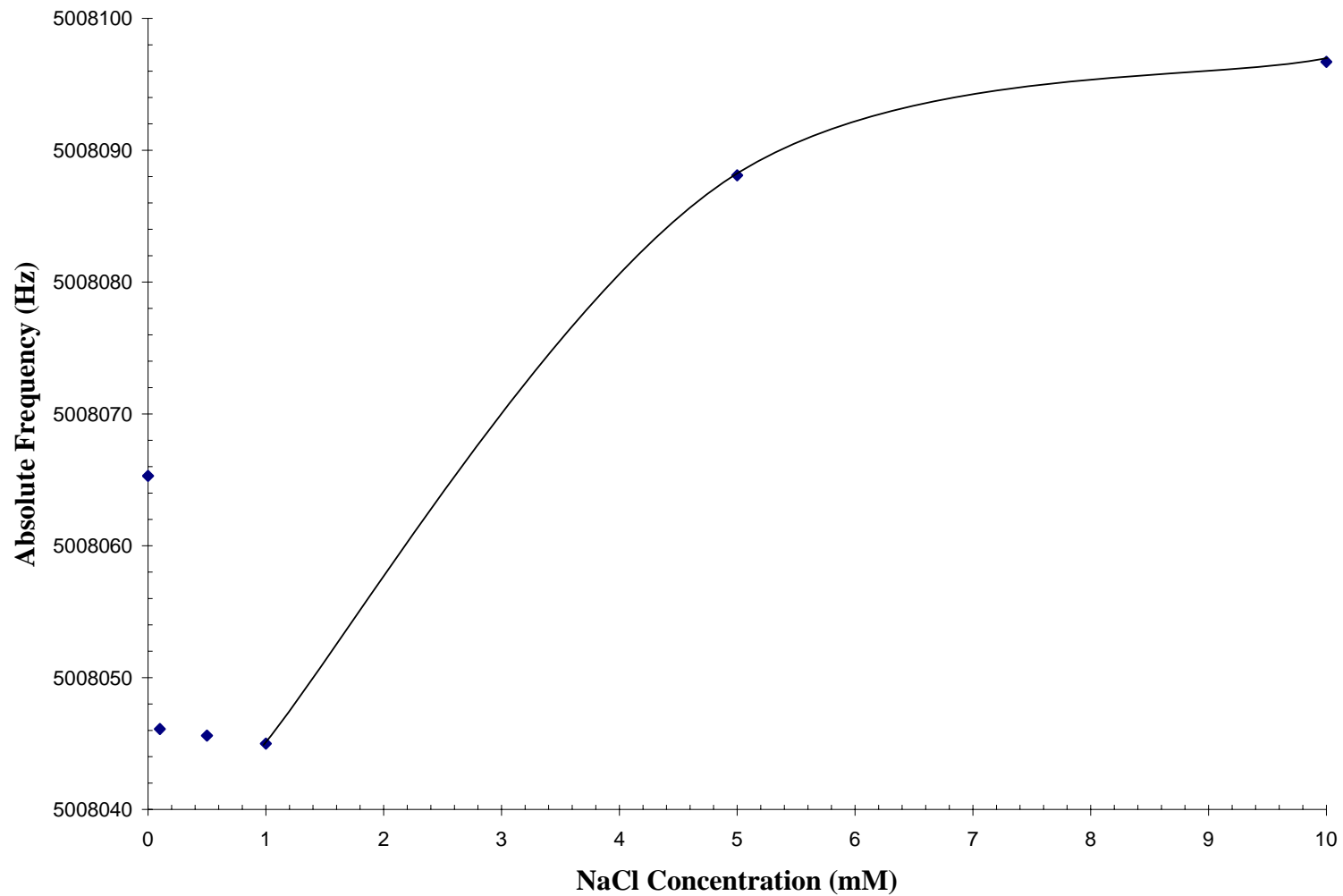
Figure 1.4   Effects of NaCl Concentration on QCM Frequency.

expressed in Equation 1 between adsorbed mass and frequency change is lost.

In the analysis of this data, it is important to remember the other influencing factors on the measured frequency change observed during this process. As stated in Equation 6, the change in frequency measured by the QCM is a result of more than just the mass changes occurring during surfactant adsorption. Pressure, surface roughness, density and viscosity, all have an effect on the measured frequency [33]. In the current study, the roughness effect, Δf_r, can be discounted because the surface of the crystal is polished smooth. The effect from the interaction of a viscous medium with the crystal surface, Δf_η, is actually influenced by the bulk properties, viscosity and density of the solution [33]. In order to solve for this value and thus correct for changes in the immediate interfacial crystal/solution environment, an application of Kanazawa's equation was necessary [20]. Density and viscosity data for the necessary concentrations of SDS and NaCl were obtained from the work of Afroz *et al*. [35]. This data was then extrapolated for solution predictions at a temperature of $25^\circ C$. Validating experiments to obtain independent measurements for the density and viscosity of each aqueous solution were also obtained as described in the Experimental Section. There were initial concerns of the ability to achieve precise density and viscosity data using the available balance, but when checked against the extrapolated data acquired from the work of Afroz *et al*, there was close agreement.

The final factor contributing to the total frequency change measured by the QCM was the compression effect, Δf_p, or the effect due to changes in pressure. Unfortunately, because of the nature of the experiments that were performed, in an open solution with no

way to control the pressure changes from the surrounding environment of an open laboratory, it was impossible to extract the pressure effects from the QCM data. This method of experimentation also proved inefficient for repetition and verification purposes. It proved impossible to recreate the experiment at a later time. Due to vast differences in the pressure effects, winter break experimentation in an empty laboratory verses summer experimentation in a crowded laboratory, the data measured was largely unrepeatable and unusable for continuing research.

1.6.0 Conclusions

The purpose of this study was to make observations about surfactant adsorption phenomenon and, if possible, provide experimental work to validate the assumptions inherent in the model presented by Morton *et al*. [1,13-17]. The QCM proved effective in measuring the minute amounts of mass changes involved in surfactant adsorption. However, due to the inability to account for pressure effects on the system, the data obtained was not useful for analysis beyond obtaining general observations about the effects of NaCl on the system. Taking this limitation into account, the addition of very small concentrations of NaCl did prove to significantly affect surfactant adsorption; this is consistent with previous observations of contact angle measurements by Davis *et al*. [4-5]. Unfortunately, the results of the current study, without further data refinement and experimentation, can not be used to validate expectations concerning monolayer formation from Morton *et al*. [1,13-17]. These results must be viewed as being qualitative due to the inability to account for pressure effects and a new method of experimentation is necessary in order for use in analysis in relation to the work of Morton, *et al*.

In order to address the problem of pressure effects on frequency measurement using the QCM, a more exact method of experimentation is required.   Therefore, a system incorporating the use of a flow cell and pump was developed. A flow cell represents a closed system that will negate the need to account for pressure affects on the QCM data. This system will allow for the verification of the assumptions made in the current study and further enhance knowledge about adsorption phenomenon.

CHAPTER 2

Effects of Electrolyte on Surfactant Adsorption to a QCM

2.1.0 Introduction

The adsorption of surfactants on solid surfaces is a key phenomenon in the cleaning and degreasing of metal surfaces. Morton *et al*. [1,13-17] developed a thermodynamically-based model for the prediction of equilibrium oil droplet contact angles on solid surfaces immersed in aqueous surfactant solutions. This model assumes competition between oil and surfactant on the metal surface as a basis for predictions. By applying classical thermodynamics, relevant surfactant self-assembly modeling theory and an estimation of the impact of ionic strength and other systemic parameters on the prediction of oil droplet contact angle, this model provides a foundation upon which to further understand and subsequently enhance industrial aqueous cleaning processes [1,13-17]. With the established relationship between surface cleaning and contact angle, a sound model relating the extent of surface cleaning and system parameters was thus established. These modeling efforts overlap existing data on surfactant adsorption data and require an estimation of surfactant adsorption phenomena, especially the transition between monolayer adsorption and multi-layer adsorption, which corresponds to the critical micelle concentration (CMC).

