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

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Abstract: We report the results of a theoretical study of the complex phenomena relating to contact angle changes for hexadecane droplets on a gold surface in aqueous ionic surfactant solutions. This approach integrates changes in the nature of the solid absorbed surfactant phase through use of the quasi-chemical approximation. This improvement is accomplished with minimal additional model complexity and provides evidence for changes in adsorbate structure as aqueous surfactant concentration is increased. The theoretical predictions are tested using previously published data regarding the contact angle of hexadecane on gold in sodium dodecyl sulfate and cetyl-trimethylammonium bromide solutions.

Keywords: Contact angle, ionic surfactant, interfacial tension, quasi-chemical approximation, surface adsorption, surfactant aggregation

INTRODUCTION

Contact angle measurements play an important role in the study of interfacial phenomena. Such measurements can be used to determine numerous

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

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

$$\cos(\theta) = \frac{\gamma_{\mathrm{s/a}} - \gamma_{\mathrm{s/l}}}{\gamma_{\mathrm{l/a}}} \tag{1}$$

where θ is the contact angle, $\gamma_{\mathrm{s/a}}$ is the solid/liquid (bulk) interfacial tension, $\gamma_{\mathrm{s/l}}$ is the solid/liquid(adsorbed) interfacial tension, and $\gamma_{\mathrm{l/a}}$ is the liquid (adsorbed)/liquid(bulk) interfacial tension. Elongated droplets do not lend themselves to analysis by the Young's equation. Contact angles are routinely measured for such elongated droplets through the use of axisymmetric drop shape analysis (ADSA) technique, which fits the shape of the drop numerically using the Young-Laplace equation. Chatterjee (2) discusses such droplets and provides an analytical approach to drop shape and links this to detachment. Another resource for ADSA can be found in the work of Kwok and coworkers (3, 4). For droplets examined in this present article only spherical shapes were observed and as a result only Young's equation [Eq. (1)] is required for analysis.

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

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

ANALYSIS OF CONTACT ANGLE AND INTERFACIAL TENSION DATA

From Young's equation, the inversely proportional relationship between the cosine of the contact angle and the interfacial tension at the organic/solution interface is obvious. It should be possible to determine if droplet shape changes are due simply to changes in organic/solution interfacial tension or if other factors such as solid/solution interfacial adsorption and aggregate structure exhibit a demonstrative effect. Such a determination could then validate the use of contact angle data to interpret liquid(bulk)/solid interfacial phenomena in liquid/liquid/solid systems.

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

Figure 1 shows the reported contact angle and interfacial tension data for hexadecane droplets in an aqueous SDS solution while Fig. 2 shows the reported data for hexadecane in aqueous CTAB solutions. From these figures it is obvious that the general inverse proportionality of contact angle and interfacial tension is true. It is important to note that the curve shape of

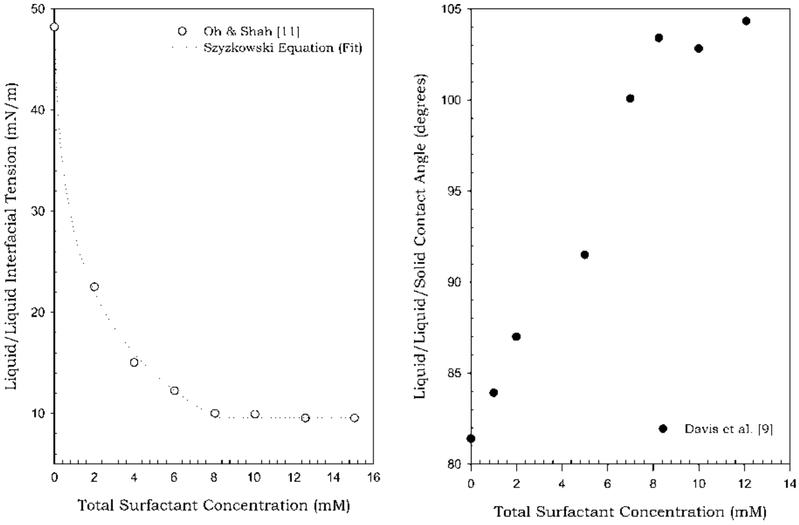

Figure 1. Interfacial tension and contact angle data for hexadecane/SDS solution.

