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

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Abstract: A theoretical approach to predict equilibrium 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 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.

Keywords: Contact angle, surfactant, adsorption, surface cleaning, ionic strength, interfacial tension, hexadecane, critical micelle concentration, sodium dodecyl sulfate, cetyl trymethyl ammonium bromide, sodium chloride, salt

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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 (29–31) 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 similar 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 improved model is then compared to experimental studies from Davis et al. (23, 24).

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 is present 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) as well as this current article. Understanding the nature of self-assembly processes, that they 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 formation of organic solid surface contact angles. It is evident from the experimental data presented by Davis that equilibrium contact angles exhibit a complex relationship to aqueous surfactant concentration and ionic strength. 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 Fig. 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.

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 it was developed for salt free conditions and does not provide direct guidance as to a method for incorporating the observed effects. Upon further study a possible empirical solution to the problem becomes evident. In the determination of the deformational free energy contribution (ΔG_{def}) Nagarajan and Ruckenstein present an earlier empirical relationship used to assist in the fitting of the CMC based on experimental data. This empirical relationship:

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

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 to as follows:

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

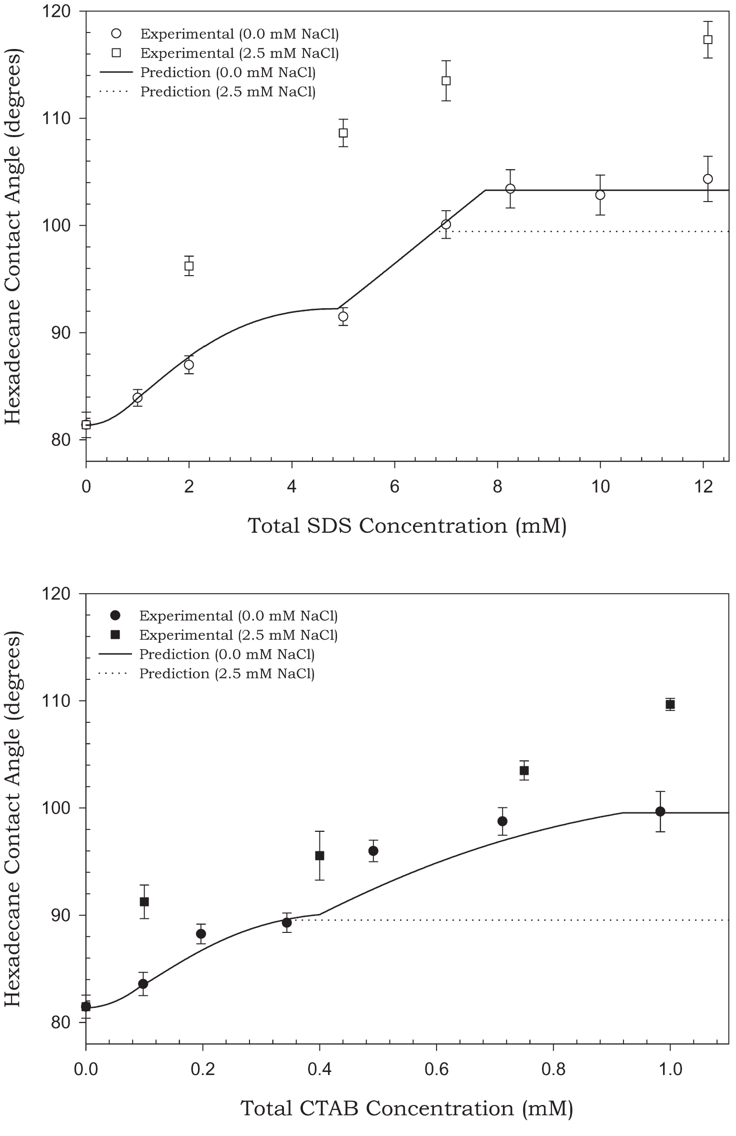

Figure 1. Model performance prior to modification to account for effects of salt on self-assembly processes.

where Φ_{CMC} becomes a parameter describing the dependence on salt concentration. It is not directly intuitive 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 effects relative to the micelle surface and the bulk solution and the steric free energy contribution (ΔG_{str}) is exclusively 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 in that as the surface area decreases the volume of the micelle decreases and the impacts of the tail chain deformation increase as an indirect function of solution ionic strength.

