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Effects of Electrolyte Concentration on Surfactant Adsorption to a QCM Immersed in Surfactant + Electrolyte Solutions

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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., directed toward the development of a thermodynamically-based model of oil removal from metal surfaces. These modeling efforts utilized existing data on surfactant adsorption data, yet required the estimation of surfactant adsorption phenomena, such as the transition between monolayer adsorption and multi-layer adsorption and the location of the critical micelle concentration (CMC). Experimental techniques utilizing the quartz crystal microbalance (QCM) have been shown to be highly reliable for measuring slight changes, on the order of a nanogram, in the adsorption behavior of surfactants from aqueous solutions. The current study demonstrates that the addition of low concentrations ($< 100\,\text{mM}$) of sodium chloride to aqueous solutions of ionic surfactant can have a significant effect on the adsorption of the surfactant to a gold surface. An analysis of the QCM measurements as well as a discussion of the effects of salt addition on various solution properties will be presented. Impacts of the current results to previously published work as well as potential applications will be discussed.

Keywords: Adsorption, critical micelle concentration, electrolyte, quartz crystal microbalance, surfactant

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INTRODUCTION

The adsorption of surfactants on solid surfaces is a key phenomenon in the cleaning and degreasing of metal surfaces. Morton et al. (1–6) 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 (1–6). 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. (7,8) 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. (1–6) was designed to predict the changes in contact angle at small surfactant and electrolyte concentrations. The reverse orientation model described by Fan et al. (9) offers a possible explanation of the adsorption phenomena present within a surfactant/salt solution and was used in the development of Morton's model. 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.

The model presented by Morton (9) required an assumption wherein the transitions between Region B and C were related to a critical aggregation concentration that linked the solid/solution aggregate structure to the concentrations of salt and surfactant in the solution. This assumption was qualitatively justified by extending the effects that increasing salt concentrations were known to have on the packing density of the solution aggregate (micelle) to a representation of the packing density of the solid surface aggregate (monolayer). 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. (1–6).

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 (10). This relationship is shown as:

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

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 (10). This equation is often simplified through the application of a linear sensitivity factor, C_f, as shown in the following equation:

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

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, $C_f = 56.6\,\text{Hz}\ \mu g^{-1}\,\text{cm}^2$, 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, 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 (monolayer), the Sauerbrey equation looses it validity. Therefore, another useful form of the

Sauerbrey equation was developed as seen below:

$$\frac{\Delta f}{f_0} = \frac{\Delta m}{m} \tag{4}$$

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 (10). 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,

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

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 (11). 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 (11).

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,

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

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 (12), 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 the 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.

EXPERIMENTAL

Materials and Equipment

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).

Experimental Method

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 (10–11).

ANALYSIS 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 Fig. 1, were performed for a 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

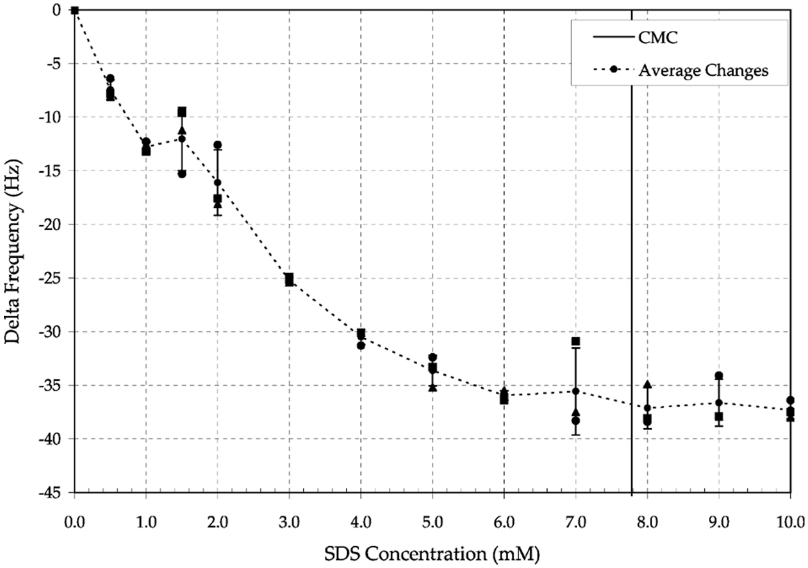

Figure 1. Changes in QCM frequency relative to SDS concentration in the absence of NaCl.