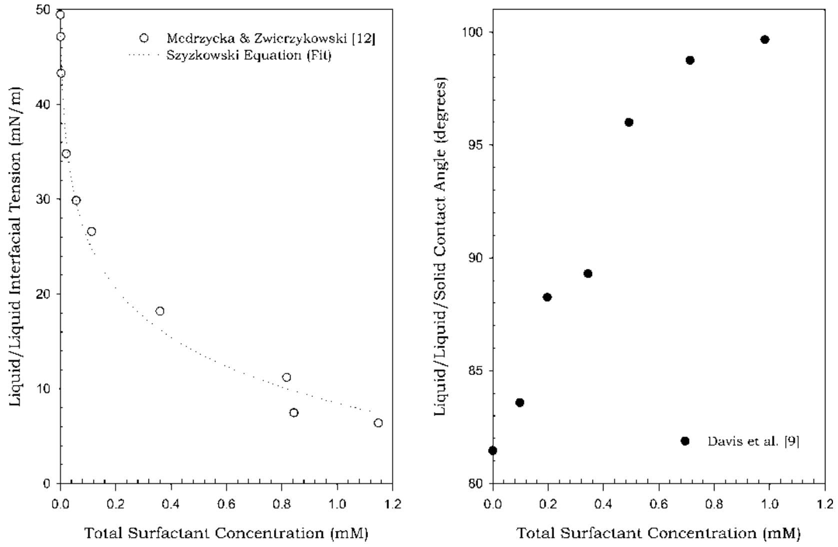

Figure 2. Interfacial tension and contact angle data for hexadecane/CTAB solution.

the contact angle data set does not mirror the shape of the interfacial tension data set. By rearranging Young's equation as follows:

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

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

$$\gamma_{l/a} = \gamma^{\circ}_{l/a} - \mathrm{RT}\Gamma^{\infty}\ln\left(1 + \frac{\mathrm{c}}{\mathrm{A}}\right) \tag{3}$$

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

After including the contact angle and liquid/liquid interfacial tension data into the modified form of Young's equation (Eq. (2)) the effect of surfactant concentration on the solid/liquid interfacial tensions can be determined.

Table 1. Szyzkowski equation parameters for SDS/hexadecane and CTAB/hexadecane interfacial tension data

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

Figure 3 shows the left-hand side of Equation (2) for both the SDS and CTAB datasets. From this figure it is evident that the trend observed in the contact angle data is manifested in the difference between the solid/liquid interfacial tensions. Davis et al. (9) first introduced the organic to the solid surface, allowed time for wetting, and then immersed the solid in the aqueous surfactant solution. The benefit from this is that the solid/liquid(adsorbed) interfacial tension, $\gamma_{s/l}$, may be assumed to be essentially constant, therefore the inflection observed in the contact angle data must be due to a subsequent inflection in the solid/aqueous interfacial tension, $\gamma_{s/a}$. Such an inflection would be logically due to a change in the adsorbed surfactant aggregate

