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Contact Angles of Surfactant Solutions on Heterogeneous Surfaces

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Abstract:

Using Gibbs' adsorption equation and a literature isotherm, a new general model to predict the contact angle of surfactant solutions on (smooth or rough) chemically heterogeneous surfaces is constructed based on the Cassie equation. The model allows for adsorption at the liquid-vapor, solid-liquid, and solidvapor interfaces. Solid-vapor adsorption is allowed in order to model the autophobic effect on hydrophilic surfaces. Using representative values for the coefficients which describe adsorption at each interface, model predictions for contact angles as a function of f parameters (area fractions) and surfactant concentration are made for heterogeneous surfaces made up of different materials. On smooth surfaces, the f parameters serve as weighting factors determining how to combine the effects of surfactant adsorption on each material to predict the behavior on the heterogeneous surface. Due to the non-linear nature of the model, the inclusion of a small amount of hydrophobic material has a greater effect on a predominantly hydrophilic material than vice versa, explaining the result seen in literature that a small amount of hydrophobic contamination (such as oil) significantly increases contact angle on a hydrophilic surface. The fact that even a small amount of heterogeneity can greatly change experimental results could lead to incorrect experimental conclusions about surfactant adsorption if the surface were wrongly assumed to be homogeneous. Model predictions rapidly become more complex as the number of differently wettable materials present on the surface increases. Also, an approximately equal weighting of different materials generally leads to more complex behaviors compared to heterogeneous surfaces composed largely of a single material. Rough heterogeneous surfaces follow previous results for surfactant wetting of rough homogeneous surfaces, leading to an amplification/attenuation of surfactant effects for penetrated/unpenetrated wetting, and further increasing the complexity of predictions. These potential complexities point to the importance of characterizing the heterogeneities of any surface under consideration. With proper characterization, the model described in this paper will allow for prediction of contact angles on all types of heterogeneous surfaces, and design of surfaces for specific interactions with surfactant solutions.

List of Symbols:

In the following list, x and y may be any two of the solid (s), liquid (l), or vapor (v) phases

C_{s}	surfactant concentration (expressed non-dimensionally as concentration/critical micelle
	concentration ($C/C_{\rm CMC}$) or as concentration/critical association concentration ($C/C_{\rm CAC}$))
f_m	weighting factors (actual wetted areas of material <i>m</i> normalized by the total projected area)
K_{xy}	product of the equilibrium constants for first and second adsorption steps
т	index denoting different materials in a heterogeneous surface
n_{xy}	empirical fitting factor
R	universal gas constant
Т	absolute temperature
γ_{xy}	interfacial tension of x-y interface
γ_{xy} γ^0_{xy}	interfacial tension of x-y interface interfacial tensions for $C_s = 0$
${\mathcal Y}_{xy} \ {\mathcal Y}^0_{xy} \ {\Gamma}_{xy}$	interfacial tension of x-y interface interfacial tensions for $C_s = 0$ coverage (surface excess per unit area) of surfactants at the x-y interface
$ \begin{array}{l} \gamma_{xy} \\ \gamma_{xy}^{0} \\ \Gamma_{xy} \\ \Gamma_{xy} \\ \Gamma_{xy}^{\infty} \end{array} $	interfacial tension of x-y interface interfacial tensions for $C_s = 0$ coverage (surface excess per unit area) of surfactants at the x-y interface limiting surface coverage
$ \begin{array}{l} \gamma_{xy} \\ \gamma^{0}_{xy} \\ \Gamma_{xy} \\ \Gamma^{\infty}_{xy} \\ \theta_{c} \end{array} $	interfacial tension of x-y interface interfacial tensions for $C_s = 0$ coverage (surface excess per unit area) of surfactants at the x-y interface limiting surface coverage Cassie contact angle
$\begin{array}{l} \gamma_{xy} \\ \gamma^{0}_{xy} \\ \Gamma_{xy} \\ \Gamma^{\infty}_{xy} \\ \theta_{c} \\ \theta^{0}_{c} \end{array}$	interfacial tension of x-y interfaceinterfacial tensions for $C_s = 0$ coverage (surface excess per unit area) of surfactants at the x-y interfacelimiting surface coverageCassie contact angleCassie contact angle for a pure liquid on a heterogeneous surface

1.0 Introduction

The contact angle that a drop of liquid makes on a solid surface is an important parameter for characterizing the surface and predicting and/or controlling its behavior in applications involving wettability and adhesion. The contact angle of water on a surface describes its hydrophobicity, with contact angles below 90° denoting a hydrophilic surface, and contact angles above 90° denoting a hydrophilic surface. The contact angle depends on the balance of the liquid-vapor, solid-liquid, and solid-vapor interfacial tensions at the contact line¹.