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). 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 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). Suffice it to say 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.

Solid/Solution Interfacial Surfactant Aggregation

The remaining balance is concerned with the distribution of surfactants between the bulk and the aggregate formed at the solid/solution interface. It follows from Fig. 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 as well as the interactions between aggregated surfactant monomers. To account for this effect the previous model (31) must be modified to include a semi-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 incorporation of a dependence on solution ionic strength for the solution/solid aggregation component is analogous to the use of the Debye screening length in the models developed for micellization (34). 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 the 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 maxima 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, $w_{22\text{-}RC}$. 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:

$$w^{salt}_{22-RC} = U^{salt}_{2}(A^{salt}_{RC} - B^{salt}_{RC}C_{surfactant}) \tag{5}$$

which will result in salt dependence for the A_{RC} and B_{RC} constants reflected in A^{salt}_{RC} and B^{salt}_{RC} 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.

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 broad enough range for the generation of correlations and trends in the low salt concentration ranges studied in the Davis's work. Figures 2 and 3 show the 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 and 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

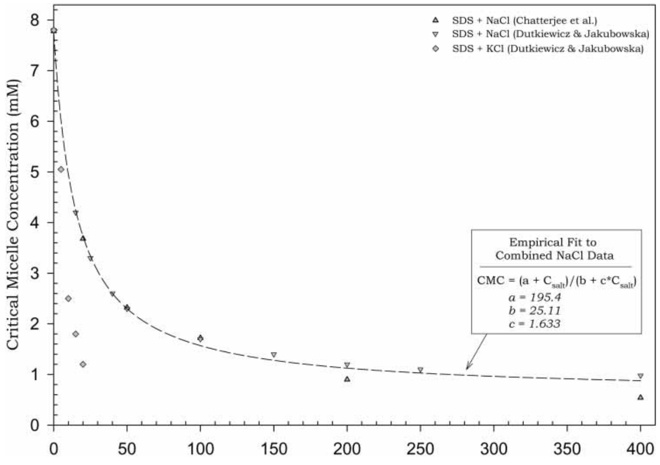

Figure 2. Effect of 1:1 electrolytes on the CMC of SDS.

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.

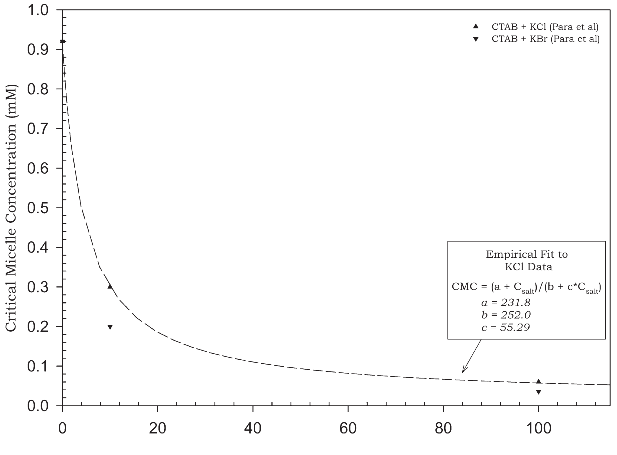

Figure 3. Effect of 1:1 electrolytes on the CMC of CTAB.

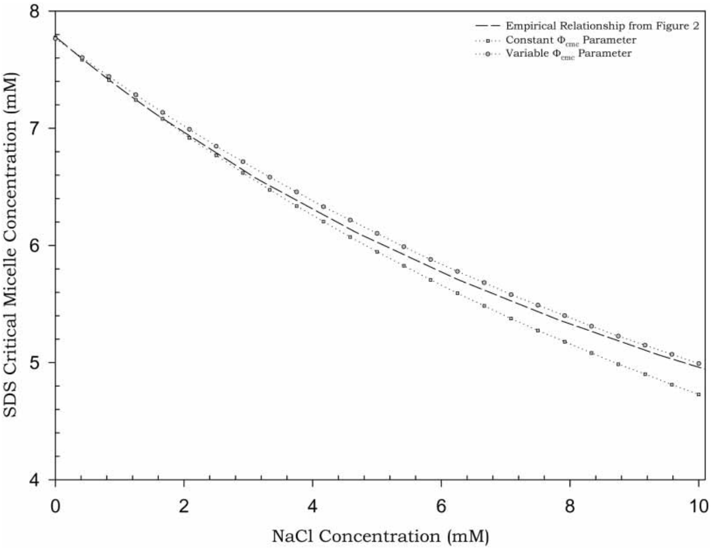

Figure 4. Model prediction for the impact of NaCl on SDS CMC.