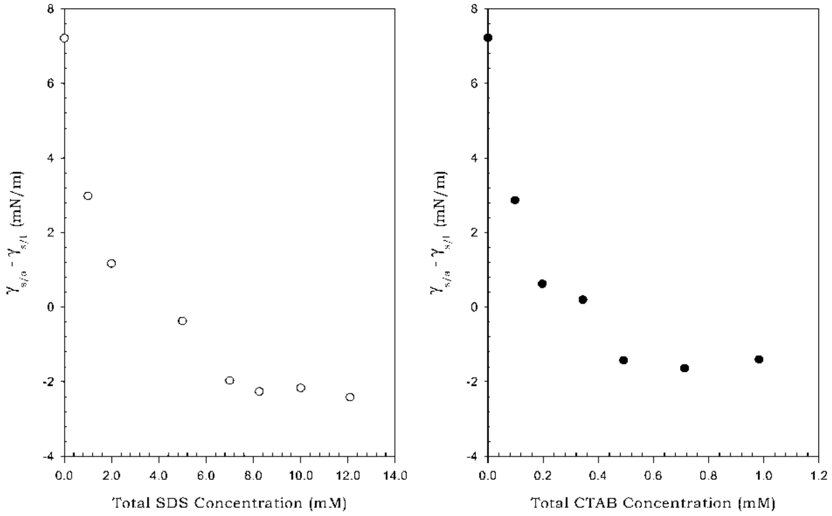

Figure 3. Analysis of modified young's equation for hexadecane/SDS and hexadecane/CTAB.

structure and increased competition for adsorption sites with the organic. This phase change in the adsorbed surfactant aggregate is supported by the work of Fan et al. (14), Goloub and Koopal (15), Somasundaran and Krisknakumar (16), and Drelich (17). These representative articles discuss the phenomena related to the adsorption of surfactants to various surfaces.

Fan et al. (14) discuss the adsorption of surfactant in terms of the reverse orientation model. This model, first proposed by Somasundaran and Fuerstenau (18), separates the adsorption of surfactant into four regions. In Region A, surfactants adsorb to the surfaces due to electrostatic considerations and display no obvious aggregation behavior. Region B surfactant adsorption shows the first indication of self-assembly behavior with progression toward a monolayer near the onset of Region C. Surfactants continue the self-assembly behavior in Region C progressing toward a bilayer near the onset of Region D. Region D falls above the critical micelle concentration (CMC) for the surfactant where additional surfactant introduced to the system is entrained in the formation of solution aggregates. We will utilize a similar adsorption region concept for the reevaluation of our previous approach to predicting contact angles of oils on metal surfaces in ionic surfactant solutions presented in this article.

THEORY AND MODEL

In our previous modeling work (10) a system of 5 component balances was developed to describe the redistribution of components in an oil/solution/solid system. The balances encompassed the partitioning of surfactant between solutions aggregates, the oil/solution interface, and the solid/solution interface, the partitioning of water between the solid/solution interface, and the partitioning of oil between the oil/solid interface. The balances pertaining to component adsorption/desorption to and from the solid surface are of particular interest to this current work. A detailed discussion of the input and output characteristics and requirements for the model is presented in an earlier work (10) and will not be repeated here. In the original work there were two preeminent assumptions:

1. with limited adsorption sites competition for sites must occur, and
2. surfactant adsorption behavior can be described by the Langmuir isotherm.

Using the indication of surfactant phase change, both from the literature and experiment, a revision of this second assumption is due.

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

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

$$\mu_i^{ad} = \mu_i^{bulk} \tag{4}$$

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

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

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

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

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

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

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

$$\mu_i^{ad} = \left(\frac{\partial \ln Q}{N_i} \right) \tag{7}$$

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

The total partition function for our model system is the product of three terms:

1. the configurational degeneracy,
2. the intra-site partition function, and
3. the energetic interactions due to neighboring atoms.

