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S. A. Morton III[a]; D. J. Keffer[a]; R. M. Counce[a]; D. W. DePaoli[b]; M. Z-C. Hu[b]
[a] Department of Chemical Engineering, The University of Tennessee, Knoxville, Tennessee, USA [b] Separations and Materials Research Group, Oak Ridge National Laboratory, Oak Ridge, Tennessee, USA

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

**S. A. Morton III,[1,*] D. J. Keffer,[1] R. M. Counce,[1]
D. W. DePaoli,[2] and M. Z-C. Hu[2]**

[1]Department of Chemical Engineering, The University of Tennessee,
Knoxville, Tennessee, USA
[2]Separations and Materials Research Group, Oak Ridge National
Laboratory, Oak Ridge, Tennessee, USA

ABSTRACT

The attachment of a droplet of oil to a solid surface in the presence of an aqueous surfactant solution may be quantified by contact angle measurements. A classical thermodynamic model has been developed to predict this characteristic contact angle. The model minimizes the Gibbs free energy for a system that includes five mass-transfer actions: micellization of surfactant monomer in aqueous solution, adsorption of surfactant at the solid–solution interface, adsorption of surfactant at the oil–solution interface, adsorption of the oil at the solid surface, and adsorption of water at

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[*]Correspondence: S. A. Morton III, Department of Chemical Engineering, The University of Tennessee, Knoxville, Tennessee 37996, USA; E-mail: samuel.morton@tennessee.edu.

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the solid surface. Limitations in the model include empirical values for the energy of steric/restrictive interactions in micellization and the interfacial free-energy term for adsorption of surfactant at the oil–solution interface. In addition, the free energies for adsorption of water, oil, and surfactant at the solid surface are adjustable parameters. The model has been validated by comparison with experimental values of contact angle measured for droplets of hexadecane on a gold surface. This approach allows for the use of published physical property data for the prediction of surfactant distribution and contact angle in a given system and may be useful in guiding aqueous cleaning applications.

Key Words: Contact angle; Surfactant; Adsorption; Surface cleaning; Thermodynamic model.

INTRODUCTION

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

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

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

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

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

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

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

THEORY

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

Mass Balances

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

$$\text{Surfactant}_{(solution)} \leftrightarrow \text{Surfactant}_{(micelle)}$$

$$\text{Surfactant}_{(solution)} \leftrightarrow \text{Surfactant}_{(solid/solution\ absorbed)}$$

$$\text{Surfactant}_{(solution)} \leftrightarrow \text{Surfactant}_{(oil/solution\ absorbed)}$$

$$\text{Oil}_{(liquid)} \leftrightarrow \text{Oil}_{(solid/oil\ absorbed)}$$

$$\text{Water}_{(solution)} \leftrightarrow \text{Water}_{(solid/solution\ absorbed)}$$

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

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

Equilibrium Constraints

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

$$K_{\alpha\to\beta} = \frac{[N_{\text{molecules},\beta}]}{[N_{\text{molecules},\alpha}]} \tag{1}$$

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

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

Rearranging the above Eq. 2 and substituting for the equilibrium constant gives us a relationship that can be used to determine the partitioning of components between states in the model system,

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

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

Micellization

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

$$\Delta G_{\mathrm{micelle}} = \Delta G_{\mathrm{hydrophobic}} + \Delta G_{\mathrm{restrictive/steric}} + \Delta G_{\mathrm{electrostatic}} \tag{4}$$

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

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

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

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

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

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

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

Oil–Solution Interfacial Surfactant Adsorption

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

$$\Delta G_{\mathrm{soln/oil\ ads}} = \Delta G_{\mathrm{hydrophobic}} + \Delta G_{\mathrm{steric}} + \Delta G_{\mathrm{restrictive}} + \Delta G_{\mathrm{electrostatic}} + \Delta G_{\mathrm{interfacial}} \tag{10}$$

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

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

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

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

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

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

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

Solid–Solution Competitive Adsorption

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

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

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

$$\theta_{\mathrm{H_2O}} = \frac{K_{\mathrm{H_2O}} N_{\mathrm{H_2O}}}{V_{aq} + K_{\mathrm{H_2O}} N_{\mathrm{H_2O}_{aq}} + K_S N_{S_{aq}} + K_{Oil} N_{Oil}(V_{aq}/V_{Oil})} \tag{16}$$

$$\theta_{Surfactant} = \frac{K_S N_{S_{aq}}}{V_{aq} + K_{\mathrm{H_2O}} N_{\mathrm{H_2O}_{aq}} + K_S N_{S_{aq}} + K_{Oil} N_{Oil}(V_{aq}/V_{Oil})} \tag{17}$$

$$\theta_{Oil} = \frac{K_{Oil} N_{Oil}}{V_{Oil} + K_{\mathrm{H_2O}} N_{\mathrm{H_2O}}(V_{Oil}/V_{aq}) + K_S N_{S_{aq}}(V_{Oil}/V_{aq}) + K_{Oil} N_{Oil}} \tag{18}$$

with the constraint that

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

With the relation of the surface coverage to the equilibrium constant, all that remains undefined is three equilibrium constants for the adsorption processes. The equilibrium constants shown in Eqs. (16 through 18), KH_2O, K_S, K_{Oil}, can be related to free-energy change as stated previously. It is known that the change in free energy contains an enthalpic and entropic contribution,

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

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

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

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

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

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

Determination of Contact Angle

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

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

where the relationships between contact angle, cap height, and theoretical sphere radius are shown in Fig. 1.