The work of Davis *et al*. [4-5] demonstrated the effect of such solution compositions on organic droplet contact angles adhering to a polished gold surface. Their work showed that even very small quantities of salt had a positive effect on contact angle evolution, but did not provide a predictive mechanism related to the

observed phenomena. The model developed by Morton *et al*. [1,13-17] was designed to predict the changes in contact angle at small surfactant and electrolyte concentrations. The reverse orientation model described by Fan *et al.* offers a possible explanation of the adsorption phenomenon present within a surfactant/salt solution and was used in the development of Morton's model. [36] Unfortunately, the experimental evidence needed to validate the necessary assumptions made by the model did not fully exist at the time. The primary assumption relative to the work presented in this article is the description of surface aggregation as four distinct regions: (1) Region A – Random charge related adsorption, (2) Region B – Aggregation resulting in an established monolayer, (3) Region C – Aggregation transitioning from the established monolayer to an established multilayer, and (4) Region D – Adsorption to surface superseded by solution aggregation in the form of micelles. Morton assumed that the transitions between these regions could be characterized by the status of adsorption in the aqueous/aggregate/solid interface. In Regions A and B, adsorption is more a factor of the liquid/solid interface but as the salt concentration is increased resulting in the formation of micelles, adsorption becomes a factor of the aggregate/solid interface. To resolve the uncertainty regarding the true nature of the solid surface aggregation in solution, experimental work using a QCM was proposed. This article is designed to validate the assumptions inherent in the model by Morton *et al.* [1,13-17].

2.2.0 Theory

The fundamental understanding of the relationship between a film of mass, *m*, deposited on an oscillating crystal surface and the change of the frequency (period) of oscillation is credited to Sauerbrey and verified first in vacuum [19]. This relationship is

shown as:

$$\Delta F = -\frac{2F_o^2}{A\sqrt{\mu_q \rho_q}}\Delta m \qquad (1)$$

where ΔF is the change in frequency, F_o is the fundamental resonance frequency of the crystal, A is the area of the electrode surface, μ_q is the shear modulus of the crystal, ρ_q is the density of the crystal and Δm is the change in mass [19]. This equation is often simplified through the application of a linear sensitivity factor, C_f, as shown in the following equation:

$$\Delta F = \frac{-C_f \Delta m}{A} \qquad (2)$$

where ΔF is the observed frequency change, Δm is the change in mass, and C_f is the sensitivity factor for the crystal used. This sensitivity factor is a fundamental property of the QCM crystal, $C_f = 56.6$ Hz $\mu g^{-1}cm^2$, and can be solved for by the following equation:

$$C_f = \frac{2F_o^2}{\sqrt{\mu_q \rho_q}} \qquad (3)$$

Given that the sensitivity factor, C_f, is a fundamental property of QCM crystal, the QCM mass sensor, in theory, does not require calibration. However, the Sauerbrey equation is only strictly applicable to uniform, rigid, thin-film deposits. As mass accumulated on the crystal surface exceeds that accommodated in a thin layer

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(monolayer), the Sauerbrey equation looses it validity. Therefore, another useful form

of the Sauerbrey equation was developed as seen below:

$$\frac{\Delta f}{f_0} = \frac{\Delta m}{m}$$

(4)

where Δf is the change in frequency, f_o is the initial resonant frequency of the crystal,

Δm is the change in mass, and m is the measured mass [19]. From this relationship it

can be seen that the change in frequency is proportional to the change in mass on the

crystal surface.

Kanazawa and Gordon apply this technology to applied films in liquid solutions

and point out the importance of the liquid viscosity and density on the frequency change

in liquid applications in the following equation,

$$\Delta f = -f_o^{3/2} \left[\frac{\rho_l n_l}{\pi \rho_q u_q} \right]$$

(5)

where ρ_1 is the density of the liquid, η_1 is the viscosity of liquid, ρ_q is the density of

quartz and μ_q is the shear modulus of quartz [20-21]. Kanazawa and Gordon also point

out that the above relationships are limited to thin films and when a thick film is present

on the oscillating crystal, the relationship between deposited mass and frequency

change will become more complicated. Thin film thickness is governed by the amount

of material deposited on the crystal during experimentation [20-21].

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Experimentation involving the use of a QCM requires that these effects due to outside forces be taken into account. The frequency change measured by the QCM, Δf, is actually the sum of frequencies due to different factors as shown by the expression below,

$$\Delta f = \Delta f_m + \Delta f_p + \Delta f_\eta + \Delta f_r + \Delta f_v \qquad (6)$$

where Δf_m is the frequency due to the mass effect discussed by Sauerbrey, Δf_p is the compression effect due to changes in pressure, Δf_η is an effect due to the interaction of the smooth surface of a vibrating crystal with a viscous medium, and Δf_r is the roughness effect due to the interaction of the rough surface with the fluid [33], Δf_v, is the change due to viscosity and density variations of the immersion solution from Equation 5.

For the study of surfactant adsorption presented in this article, the mass effect, Δf_m, and the viscous effect, Δf_v, are the primary variable factors among those above. The pressure compression factor is rendered negligible through use of the QCM flow cell. The remaining factors are assumed to be negligible and constant as they are related to the interaction between the crystal and the immersion medium absent adsorption.

2.3.0 Experimental Setup and Operations

Sodium dodecyl sulfate (SDS) [CAS 151-21-3] and sodium chloride (NaCl) [CAS 7647-14-5] were purchased from Fisher Scientific. All chemicals were used as received. Aqueous solutions of SDS and NaCl were prepared in deionized water and

mixed in varying ratios to create stock solutions.

QCM measurements were made using a Stanford Research Systems (SRS) QCM200 instrument. The crystals used were 5 MHz 1-inch AT-cut quartz crystals coated with gold in the center. Flow cell measurements were obtained using a Waters Associates Chromatography Pump M600A and the SRS standard axial flow cell (O100FC).

The QCM crystal was mounted vertically and attached to the SRS axial flow cell. The M600A Pump was then used to ensure constant flow of each stock solution at 0.1 mL per minute through the flow cell and over the face of the crystal. Between each solution set, the crystal face was rinsed by washing deionized water through the flow cell system for times in excess of 30 minutes (total time determined when a stable signal from the QCM is achieved). Frequency measurements were obtained using the provided data acquisition software. The data gained from this experiment was then analyzed using Sauerbrey's QCM theory and Kanazawa's equation to account for density and viscosity effects on the system [19-21].

2.4.0 Results and Discussion

In developing the flow system for experimentation, the main goal was to gain a clearer picture of the monolayer formation activity that is expected to occur at the salt-aqueous-surfactant solution-solid interface. A series of experiments was performed encompassing variations in both surfactant concentrations (0 mM to 10 mM SDS) and electrolyte concentrations (0 mM, 1 mM, 10 mM, and 100 mM) at constant temperature.

The first series of experiments, shown in Figure 2.1, were performed for a
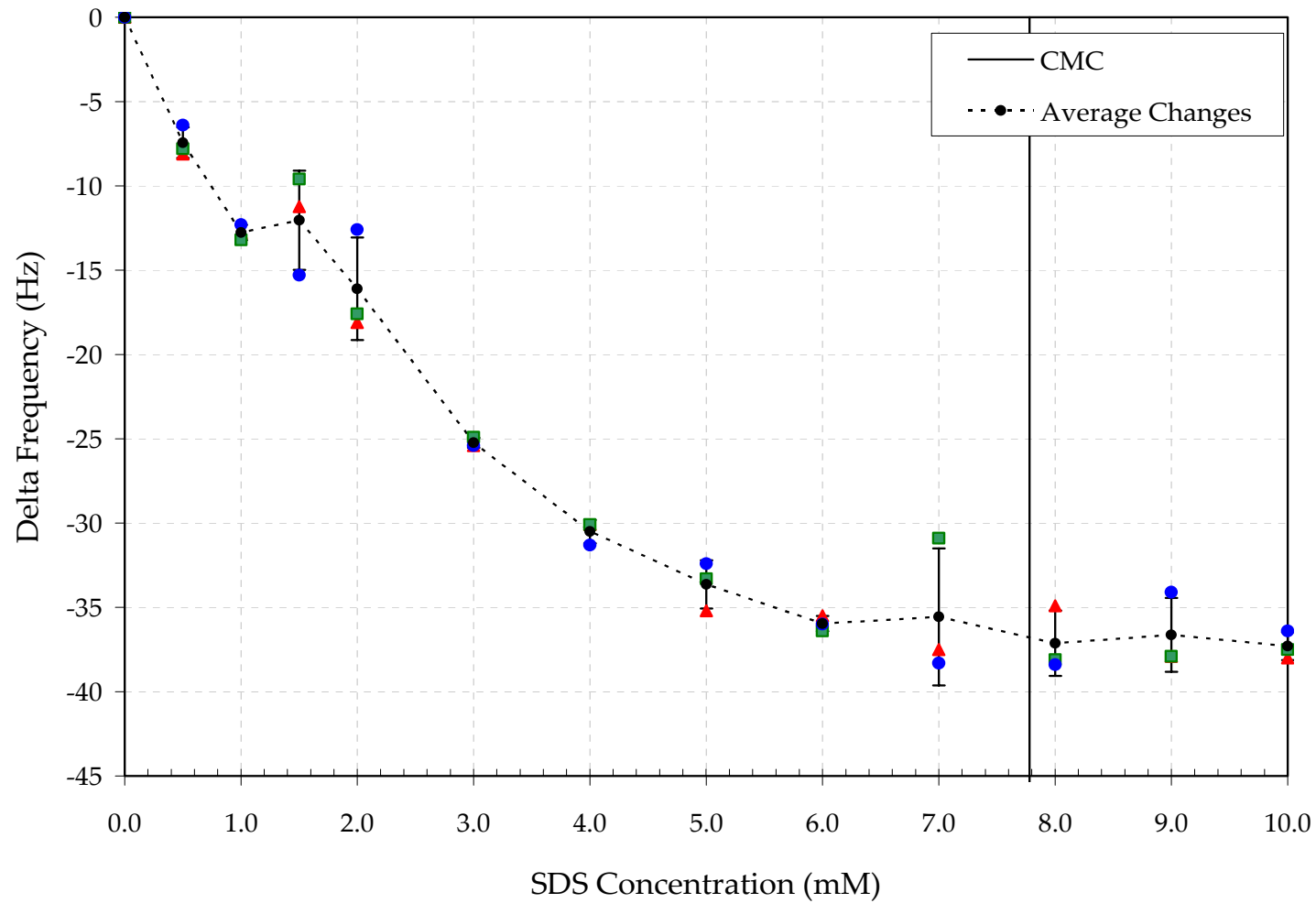
Figure 2.1 Changes in QCM frequency relative to SDS concentration in the absence of NaCl.