The general form for this relationship is as follows:

$$Q(N, M, T) = g(N, M)\, q_s(T)\, q_N\,(N_{xy}) \tag{8}$$

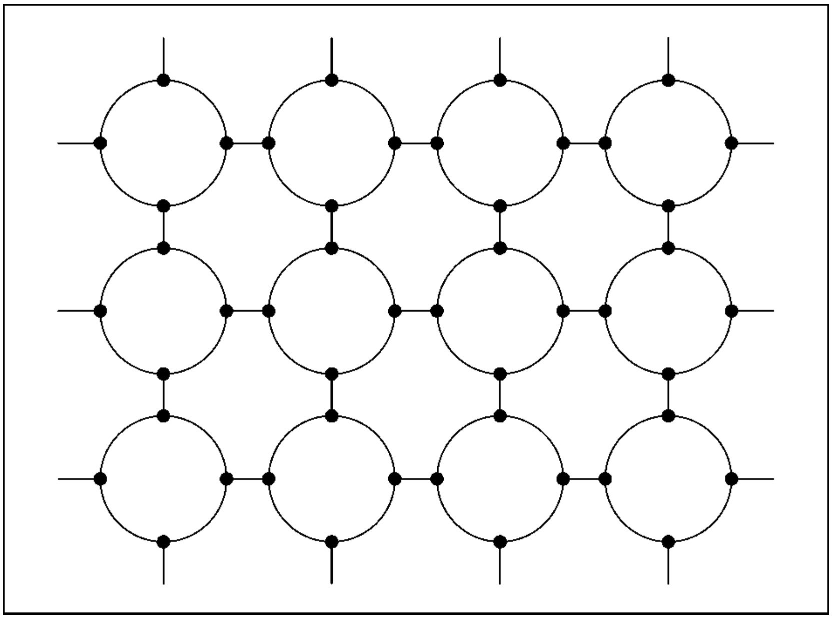

Figure 4. Hypothetical adsorption site lattice configuration.

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

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

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

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

$$\mathrm{M} = \mathrm{N}_1 + \mathrm{N}_2 + \mathrm{N}_3 \tag{10}$$

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

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

$$\mathrm{N}_{\mathrm{xy}} = N_{\mathrm{yx}} \qquad \text{where } \mathrm{x} \neq \mathrm{y} \tag{11}$$

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

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

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

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

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

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

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

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

where w_{11} is the lateral interaction parameter for water-water interactions, w_{22} is the lateral interaction parameter for surfactant-surfactant interactions, w_{33} is the lateral interaction parameter for oil-oil interactions, and w_{12}, w_{13}, and w_{23} are determined as follows:

$$\mathrm{W_{xy}} = \sqrt{\mathrm{W_{xx}W_{yy}}} \quad (18)$$

The intra-site partition function term, $q_S(T)$, is defined by the following function:

$$q_s(T) = \prod_{i=1}^{3} q_i^{N_i} = q_1^{N_1} q_2^{N_2} q_3^{N_3} \quad (19)$$

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

$$\mathrm{q_i} = \frac{\mathrm{V_{site}}}{\Lambda_i} e^{\left(\frac{-U_i}{k_b T}\right)} \quad (20)$$

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

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

$$q_N(N_{xy}) = \exp\left(\frac{\sum_{x=1}^{n}\left(N_{xx}w_{xx} + \sum_{y=1}^{n}\frac{N_{xy}w_{xy}}{2}\right)}{k_b T}\right) \quad (21)$$

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

With the total partition function defined the chemical potentials for the adsorbed water and surfactant molecules can be generally calculated as follows:

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

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

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

RESULTS AND DISCUSSION

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

Since the Langmuir case neglects lateral adsorbate-adsorbate interactions it is necessary to evaluate the model results when the Langmuir assumption is replaced with the quasi-chemical approximation. As surfactants are known to exhibit self-assembly behavior while hexadecane and water do not, it is a reasonable assumption that only the surfactant molecules will exhibit an affinity for one another. This affinity can be established in the presented model by selecting a new value for the surfactant-solid interaction parameter, $U_{2,}$ and a value for the surfactant-surfactant interaction parameter, w_{22}. Figure 6 shows the results for this approach for both SDS