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

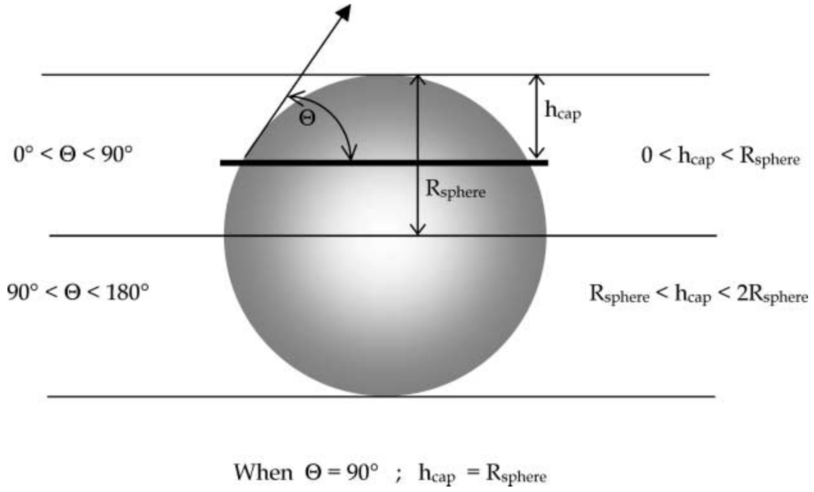

Figure 1. Droplet geometric relationships.

EXPERIMENTAL METHOD

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

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

The gold slide was repeatedly washed with acetone and deionized water to remove any contaminants from handling and to ensure consistent wetting of

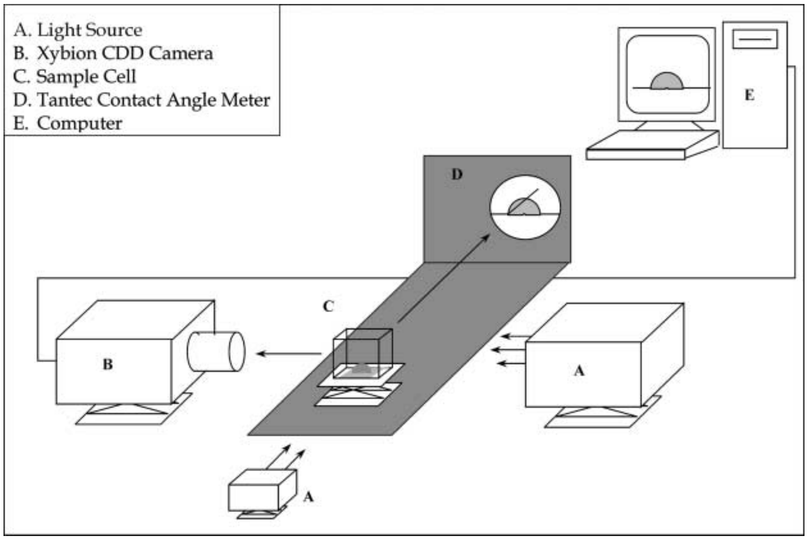

Figure 2. Contact angle study apparatus.

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

RESULTS AND DISCUSSION

Comparison with Experimental Data

The change in contact angle of the droplet on the gold surface was measured as a function of total surfactant concentration. The drop was viewed with the CCD camera until equilibrium appeared to have been achieved. Figure 3 shows a typical droplet on the gold surface in aqueous surfactant solution.

Several equilibrium-contact angles were measured, two at SDS concentrations above the CMC, and four below the CMC value of 8.3 mM. As can be seen from Fig. 4, the values predicted by the model are in good agreement with the experimental data.

As expected, an increase in total-surfactant concentration in the system resulted in increased adsorption of surfactant to the solid surface below the CMC. This increase in adsorption resulted in competition for available surface area between the surfactant, organic, and water species. The end results show, since the adsorption of surfactant is known to be affected by the concentration of surfactant in solution, that the adsorption of organic and water displayed an inverse relationship to the solid–solution interfacial

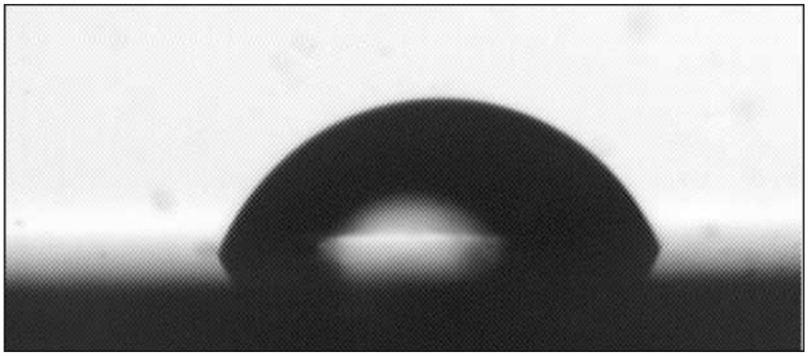

Figure 3. Hexadecane droplet on gold surface in 5-mM SDS solution.