concentration of 0 mM NaCl for each of the stock solutions of increasing SDS

concentration. Multiple experimental runs were performed and are shown (symbols

without connective lines) along with the average of the data (symbols with connective

lines) and an approximation of error. The data shows a fairly uniform downward trend,

which indicates a gradual increase in surfactant adsorption to the surface as the solution

concentration approaches the CMC. The CMC for SDS in the absence of NaCL is

approximately 7.78 mM SDS in water (values for the CMC as a function of NaCl

concentration were taken from the work of Morton *et al*. [1,13-17]. Beyond the CMC,

the change in frequency becomes essentially constant.

Figure 2.2 shows the next set of experiments performed for solutions with

increasing concentrations of SDS and NaCl concentrations equal to 1.0 mM NaCl. The

data obtained from this concentration were similar to those observed for 0.0 mM NaCl.

As the SDS concentration is increased (approaching the CMC of 7.34 mM SDS),

ΔF decreases as expected. Additionally, at SDS concentrations higher than the CMC,

ΔF again remains constant. However, there are two distinct differences in this data set.

First, the level of surfactant adsorption reaches a maximum at slightly lower

concentrations of SDS than when the NaCl concentration was zero. For this NaCl

concentration, surfactant adsorption reaches its maximum closer to 7.0 mM SDS instead

of 8.0 mM SDS as in Figure 2.1. The second difference is that surfactant adsorption

appears to become relatively constant well before the CMC, indicating monolayer

formation, beginning at smaller SDS concentrations.

The next concentration of NaCl studied was that of 10.0 mM as seen in Figure

2.3. The findings for this data set agreed with those observed in the previous two data
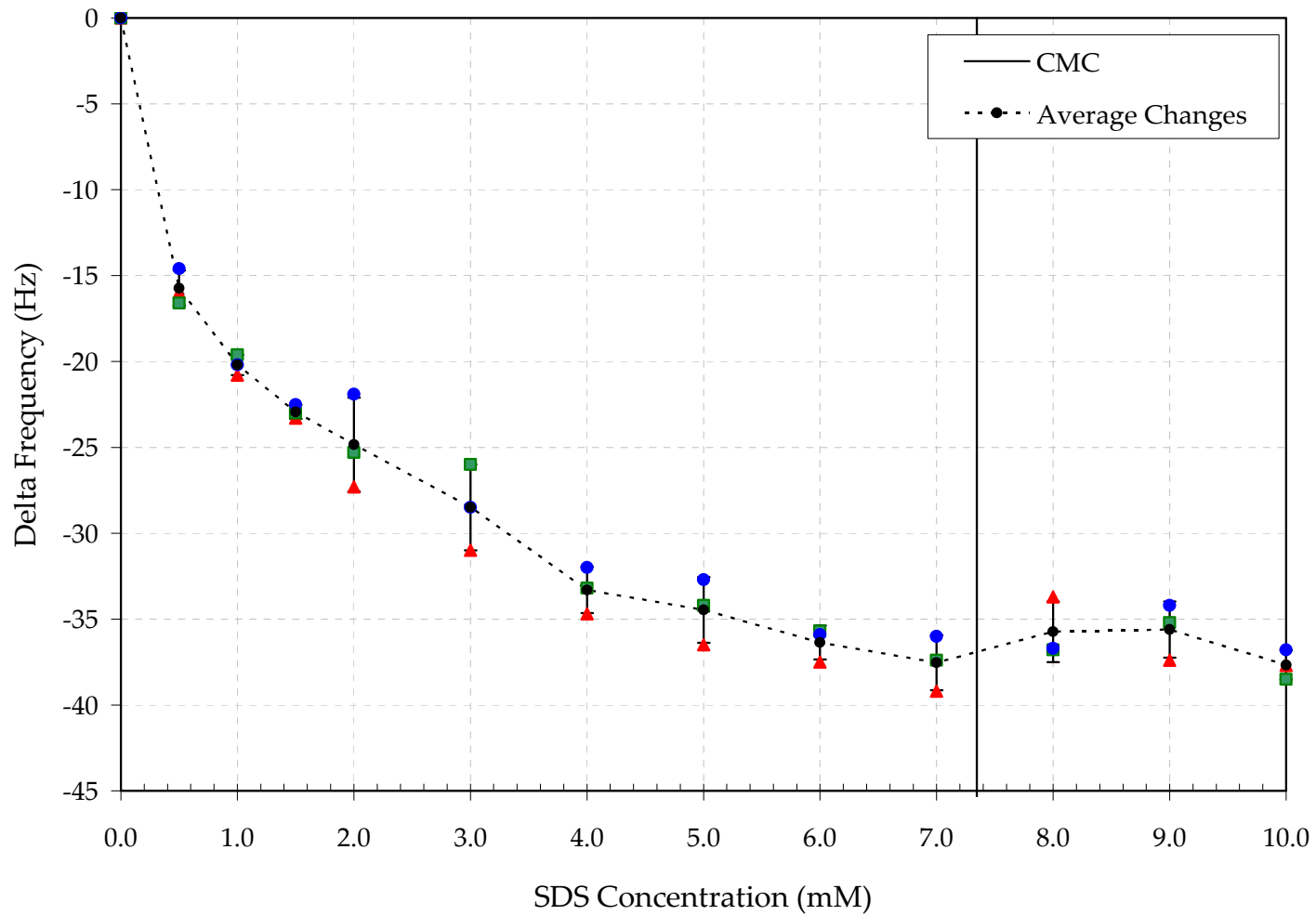
Figure 2.2   Changes in QCM frequency relative to SDS concentration for a NaCl concentration of 1.0 mM.
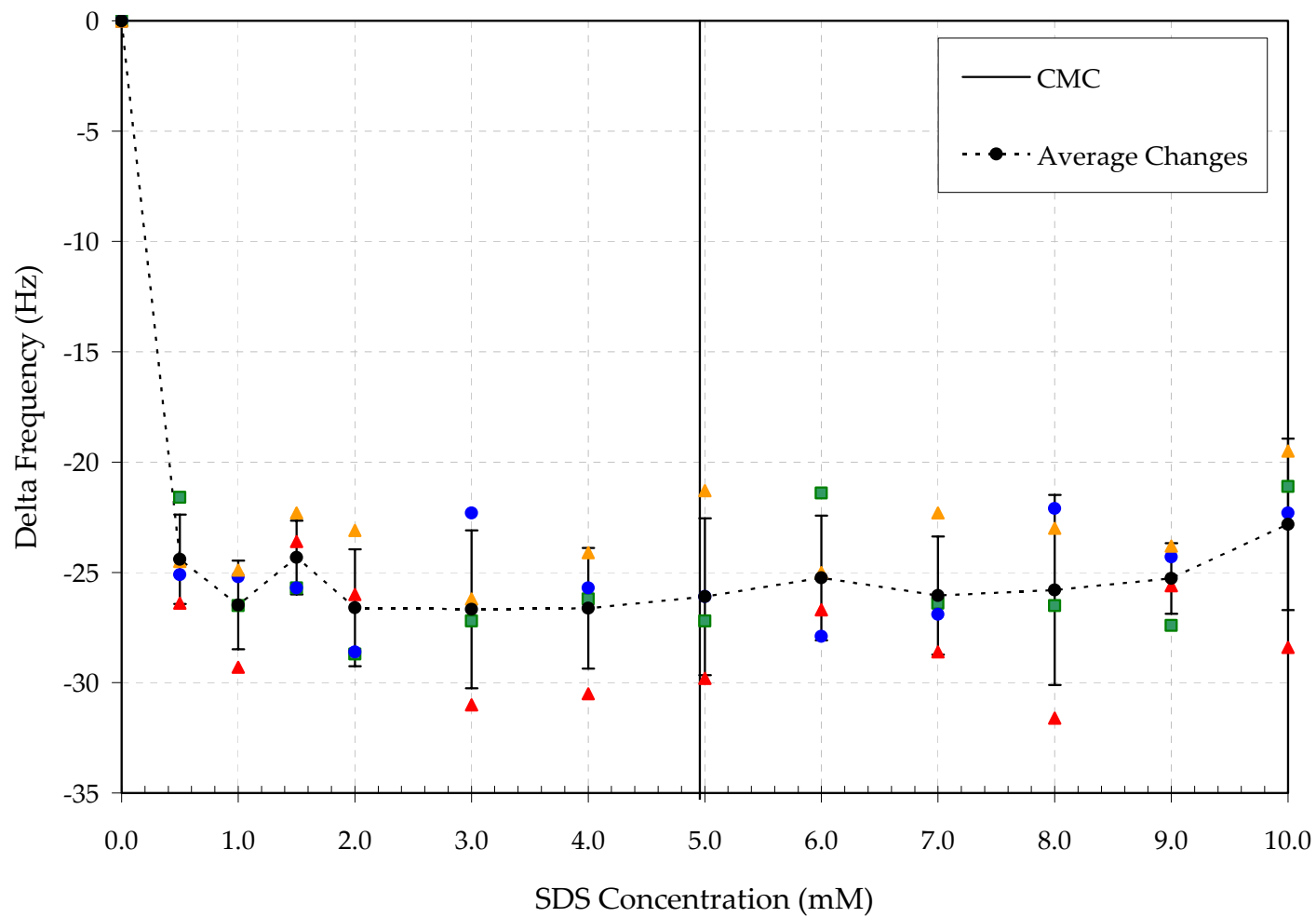
Figure 2.3   Changes in QCM frequency relative to SDS concentration for a NaCl concentration of 10.0 mM.