SDS and 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 Fig. 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 determined and is shown in Fig. 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 was determined for the optimized values of Φ_{U2} and is shown in Fig. 6. From this we can imply that as the salt concentration increases, the effective surfactant-solid interaction increases.

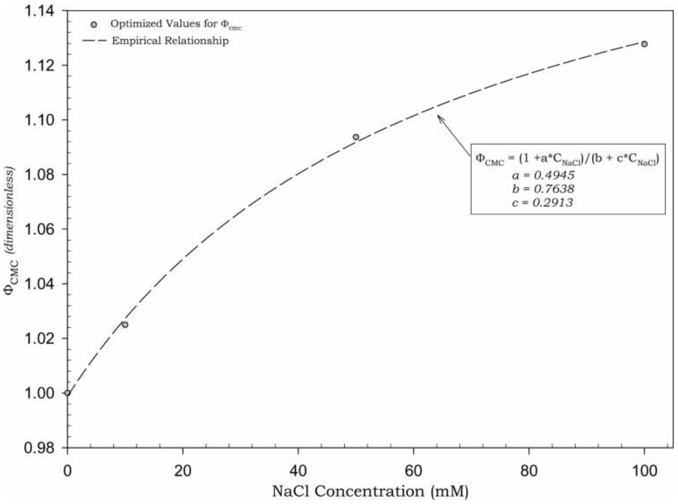

Figure 5. Analysis of NaCl concentration effects on the salt dependent CMC parameter.

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

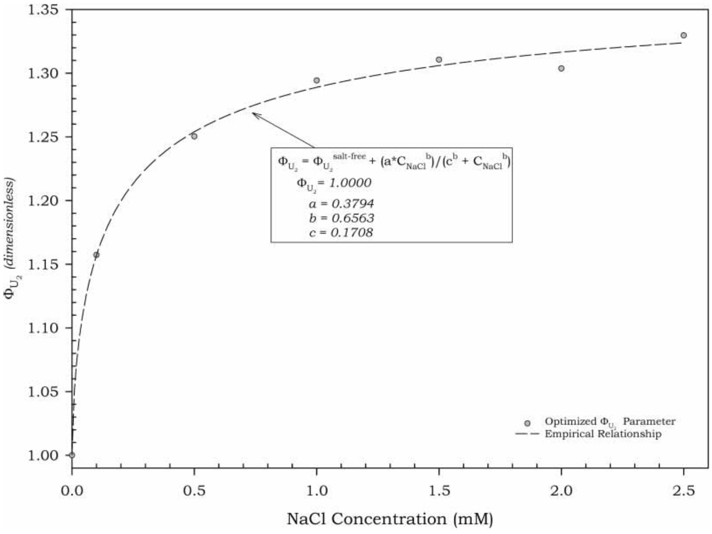

Figure 6. Impact of NaCl on the salt dependent surfactant/solid interaction parameter for a SDS/gold system.

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 Fig. 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 Fig. 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 to the SDS solution experimental data from Davis et al. (23) in Figs. 8 and 9. Not only do these figures demonstrate that the model's prediction is greatly improved from Fig. 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.