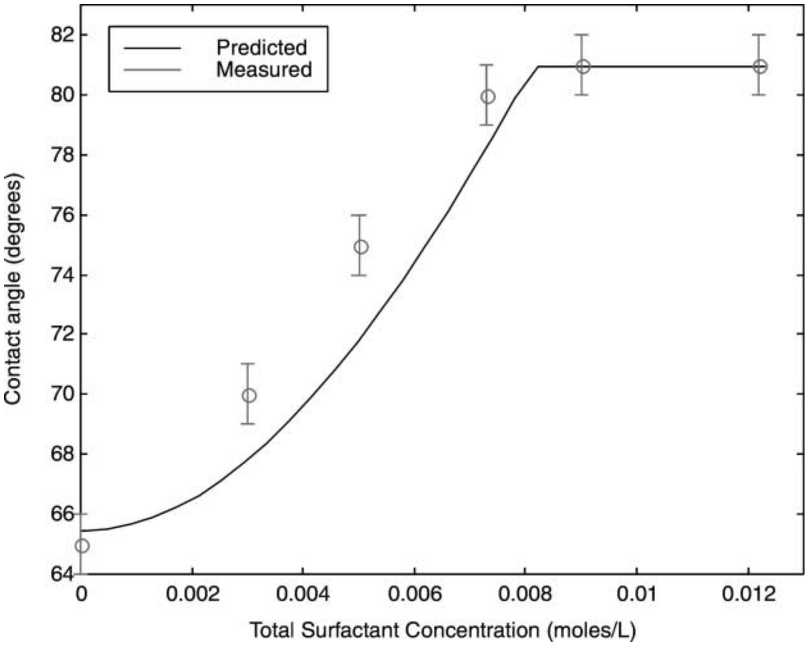

Figure 4. Comparison of predicted and measured contact angle.

Table 1. Approximate interaction parameters.

E_{Oil}	− 0.761 kJ/mol
E_{Water}	− 5.603 kJ/mol
$E_{Surfactant\ (solid/soln\ ads)}$	− 39.27 kJ/mol

adsorbed surfactant concentration. The values of the energetic interaction parameters, E_i, used in the calculation of the change in free energy of adsorption, resulting in the best correlation to the experimental data are shown in Table 1.

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

Discussion of Model Performance

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

CONCLUSIONS

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

NOMENCLATURE

Symbol	Units	Definition/value
K_i	—	Equilibrium constant for process i
N_i	molecules	Number of molecules of species i
R	J/(molecules∗K)	Ideal gas constant (1.38083×10^{-23})
T	K	System temperature
ΔG_i	J/molecule	Change in Gibbs free energy of process i
N_c	—	Number of carbons in surfactant tail chain
ΔG_{CH3}	J/molecule	Change in free energy for transfer of CH3 group
ΔG_{CH2}	J/molecule	Change in free energy for transfer of CH2 group
$A_{micelle}$	m^2	Surface area of micelle hydrocarbon core
$N_{aggregation}$	—	Micelle aggregation number
$\gamma_{micelle}$	J/m^2	Surface tension of micelle core
$\alpha_{micelle}$	J/molecule	Restrictive/steric contribution correction factor
k_b	J/(molecules∗K)	Boltzmann constant (1.3806×10^{-23})
κ	m^{-1}	Inverse Debeye–Huckel screening length
e_c	C	Unit charge (1.602177×10^{-19})
$N_{aq\ ion}$	molecules	Number of ions in solution
εH_2O	—	Dielectric constant for water
ε_v	C/(J∗m)	Permittivity of a vacuum (8.85419×10^{-12})

S	—	Dimensionless surface charge density
$R_{micelle}$	m	Radius of micelle hydrocarbon core
A_{mon}	m^2/molecule	Area of surfactant square footprint
$A_{effective}$	m^2/molecule	Area of surface per surfactant monomer
E	—	Packing parameter
τ	m	Depth of surfactant tail group penetration into oil
N_{sites}	—	Number of available adsorption sites
θ_i	—	Fractional coverage of surface
C_i	molecules/m^3	Concentration of species i
V_i	m^3	Volume of species i
ΔH_i	J/molecule	Change in enthalpy for adsorbing component I
ΔS_i	J/molecule	Change in entropy for adsorbing component I
$V_{i,adsorbed}$	m^3	Free volume of adsorbed species i
$V_{i,bulk}$	m^3	Free volume of species i in bulk phase
E_i	J/molecule	Adsorption interaction parameter
Cp_i	J/(molecules*K)	Heat capacity of component i
Θ	radians	Contact angle
R_{sphere}	m	Radius of theoretical sphere
h_{cap}	m	Maximum height of spherical cap
$N_{moles\ i}$	moles	Number of moles of species i

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