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. (1,6). Beyond the CMC, the change in frequency becomes essentially constant.

Figure 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 the was zero. For this NaCl concentration, the surfactant adsorption reaches its maximum closer to 7.0 mM SDS instead of 8.0 mM SDS as in Fig. 1. The second difference is that the 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 Fig. 3. The findings for this data set agreed with those observed in the

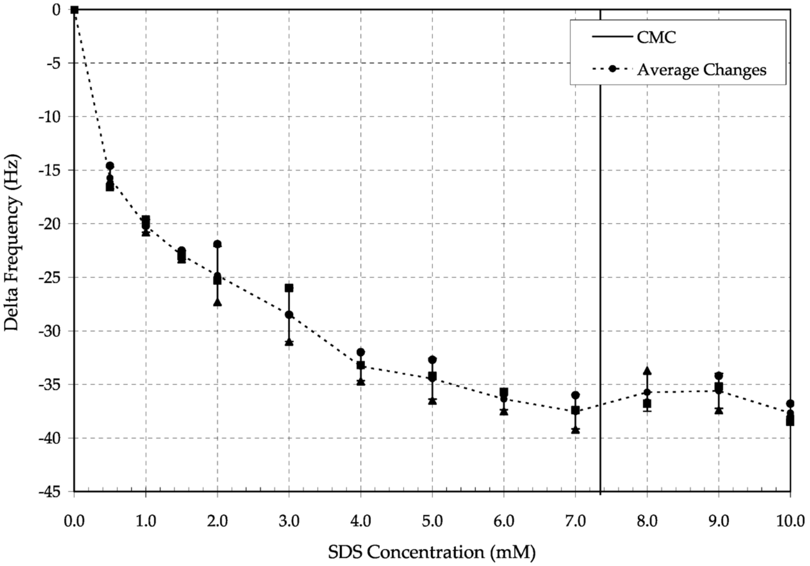

Figure 2. Changes in QCM frequency relative to SDS concentration for a NaCl concentration of 1.0 mM.

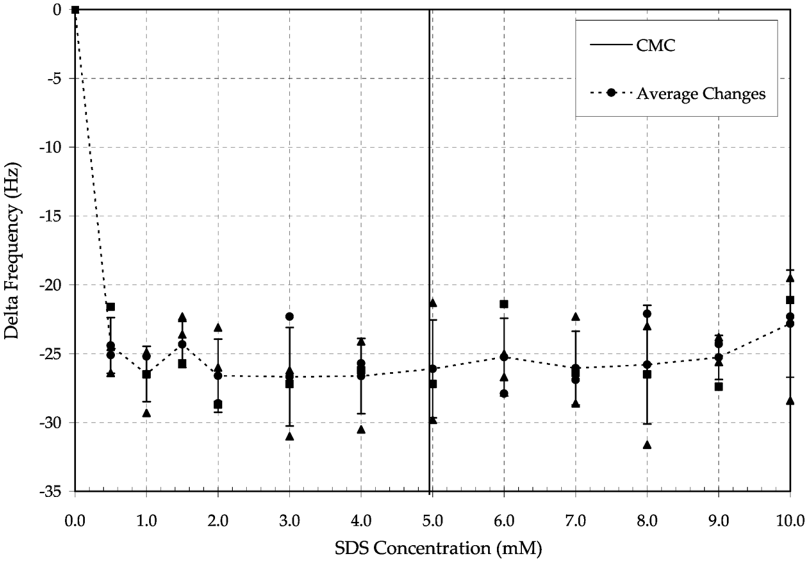

Figure 3. Changes in QCM frequency relative to SDS concentration for a NaCl concentration of 10.0 mM.

previous two data 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 3 shows that the 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 Fig. 4, vary greatly from that of the previous NaCl concentrations. Ats 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 is highly suspect. 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.