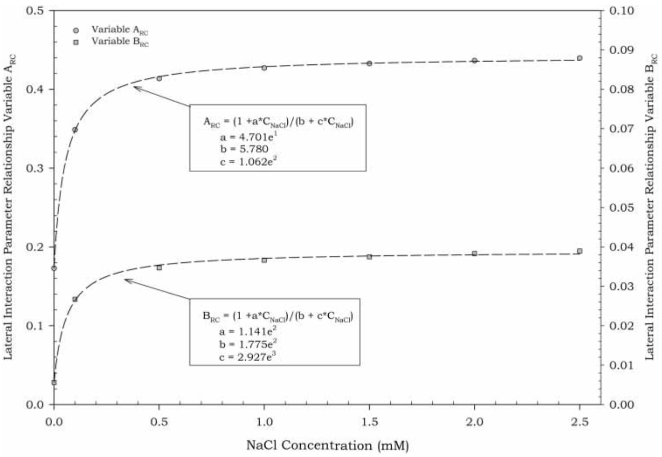

Figure 7. Effect of NaCl on the surfactant concentration dependent relationship for w_{22} in region C.

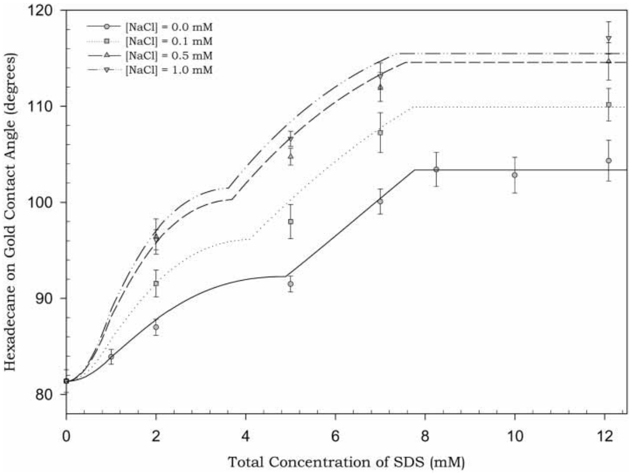

Figure 8. Experimental and predicted hexadecane contact angles in SDS/NaCl solutions: 0.0 mM to 1.0 mM NaCl.

CTAB and 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

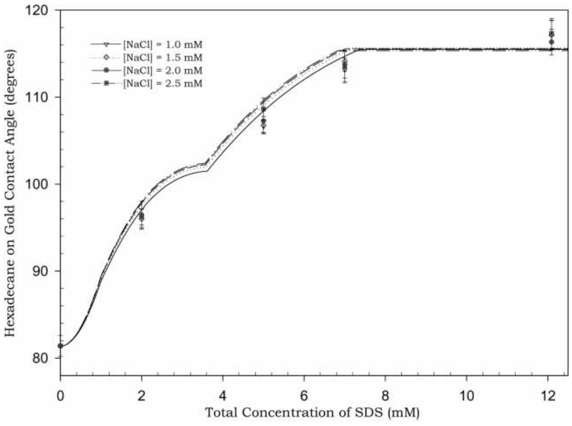

Figure 9. Experimental and predicted hexadecane contact angles in SDS/NaCl solutions: 1.0 mM to 2.5 mM NaCl.

system, shown in Fig. 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 computational 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 Fig. 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 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

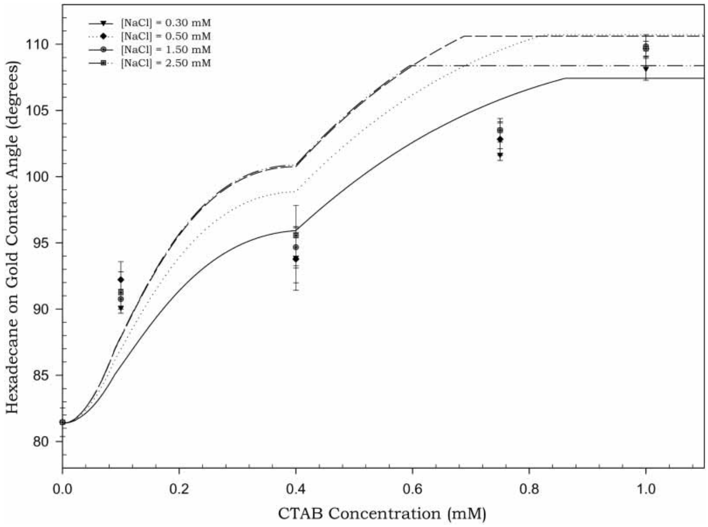

Figure 10. Experimental and predicted hexadecane contact angles in CTAB/NaCl solutions: 0.3 mM to 2.5 mM NaCl (based on KCl CMC empirical relationship).