sets. Once again, an increase in surfactant adsorption with greater concentrations of SDS was observed. However, for this level of NaCl concentration there was a significant increase in surfactant adsorption at a much lower concentration of SDS. Figure 2.3 shows that surfactant adsorption reaches a maximum level at approximately 2.0 mM SDS, where there is an apparent monolayer formed, and stays constant during the consecutive increases in SDS. This value is significantly lower than the CMC of 4.96 mM SDS.

Finally, a set of experiments were performed in which a concentration of 100.0 mM NaCl was added to the stock solutions of increasing SDS concentrations. The results, shown in Figure 2.4, vary greatly from that of the previous NaCl concentrations. At this level of NaCl concentration, it appears to be a near zero change in frequency that would indicate negligible adsorption. It is well understood that this is not true, thus the data shown must have other implications. A logical explanation for this deviation from the expected performance is that as the surface aggregate becomes more developed at lower and lower concentrations the crystal is shielded from the solution at lower and lower concentrations. Thus what appears to be indicative of no surfactant adsorption is in fact indicative of significant and rapid crystal shielding surfactant adsorption.

To get a clear understanding of the overall effects of NaCl concentration on SDS surfactant adsorption as measured by the QCM, it is helpful to compare the data sets on one graph, as seen in Figure 2.5. However, it is necessary to correct for density and viscosity effects on the system before making any observations to ensure the accuracy of the data [33]. Therefore, Figure 2.6 shows a comparison of each of the averaged data sets, this time taking into account density and viscosity effects. This plot was created
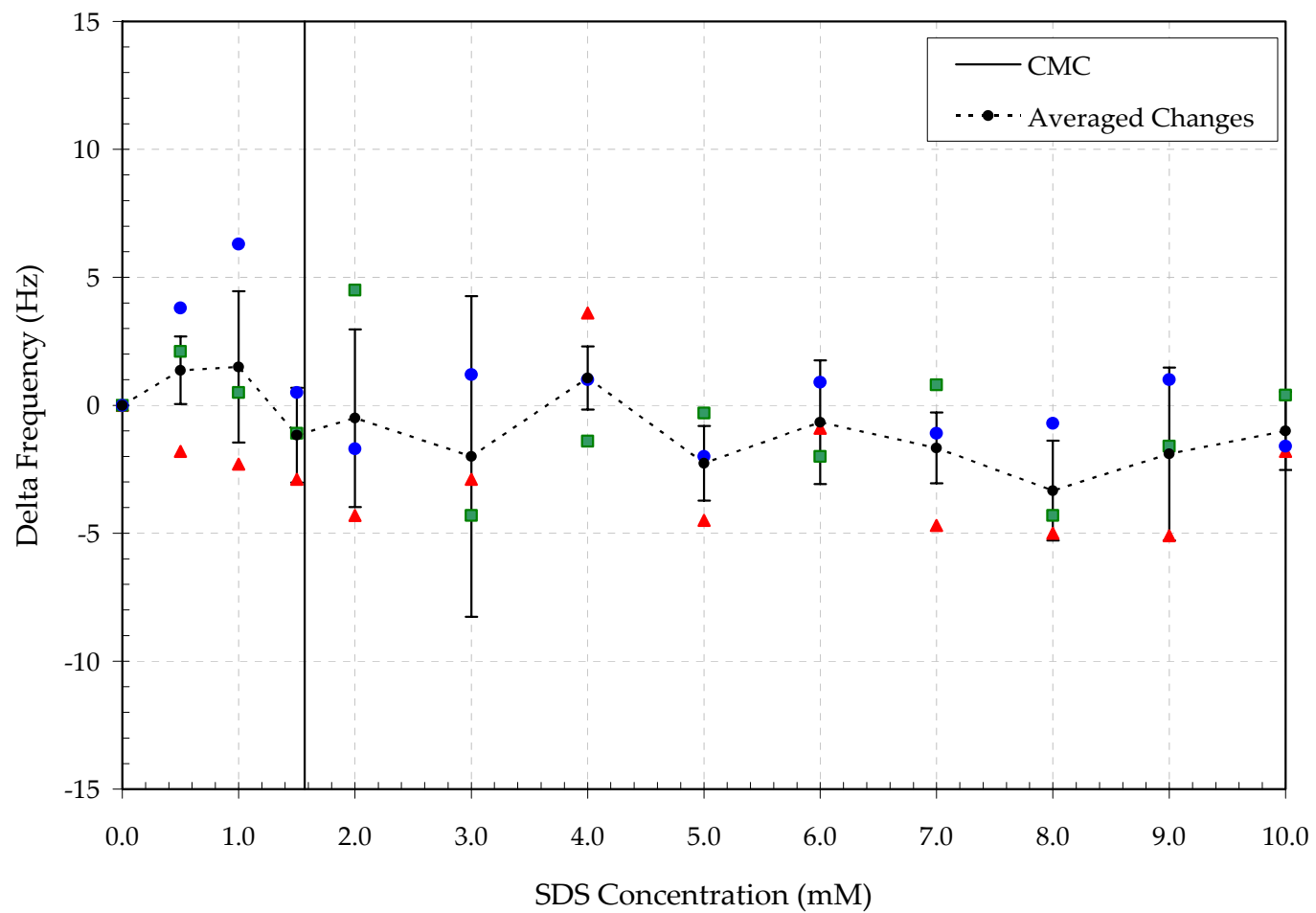
Figure 2.4   Changes in QCM frequency relative to SDS concentration for a NaCl concentration of 100.0 mM.
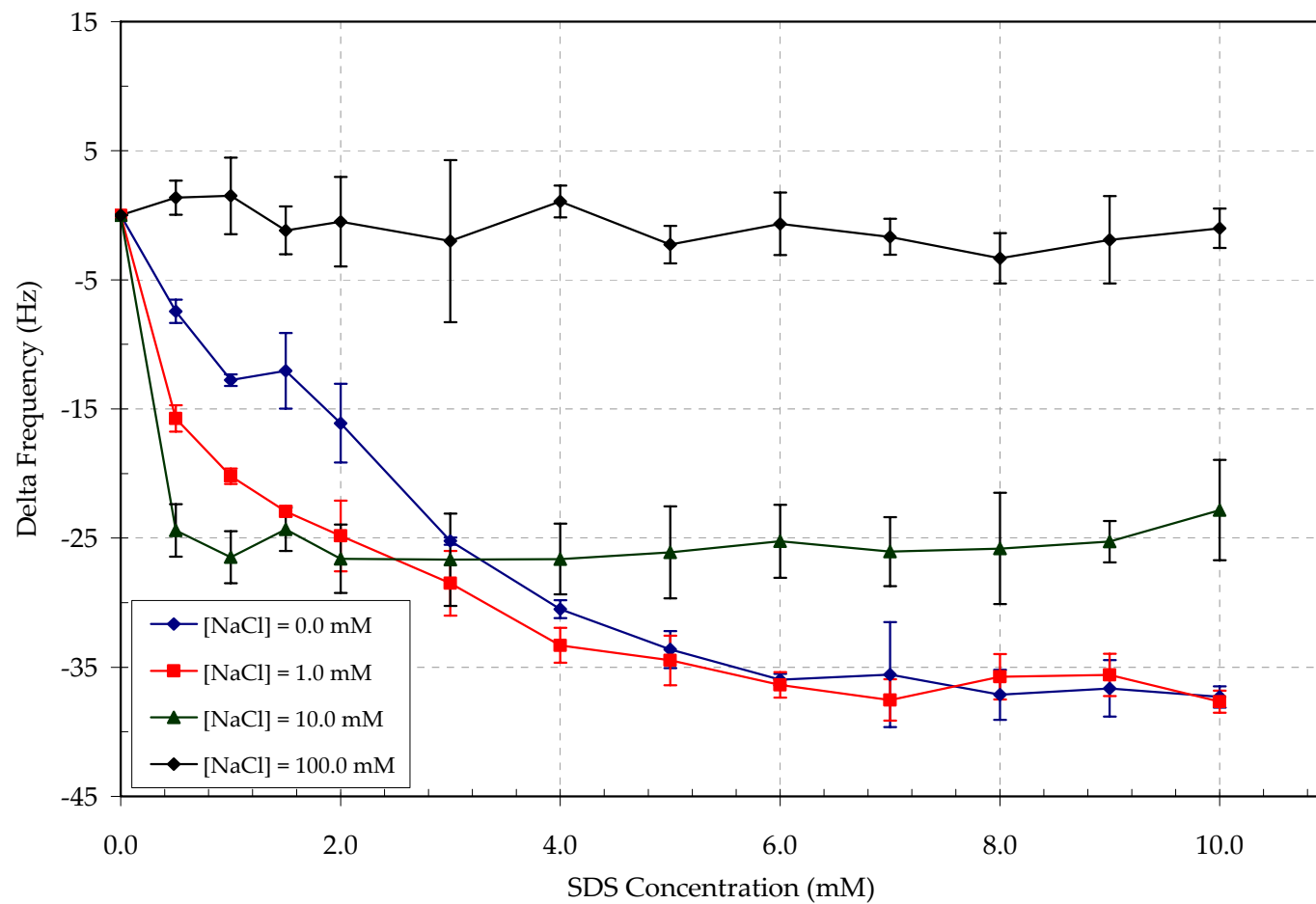
Figure 2.5   Comparison of frequency changes for all data sets.