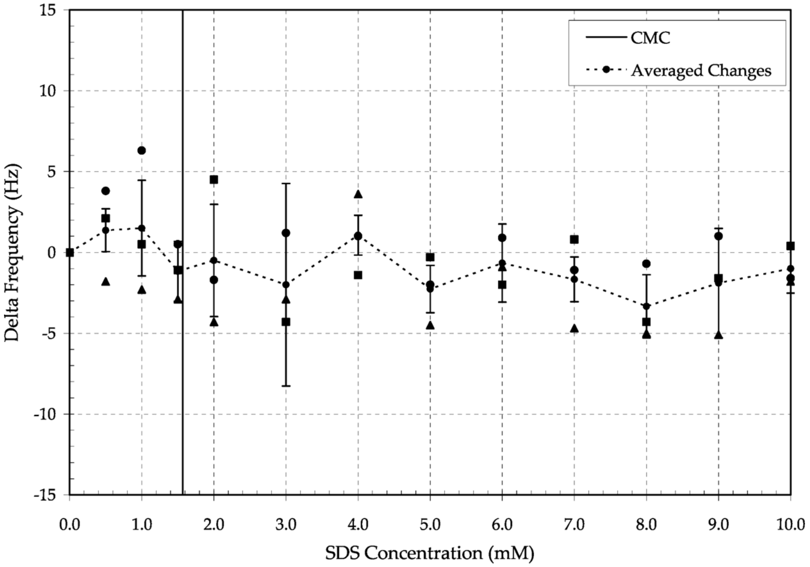

Figure 4. Changes in QCM frequency relative to SDS concentration for a NaCl concentration of 100.0 mM.

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 Fig. 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 (12). Therefore, Fig. 6 shows a comparison of each of the averaged data sets, this time taking into account density and viscosity effects. This plot was created by applying a correction for density and viscosity effects on the solution relative to changes in SDS concentration for each of the NaCl concentrations (13–14). 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 (11). Density and viscosity data for the necessary concentrations of SDS and NaCl were obtained from the work of Afroz et al. (15). 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 (15). From the corrected plot, it is evident that 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

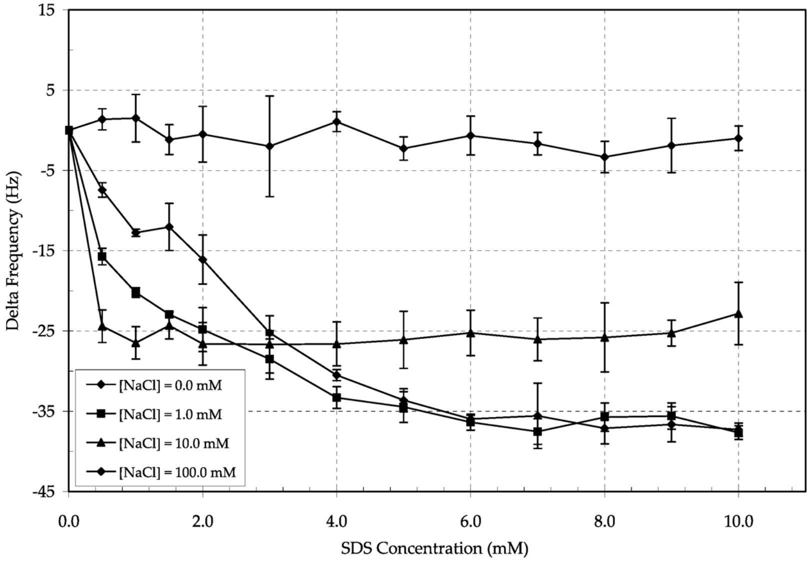

Figure 5. Comparison of frequency changes for all data sets.