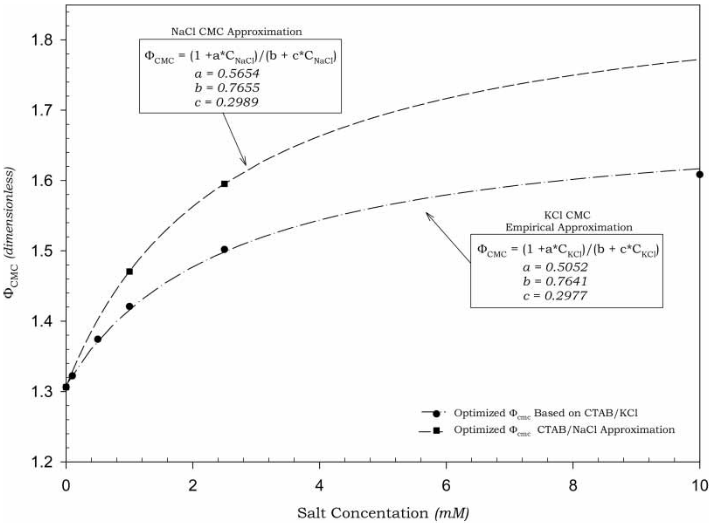

Figure 11. Estimation of improved Φ_{CMC} for CTAB/NaCl solutions.

CTAB/NaCl system is of a similar degree to the SDS/NaCl system, approximate values for the Φ_{CMC}, Fig. 11, and the Φ_{U2}, Fig. 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

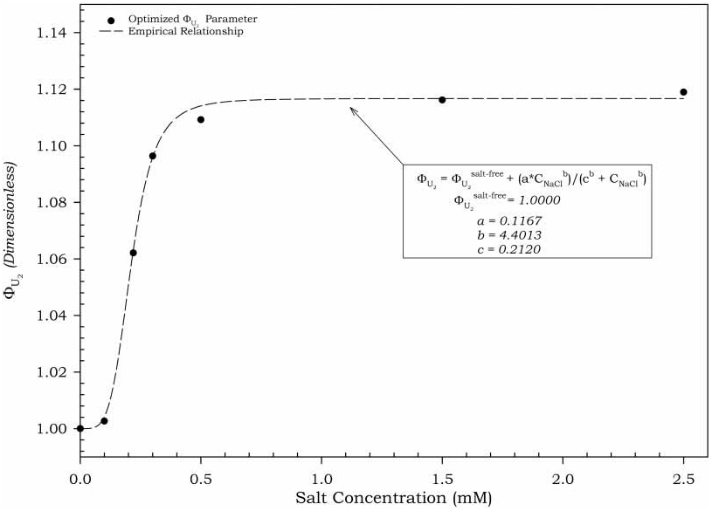

Figure 12. Estimation of surfactant/solid interaction parameter using the improved CMC approximation.

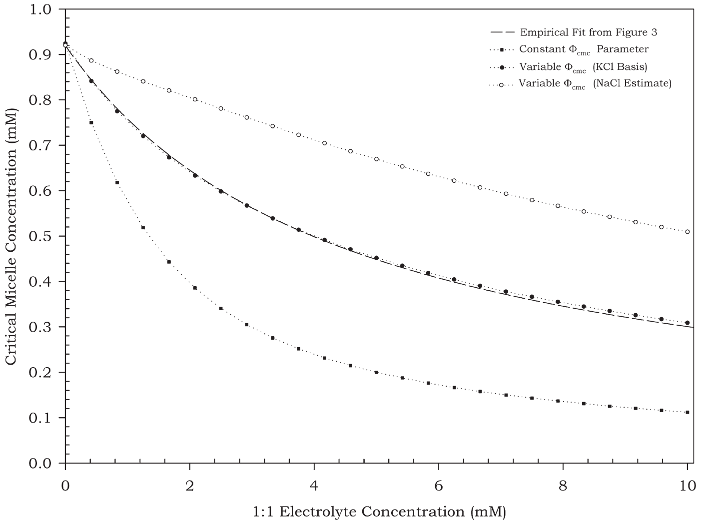

Figure 13. Model predicted values for the CMC of CTAB solutions as affected by salt in low concentration.