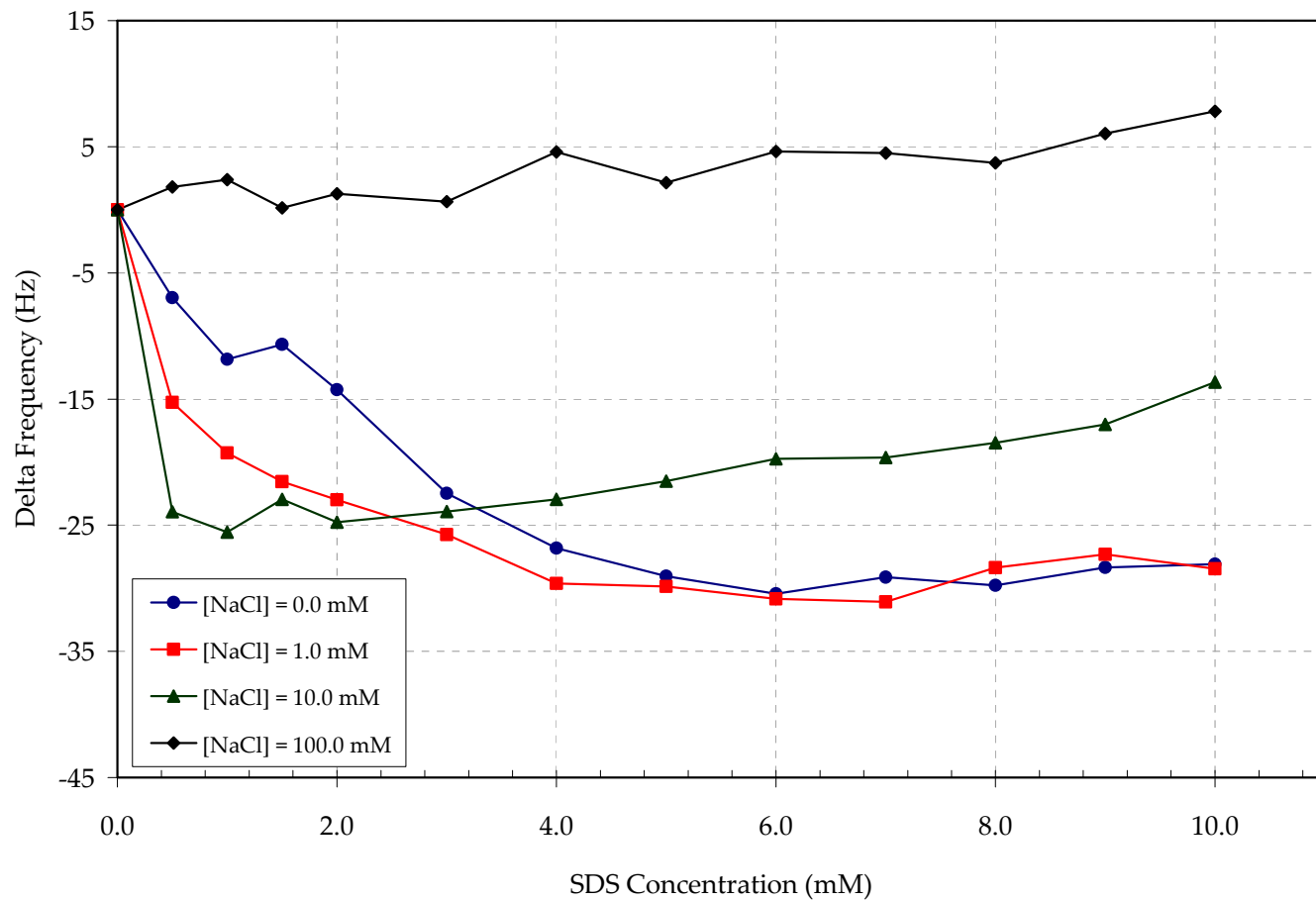
Figure 2.6 Comparison of frequency changes with correction for density and visocity changes in solution.

by applying a correction for density and viscosity effects on the solution relative to changes in SDS concentration for each of the NaCl concentrations [26-27]. In order to solve for this value and thus correct for changes in the immediate interfacial crystal/solution environment, an application of Kanazawa's equation was necessary [20-21]. Density and viscosity data for the necessary concentrations of SDS and NaCl were obtained from the work of Afroz *et al* [35]. This data was then used to extrapolate for solutions at a temperature of $25°$ C. Validating experiments to obtain independent measurements for the density and viscosity of each aqueous solution were also performed. When checked against the extrapolated data acquired from the work of Afroz *et al*, the newly measured values were in close agreement [35]. From the corrected plot, it is evident there was only a slight quantitative change to the data sets at points beyond the CMCs. Though quantitatively there is a small change in the measured frequency, the measured results exceed any density and viscosity effects present in the environment.

Comparing the 3 data sets for 0.0 mM NaCl, 1.0 mM NaCl, and 10.0 mM NaCl respectively, shows that even relatively small increases in NaCl concentration can cause surfactant adsorption to increase significantly initially. At a NaCl concentration of 0.0 mM there is lack of change in ΔF with the increasing surfactant concentration after reaching approximately 6.0 mM SDS. This phenomenon suggests the formation of a complete monolayer near this concentration. However, upon the addition of NaCl at a concentration of 1.0 mM there is a slight but noticeable change. Maximum surfactant adsorption is both reached and then remains constant at a smaller concentration of SDS

than when NaCl concentration was at zero. These changes imply that the addition of

NaCl, even in extremely small amounts, can significantly affect surfactant adsorption.