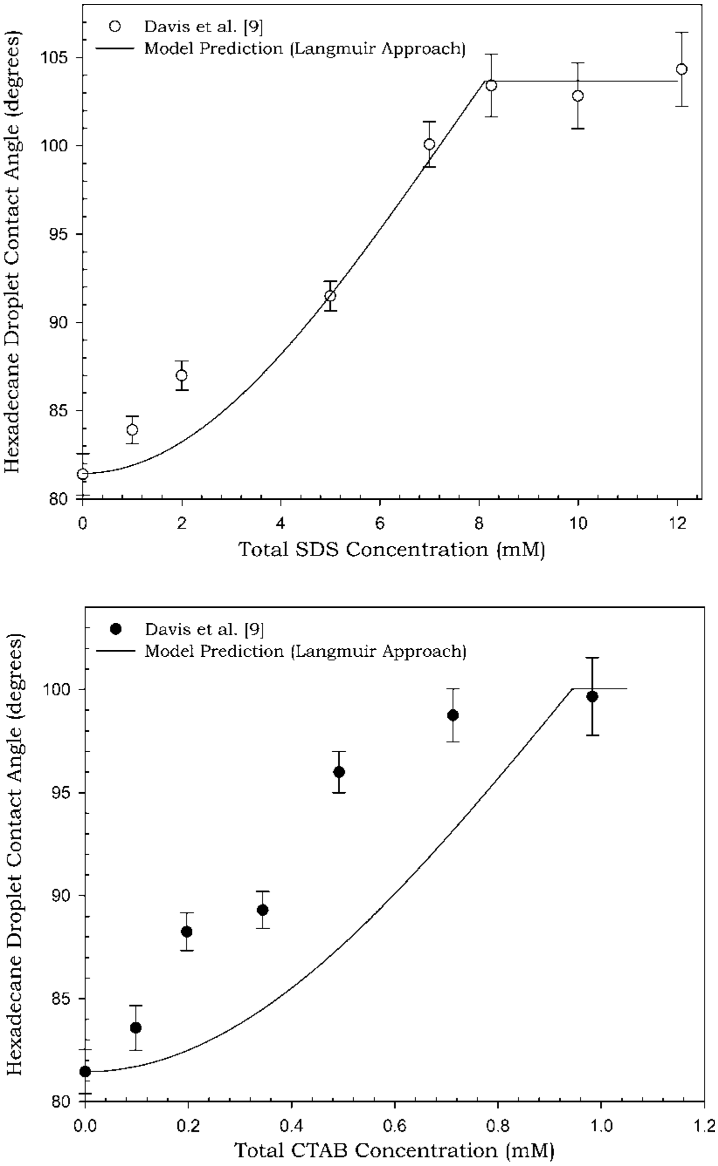

Figure 5. Contact angle prediction based on the langmuir adsorption case.