these optimized relationships, the model predicted contact angles for hexadecane on gold in CTAB/NaCl solutions are shown in Figs. 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

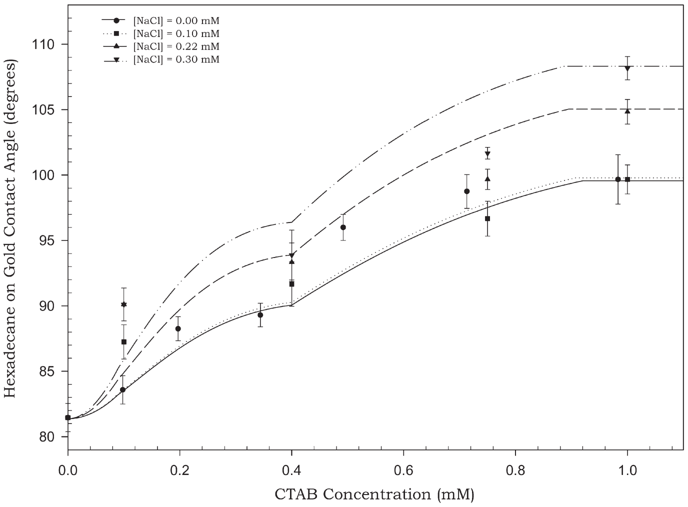

Figure 14. Experimental and predicted hexadecane contact angles in CTAB/NaCl solutions: 0.0 mM to 0.3 mM NaCl (based on improved CMC empirical relationship).

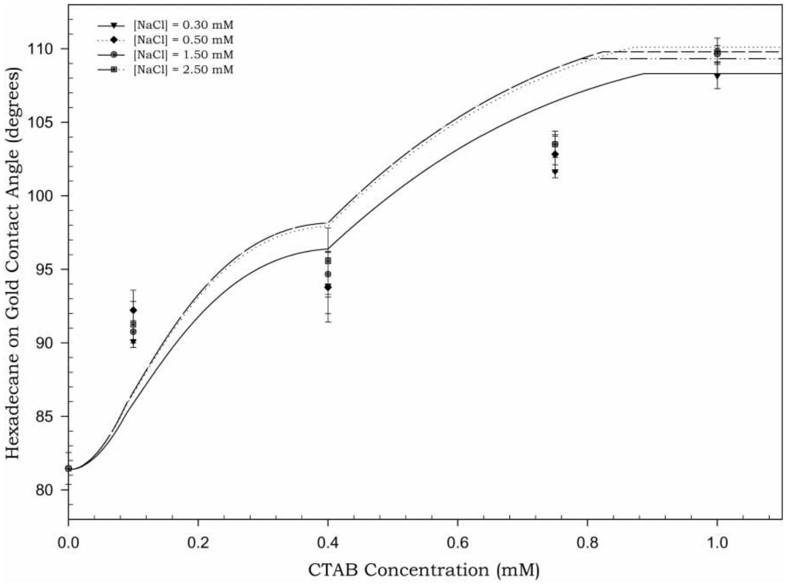

Figure 15. Experimental and predicted hexadecane contact angles in CTAB/NaCl solutions: 0.3 mM to 2.5 mM NaCl (based on improved CMC empirical relationship).

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 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.

CONCLUSIONS

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 improvements presented in this work are semi-empirical in nature and as such do pose some concerns for the broader applications of our approach. The complexity of the systems analyzed in this work dictates that the approach taken be more than a simple empirical fit. To this end, data from a number of sources was employed to augment the model (surface tension data to provide validation of the solution/organic interface change, CMC data to provide validation of the limit for continued surfactant aggregation in at the solution/organic and solution/solid interfaces, etc.); therefore, the model as presented relies on empirical parameters only to incorporate the information presented in qualitative models for surface adsorption in an effort to bridge the gaps in the data present in the literature. The empirical factors employed do not have a clear meaning from a deeper theoretical viewpoint at this time; however, it is the goal of the model as presented to serve as a primary step toward a fundamental understanding of the phenomena observed.

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 1 M. 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. It is clear however, that 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.

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