Both of these effects may be a result of reaching the formed monolayer at lower

concentrations of SDS (in this case, approximately 4.0 mM instead of 6.0 mM SDS).

At the higher concentration of 10.0 mM NaCl, the affect is much more apparent.

Maximum surfactant adsorption occurs around 0.5 mM SDS and then remains relatively

constant until the CMC is reached.

As expected, comparing these three data sets shows the CMC occurring at

decreasing concentration of SDS for increasing concentrations of NaCl.   Additionally,

the observed behavior of the frequency changes (when corrected for density and

viscosity variations) also lends credibility to the earlier onset of monolayer aggregation

at the solid-solution interface. However, ultimately, there is a limit to the ability to

experimentally determine via the QCM the effect of NaCl concentrations to increase

surfactant adsorption, as is apparent from the 100.0 mM NaCl data set when compared

with the data sets from the three lower concentrations of NaCl.

To fully understand the surfactant adsorption phenomena occurring during this

experiment, it is necessary to relate the observed trends to the model presented in

Morton *et al*. [1,13-17]. The trends observed in this experiment can be explained as a

phenomenon resulting from an application of the reverse orientation model described by

Fan *et al.* [36] In Figure 2.7, the plot for NaCl concentration of 1.0 mM was used to

clearly show how the data acquired in the current study both relates to the reverse

orientation model and validates the model presented by Morton *et al*. The four distinct

regions described in the reverse orientation model: (1) Region A – Random charge
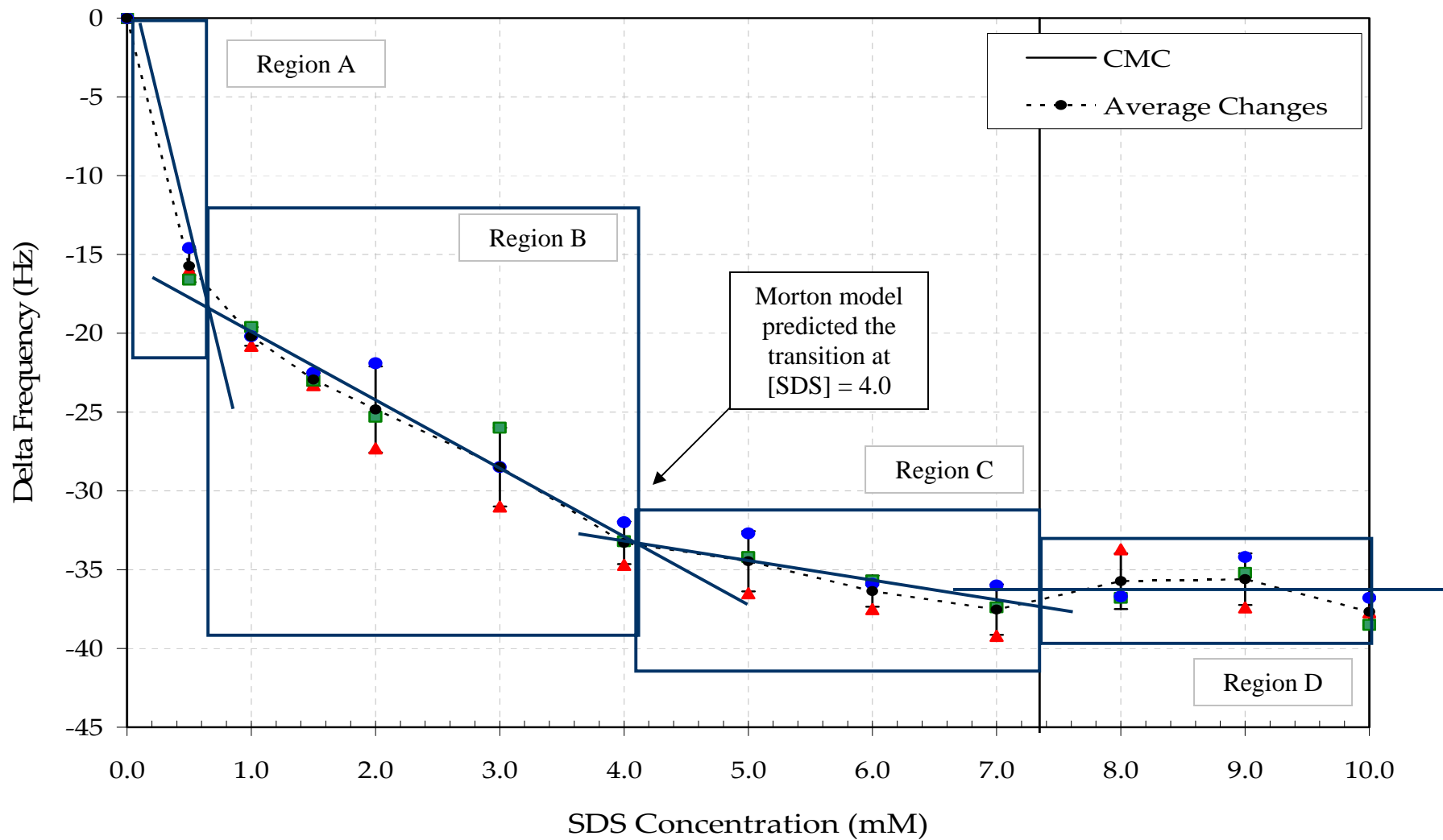
Figure 2.7 Demonstration of Validity of Morton *et al* [1, 13-17] for NaCl = 1.0 mM.

related adsorption, (2) Region B – Aggregation resulting in an established monolayer, (3) Region C – Aggregation transitioning from the established monolayer to an established multilayer, and (4) Region D – Adsorption to surface superseded by solution aggregation in the form of micelles; are each witnessed upon careful consideration of the measured data. The trend of the data for NaCl concentration of 1.0 mM distinctly represents each of these four regions. The frequency decline witnessed in each data set shows that the organized interfacial aggregates are forming at lower concentrations of SDS, and are forming more extensively. This trend is in line with the assumption of the moving initiation location for the Region B aggregate as predicted by Morton *et al*. [1,13-17]. In fact, Morton's model predicted that the location for the transition between Regions B and C would occur at approximately 4.0 mM SDS for a solution with a NaCl concentration of 1.0 mM and, as seen in Figure 2.7, this is proven to be true. The CMC occurs later than the point of maximum surfactant adsorption when salt is added to increase micelle formation. This maximum point can be assumed to correspond to an earlier organized aggregate, or the formation of the completed monolayer, which provides initial shielding and the onset of the viscous effects relative to the film. This data qualitatively validates the multiple adsorption region approach. First, that the trends showing an increase in surfactant adsorption past the CMC due to a more developed surface layer and the effects of viscous shielding. Inherently, as the interfacial layer grows, the crystal surface comes into contact with less of the bulk solution. In effect there is a layer of "hydrocarbon" forming at the interface which is the surfactant tails.

In the previous discussion and figures, frequency changes have been treated as a

proxy for mass changes in the system. Thru an application of the equation by Sauerbrey (Equation 2), it is possible to relate these two factors by rearranging the equation in the following manner:

$$\frac{m}{A} = \frac{\Delta F}{-C_f} \qquad (7)$$

This equation allows us to relate the change in mass per unit of area to the frequency changes that are a measurable quantity [19]. Figure 2.8 shows the calculated mass per unit area for NaCl concentrations of 0.0 mM to 10.0 mM. The trends observed on this graph again validate the assumptions made in the model developed by Morton *et al*. 1,6] and lends experimental evidence to the ability of salt to increase surfactant adsorption. The data for a NaCl concentration equal to 100 mM is omitted as the positive values for the frequency changes indicate that the crystal surface was likely shielded from the bulk solution by the formed surface aggregate at a very low concentration. The trend for this data set suggests that there was a desorption occurring at this level of NaCl concentration which is scientifically unsound and logically not valid.