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

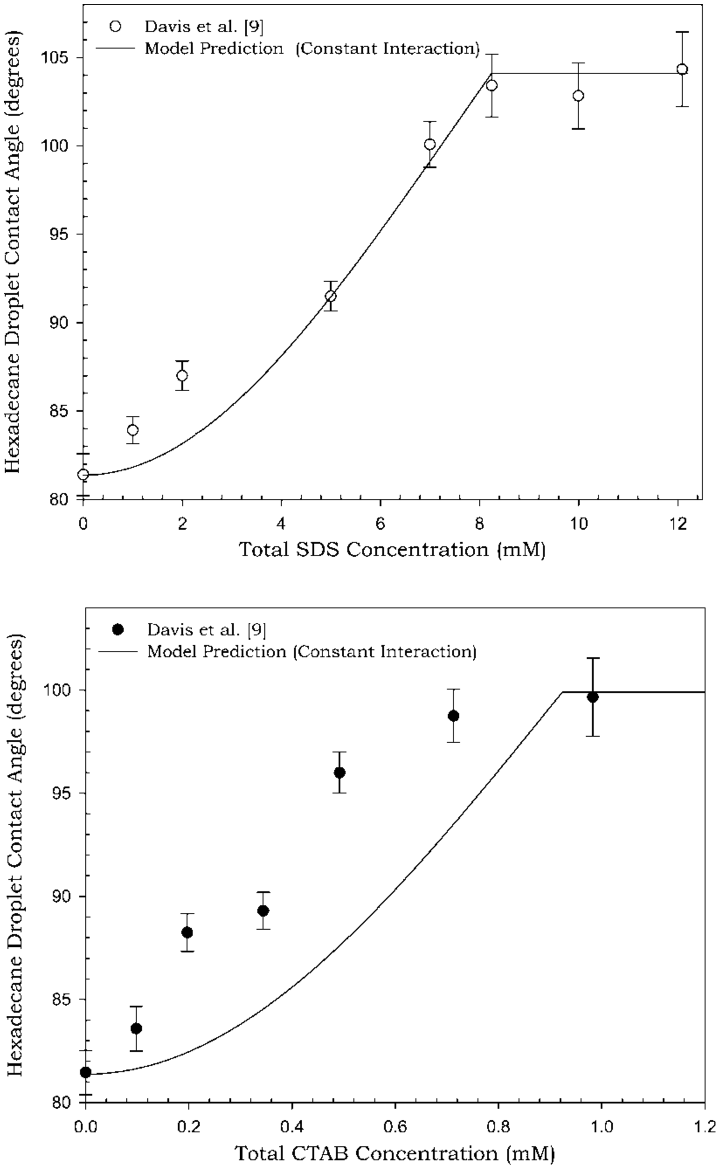

Figure 6. Contact angle prediction based on quasi-chemical approximation with constant lateral interactions.

The four regions of the reverse orientation model can be used as a basis for guidance in manipulating the lateral interaction parameters for adsorbed surfactant molecules. First values for w_{22} that begin with a constant value are selected to satisfy the case for initial adsorption found in Region A.

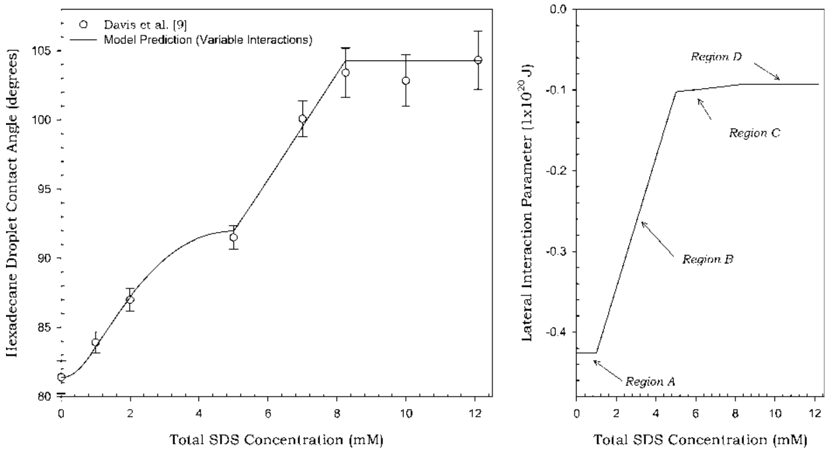

Figure 7. Contact angle prediction based on quasi-chemical approximation with variable lateral interactions for SDS solutions.

Since Region B contains the onset and formation of a monolayer in our approach a linear change in the w_{22} value until the onset of Region C, where a different linear change is utilized to describe the formation of a compressed bilayer. As Region D is above the CMC for each surfactant no additional changes to the lateral interaction parameter is required. Figure 7 shows the predicted contact angle values a variable lateral interaction parameter for the SDS experimental contact angle data as well as a plot of the values of the w_{22} parameter. Figure 8 contains the same information for