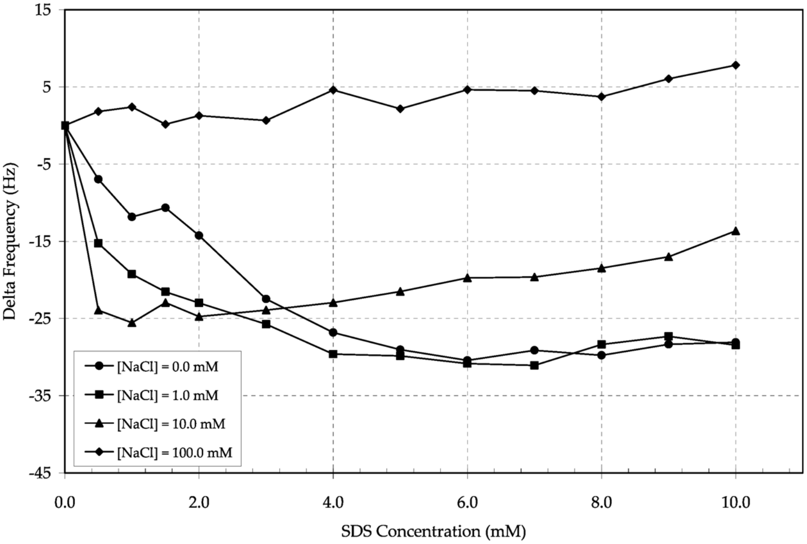

Figure 6. Comparison of frequency changes with correction for density and visocity changes in solution.

frequency, the measured results exceed any density and viscosity effects present in the environment.

Comparing the three 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 phenomenon occurring during this experiment, it is necessary to relate the observed trends to the model presented in Morton et al. (1,6). Morton's model assumed that the transitions between Region B and Region C could be characterized by changes in the adsorption of surfactant to the solid surface in much the same way that the transition between Region C and Region D can be characterized by the formation of micelles. A second assumption related the shifting of both the Region B to Region C and the Region C to Region D transitions directly to the concentrations of salt present in the solution. These assumptions have been given greater strength (although not absolutely confirmed) by the data presented above.

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. (1,6). 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. Through 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:

$$\frac{m}{A} = \frac{\Delta F}{-C_f} \tag{7}$$

This equation allows us to relate the change in mass per unit of area to the frequency changes that are a measurable quantity (10). Figure 7

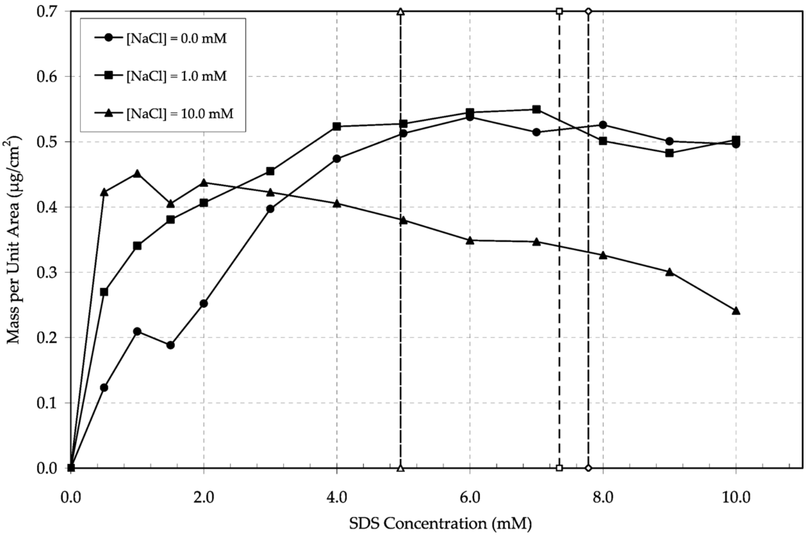

Figure 7. Mass per unit area for changing SDS concentration at NaCl concentrations of 0.0, 1.0, and 10.0 mM.

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.

CONCLUSIONS

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 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. 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.

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