2.4.0 Conclusion

The governing factors controlling surfactant adsorption phenomena are still an area of science requiring extensive research and experimentation. The purpose of the research conducted in this study was to add to what is already known about surfactant adsorption. In the work of Morton *et al.*, a model predicting surfactant adsorption behavior was developed and the trends observed experimentally in this study lend validation to the approximations made by that model. The addition of minute amounts of salt was shown to significantly affect surfactant adsorption and highlighted the link
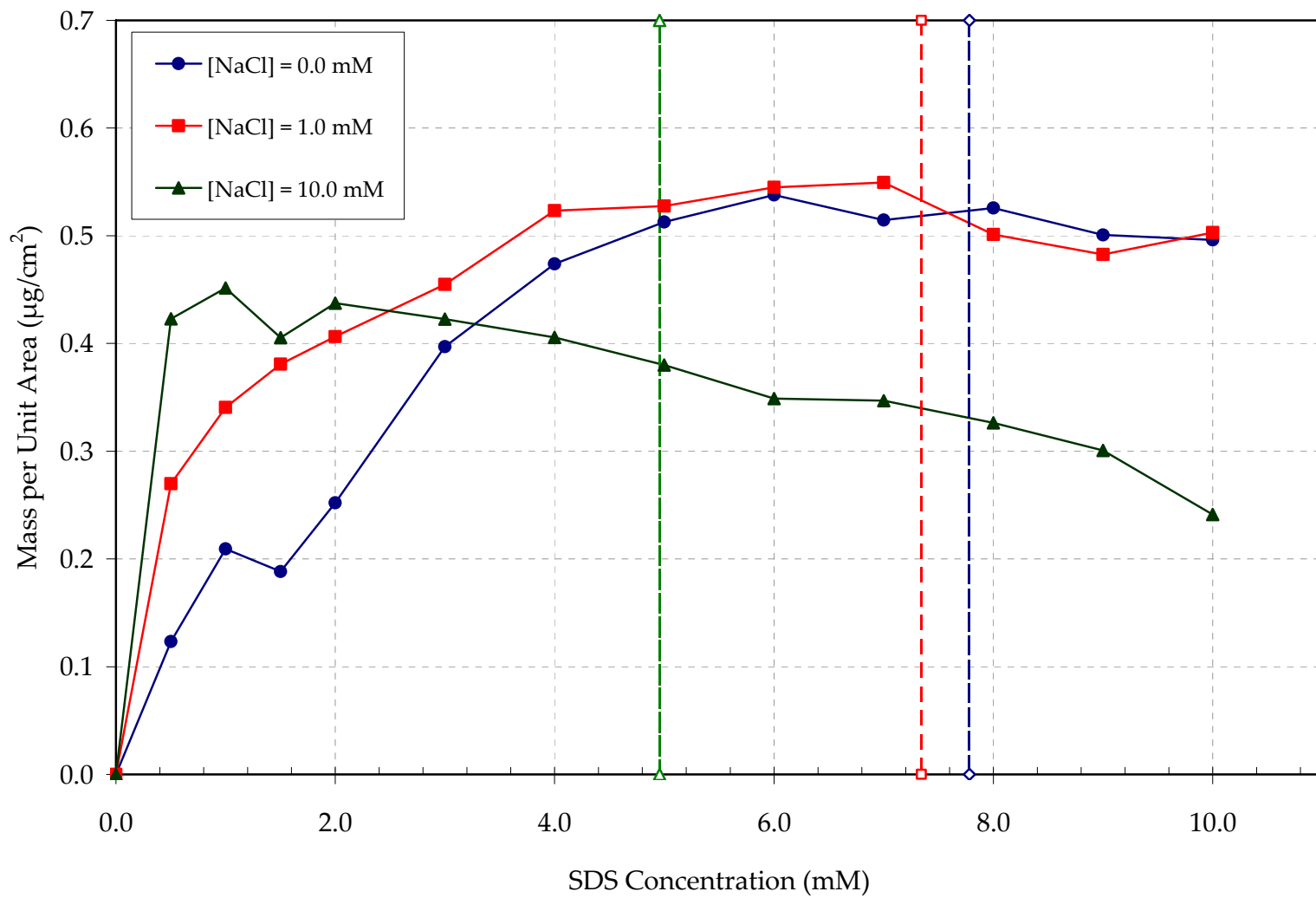
Figure 2.8   Mass per unit area for changing SDS concentration at NaCl concentrations of 0.0 , 1.0, and 10.0 mM

between micelle formation, monolayer formation and increased surfactant adsorption. Relating mass changes to frequency changes also demonstrated the trends in monolayer and multilayer formation predicted by Morton *et al*. The ability to better comprehend these phenomena increases our understanding of the governing principles of cleaning and degreasing. Clearly, there is merit in mixing salt-surfactant solutions to increase adsorption, and thus cleaning efficacy, but there appears to be a limit to the amount of improvement that can be gained by simply adding NaCl and other avenues will need to be explored in order to increase this efficacy.

CHAPTER 3

3.1.0 Future Studies

The purpose of this research was to study adsorption of surfactant molecules from bulk solution on to a gold surface. Future work should include experiments that would study desorption from the surface to the bulk solution. This could be accomplished in a couple different ways.

In the current study, sodium chloride was the salt chosen to interface with the surfactant in solution. A look at different salts with differing anions and cations may cause changes in adsorption levels that would prove beneficial for cleaning applications. For example, sodium bromide, magnesium chloride, magnesium bromide, potassium chloride and potassium bromide would all prove interesting subjects to observe the changes in the charge on the solid surface. This change in the anion and cation will cause the molecules to act in differing manners, either attracting or repelling charges, thus affecting adsorption to the bulk solution.

Another possible avenue for future experimentation would be to explore a change in surfactant. Using different surfactants in this experiment would change the way the aggregation behaves. Any change in aggregation behavior causes a corresponding change in adsorption and may help in making this overall course of study more useful to cleaning applications.

Applying an electric potential to the solution will allow us to look at the electric double layer. An electric double layer is made up of two parallel layers with opposite electrical charge. These two sheets of charge result in a strong electric field and a

correspondingly sharp change in voltage across the double layer. Ions and electrons which enter the double layer are accelerated, decelerated, or reflected by the electric field depending on charge. Applying a potential in varying amounts and in alternating positive and negative charges, would most likely affect adsorption and thus be worth further study.

It would also be worthwhile in the future to improve areas in the current experimentation process. There were several difficulties encountered in the current study, e.g. problems with an adequate flow cell, good temperature control, pump control and pressure control.   Many of these problem could be solved by the implementation of a three pump automated system in place of the current flow cell system. Using three pumps would allow one pump for the DI water, one pump for the appropriately measured surfactant solution, and one pump for the measured salt solution. In addition, automating the apparatus would eliminate previously uncontrollable factors such as changes in temperature and pressure due to ambient temperature changes in the environment around the experiment.

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APPENDICES

Table A1. Equilibrium Method Data Values

NaCl Concentration = 0.0 mM		NaCl Concentration = 0.1mM	
SDS Concentration (mM)	Frequency (Hz)	SDS Concentration (mM)	Frequency (Hz)
0	5008081.1	0	5008046.0
2	5008062.8	2	5007968.0
3	5008053.6	3	5007992.0
4	5008064.6	4	5008051.0
5	5008068.8	5	5008045.0
6	5008069.2	6	5008056.0
7	5008072.0	7	5008064.0
8	5008083.1	8	5008062.0
9	5008076.9	9	5008063.0
10	5008081.0	10	5008072.0
NaCl Concentration = 0.5 mM		NaCl Concentration = 1.0 mM	
SDS Concentration (mM)	Frequency (Hz)	SDS Concentration (mM)	Frequency (Hz)
0	5008045.6	0	5008045.0
2	5008007.6	2	5008026.0
3	5008018.5	3	5008033.0
4	5008045.3	4	5008057.0
5	5008054.0	5	5008063.0
6	5008056.1	6	5008061.0
7	5008060.6	7	5008071.0
8	5008062.0	8	5008081.0
9	5008065.3	9	5008077.0
10	5008065.3	10	5008071.0

Table A1 Continued.