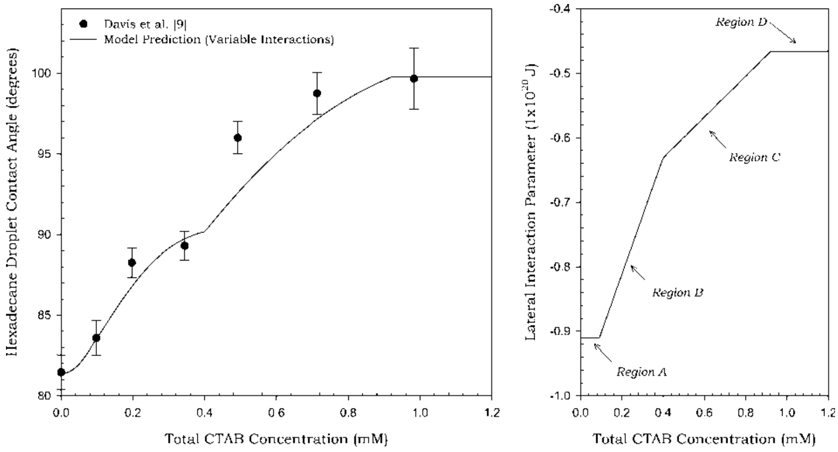

Figure 8. Contact angle prediction based on quasi-chemical approximation with variable lateral interactions for CTAB solutions.

Table 2. Interaction parameters for SDS/hexadecane/gold and CTAB/hexadecane/gold systems from the quasi-chemical approximation

	U_1 (J/molecule)	U_2 (J/molecule)	U_3 (J/molecule)		w_{22} (J/molecule)
Hexadecane/SDS/Gold System					
Langmuir	-1.0087×10^{-20}	-6.8310×10^{-20}	-9.6624×10^{-20}		N/A
Quasi-Chemical (Constant Interactions)	-3.1083×10^{-20}	-6.9693×10^{-21}	-8.9012×10^{-21}		-9.7575×10^{-22}
Quasi-Chemical (Variable Interactions)	-3.1085×10^{-20}	-7.0970×10^{-21}	-8.9016×10^{-21}	Region A	U_2*(0.60)
				Region B	U_2*(0.7138−0.1138*C_{SDS})
				Region C	U_2*(0.1448−0.0041*C_{SDS})
				Region D	U_2*(0.1111)
Hexadecane/CTAB/Gold System					
Langmuir	-1.0087×10^{-20}	-7.8193×10^{-20}	-9.6624×10^{-20}		N/A
Quasi-Chemical (Constant Interactions)	-3.1083×10^{-20}	-1.5201×10^{-21}	-8.9012×10^{-21}		-4.4845×10^{-22}
Quasi-Chemical (Variable Interactions)	-3.1085×10^{-20}	-1.4821×10^{-21}	-8.9016×10^{-21}	Region A	U_2*(0.6149)
				Region B	U_2*(0.6698−0.6098*C_{CTAB})
				Region C	U_2*(0.5113−0.2135*C_{CTAB})
				Region D	U_2*(0.3149)

the CTAB experimental contact angle data. As can be seen from these figures the model has a much greater correlation to the experimental data when lateral interactions are considered and allowed to vary within the adsorption regions. Table 2 provides a listing of the component-solid interaction and surfactant-surfactant lateral interaction parameter for each tested case.

SUMMARY

In this work we have presented a significant improvement of an earlier approach to the prediction of liquid/liquid/solid contact angles. This new approach replaces the limiting assumption of a Langmuir adsorption case with the quasi-chemical approximation with variable adsorbate-adsorbate interactions. Additionally this approach utilizes sessile droplet contact angle data acquired in the manner explained by Davis et al. (9) to assist in the interpretation of surfactant solid surface aggregate structure and composition. This highlights an opportune application for the use of more detailed molecular thermodynamic modeling techniques to further refine the surfactant aggregate structure. The modified model presented in this work is currently being applied to the case of minute non-surfactant electrolyte addition to the liquid/liquid/solid system as well as certain cases where droplet contact angles are altered in the presence of a low voltage applied potential.

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