NaCl Concentration = 5.0 mM		NaCl Concentration = 10.0 mM	
SDS Concentration (mM)	Frequency (Hz)	SDS Concentration (mM)	Frequency (Hz)
0	5008088.1	0	5008046.0
2	5008064.0	2	5007968.0
3	5008082.1	3	5007992.0
4	5008089.1	4	5008051.0
5	5008089.3	5	5008045.0
6	5008090.7	6	5008056.0
7	5008088.1	7	5008064.0
8	5008101.0	8	5008062.0
9	5008085.4	9	5008063.0
10	5008092.6	10	5008072.0

Appendix B

Table B1. Flow Cell Method Data For NaCl = 0.0 mM

NaCl Concentration = 0.0 mM			
SDS Concentration (mM)	Frequency (Hz)	Frequency (Hz)	Frequency (Hz)
0.0	4996923.2	4996923.5	4996917.3
0.5	4996915.1	499615.70	4996910.9
1.0	4996911.6	4996910.8	4996906.9
1.5	4996913.1	4996913.0	4996903.5
2.0	4996911.4	4996912.0	4996905.7
3.0	4996897.0	4996906.0	4996901.3
4.0	4996892.8	4996891.9	4996897.1
5.0	4996889.2	499888.4	4996887.0
6.0	4996886.9	4996885.4	4996884.9
7.0	4996886.0	4996889.4	4996883.5
8.0	4996891.6	4996889.4	4996882.5
9.0	4996891.9	4996890.0	4996886.1
10.0	4996892.0	4996889.9	4996889.1

Table B2. Flow Cell Method Data For NaCl = 1.0 mM

NaCl Concentration = 1.0 mM			
SDS Concentration (mM)	Frequency (Hz)	Frequency (Hz)	Frequency (Hz)
0.0	4996917.3	4996919.3	4996915.1
0.5	4996901.3	4996902.7	4996900.5
1.0	4996897.8	4996898.9	4996896.8
1.5	4996894.4	4996895.9	4996893.8
2.0	4996892.3	4996893.1	4996894.2
3.0	4996889.3	4996894.0	4996892.9
4.0	4996886.2	4996892.1	4996890.1
5.0	4996883.1	4996882.4	4996879.6
6.0	4996882.0	4996882.3	4996877.9
7.0	4996881.2	4996881.2	4996876.6
8.0	4996886.1	4996880.2	4996875.2
9.0	4996887.9	4996885.4	4996880.9
10.0	4996888.3	4996886.6	4996882.1

Table B3. Flow Cell Method Data For NaCl = 10.0 mM

NaCl Concentration = 10.0 mM			
SDS Concentration (mM)	Frequency (Hz)	Frequency (Hz)	Frequency (Hz)
0.0	4996908.3	4996905.4	4996957.7
0.5	4996881.9	4996883.8	4996932.6
1.0	4996879.1	4996884.0	4996931.5
1.5	4996882.0	4996874.9	4996930.1
2.0	4996880.3	4996873.7	4996929.6
3.0	4996880.5	4996873.1	4996936.0
4.0	4996875.9	4996880.6	4996933.4
5.0	4996876.3	4996882.1	4996933.2
6.0	4996882.9	4996930.4	4996933.3
7.0	4996884.8	4996930.5	4996933.2
8.0	4996882.9	4996930.8	4996937.2
9.0	4996876.5	4996932.0	4996940.0
10.0	4996877.7	4996937.2	4996932.3

Table B4. Flow Cell Method Data For NaCl = 100.0 mM

| NaCl Concentration = 100.0 mM			
SDS Concentration (mM)	Frequency (Hz)	Frequency (Hz)	Frequency (Hz)
0.0	4996968.9	4996950.8	4996942.8
0.5	4996967.1	4996952.9	4996946.6
1.0	4996963.1	4996947.6	4996943.4
1.5	4996968.9	4996948.0	4996944.9
2.0	4996953.8	4996952.3	4996940.7
3.0	4996953.7	4996946.1	4996940.2
4.0	4996960.6	4996945.6	4996939.9
5.0	4996950.7	4996944.9	4996938.9
6.0	4996952.5	4996943.6	4996944.8
7.0	4996951.9	4996947.9	4996939.0
8.0	4996957.0	4996943.8	4996938.6
9.0	4996951.3	4996943.2	4996938.3
10.0	4996951.2	4996946.8	4996937.1

Appendix C
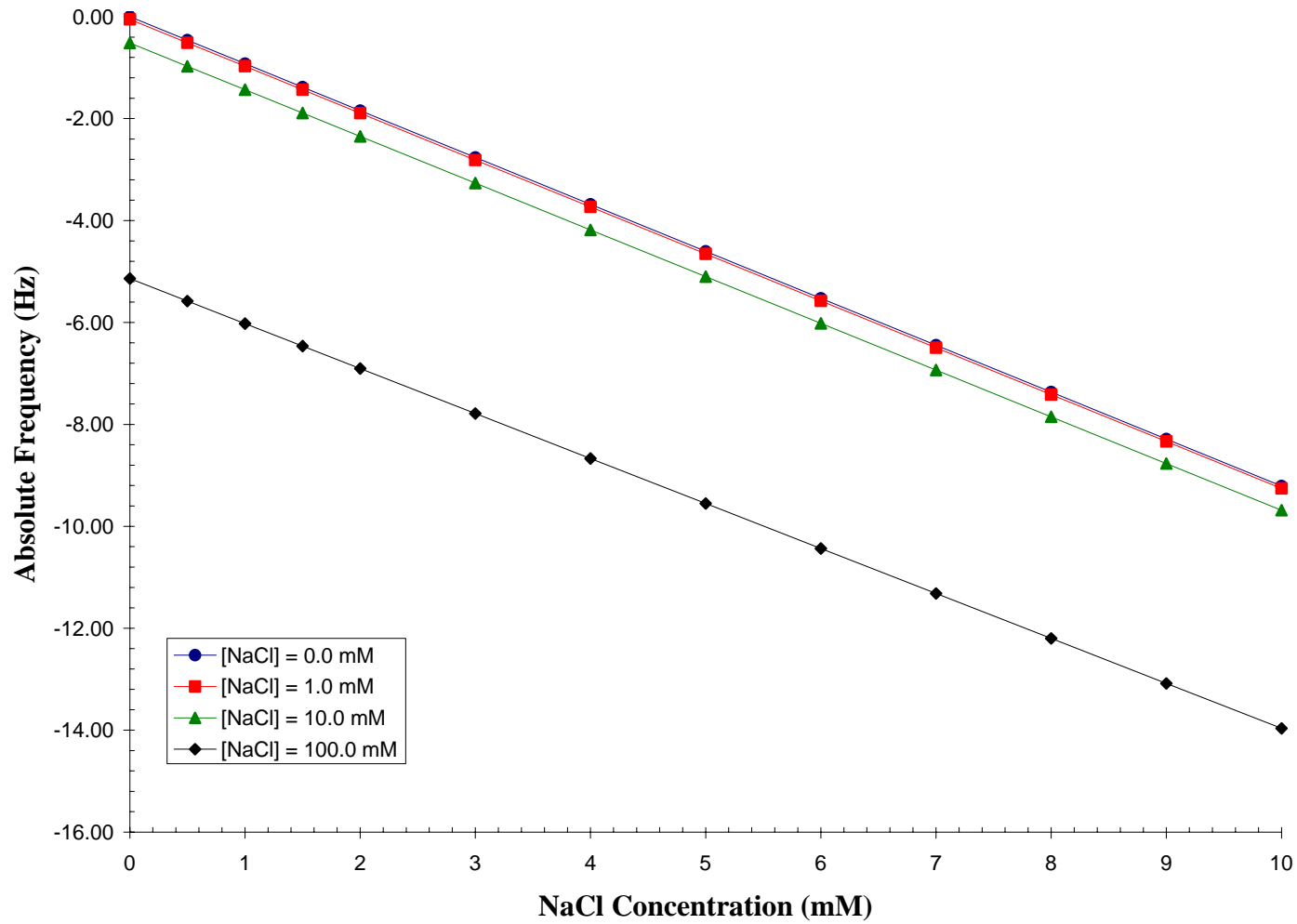
Figure C1. Effective Frequency Change Due to Solution Density and Viscosity Changes.

VITA

Shannon Joanne Ray was born on August 9th, 1979 in Oak Ridge, Tennessee, to parents Anne Laurel and John Michael Ray. Her father was a high school biology and chemistry teacher, football coach, and later a public health and safety consultant; her mother was a high school mathematics teacher. She grew up on a small cattle farm in Spring City, Tennessee, with her three sisters. At age 8, she moved to Chattanooga, followed four years later by a move to Knoxville, Tennessee, where she attended Farragut High School, was a member of the band, and enjoyed her history, honors english, and physics classes. After graduation in May 1997, she enrolled at Tennessee Technological University in Cookeville, Tennessee. After her first year at TTU, she chose to serve her country and enlist in the United States Air Force, specializing in combat communications. While in the armed forces her job was to set-up internet and phone lines for fighting wings. When she returned to college the next year she majored to mechanical engineering based on her experiences in the military. Shortly after returning to college in August 2001, she was called to active duty service with the 228th Combat Communications Division in response to the terrorist bombings in New York City on September 11th, 2001. She served bravely for six months in the deserts of Qatar. She graduated in May 2004 with a Bachelor of Science degree in mechanical engineering and continued on to receive her Masters of Science degree in chemical engineering at the University of Tennessee, Knoxville. She studied surfactant adsorption from aqueous electrolyte solutions onto metal surfaces using a Quartz Crystal Microbalance (QCM) under the direction of Professor Robert M. Counce.