Amphiphilic surfactants have hydrophobic tail groups and hydrophilic head groups. This difference in interaction energy between the head(s) and tail(s) of a surfactant molecule causes surfactants to

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accumulate at the interface between phases. By adsorbing at an interface, surfactants modify the interfacial tension of the interface, and consequently the contact angle.

For smooth, homogeneous surfaces, Young's equation for contact angle and Gibbs' adsorption equation can be combined to obtain a differential equation describing the change of contact angle due to surfactant adsorption. This or similar ideas have been pursued before^{2,3}. Other researchers^{4–7} have taken the further step of applying an isotherm equation to describe the surface coverage (surface excess per unit area) parameter used in Gibbs' adsorption equation. This non-exhaustive list of references illustrates the relatively advanced state of understanding regarding the effects of surfactant adsorption on contact angles on surfaces which are smooth and homogeneous.

In a previous work⁸, we expanded the field by modeling the contact angles of surfactant solutions on rough surfaces. All previous models^{2–8}, however, have dealt only with chemically homogeneous surfaces (whether smooth or not). Chemically *heterogeneous* surfaces are nonetheless common, either naturally occurring (e.g. due to different crystal facets in a solid), or created intentionally (e.g. a surface energy gradient) or unintentionally (e.g. due to incomplete or damaged coating of a surface). In this paper, therefore, a model is presented to describe surfactant adsorption from sessile drops on heterogeneous surface is predominantly one material, with patches of other materials. Therefore, a general understanding of the effect of surfactant adsorption on different types of materials is needed.

Experimental data from literature⁴⁻⁹ generally shows that increasing surfactant adsorption leads to decreased contact angle on hydrophobic materials, and can do so on hydrophilic materials as well. Data can also be found describing an *increase* in contact angle with surfactant adsorption to some hydro*philic* materials^{10–20}. This can be understood as indicating an auto*phobic* effect similar to that identified by Zisman²¹ for pure liquids, but involving surfactant solutions. The autophobic effect occurs when surfactants adsorb to the hydrophilic solid-vapor surface decreasing its surface energy. This leads to an

increase in contact angle and/or a spontaneous receding of a drop which initially spread on the surface. The adsorption is understood to occur through a pre-wetting film (in which case higher contact angles are seen than would be expected without this adsorption), or after the bulk of the drop advances across the surface (in which case spontaneous receding can be seen). Considering that a heterogeneous surface may contain at least some regions that are subject to a surfactant induced autophobic effect, this will be accounted for by allowing solid-vapor adsorption in the model developed in this paper.

An analogous 'auto*philic* effect' has been proposed^{4–7}, with surfactants adsorbing ahead of the contact line, *decreasing* contact angle on a hydro*phobic* surface by *increasing* solid-vapor surface energy on never-touched-by-solution solid surfaces. This proposed effect is questionable (with uncertainties as to magnitude, time scale, mechanism, etc)²², and hence will not be considered here. We also neglect the dynamic case of drop spreading with a fingering instability^{11,19,20,23–25}, as it leads to non-axisymmetric drops and is outside the scope of this work.

In this study then, a predictive model describing the effects of surfactant adsorption for drops on heterogeneous surfaces is derived. This model is based upon fundamental equations, and predicts the effects of surfactant adsorption on the thermodynamic contact angle. It also allows for solid-vapor adsorption to account for the autophobic effect. To our knowledge, this is the first such comprehensive model reported in the literature. Throughout this paper, constants in the adsorption isotherms were chosen and the model used to explore the wetting of heterogeneous surfaces with patches varying in intrinsic water contact angles from 0° to 120° .

2.0 Model Derivation

As described in our previous work⁸, for an ideal dilute solution Gibbs' adsorption equation describes the differential change in surface energy with a differential change in surfactant concentration as:

$$d\gamma_{xy} = -\Gamma_{xy} RTd \ln(C_s) \tag{1}$$

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where γ_{xy} is the interfacial tension and Γ_{xy} is the coverage (surface excess per unit area) of surfactants for the *x-y* interface, where *x* and *y* can be the solid (*s*), liquid (*l*), or vapor (*v*) phases (e.g. γ_{lv} is liquidvapor interfacial tension). Further, *R* is the universal gas constant, *T* is the absolute temperature, and C_s is surfactant concentration (expressed non-dimensionally throughout this paper as concentration/critical micelle concentration (C/C_{CMC}) or as concentration/critical association concentration (C/C_{C4C})).

Equation 1 can be integrated to find interfacial tension by applying a suitable isotherm equation relating Γ_{xy} to $\ln(C_s)$. Here, the general isotherm equation proposed by Zhu and Gu²⁶ is applied. The generality of the Zhu and Gu²⁶ isotherm allows its application to the solid-liquid, solid-vapor, and liquid-vapor interfaces, and for the expression of several 'types' of adsorption (*e.g.* Langmuir, S-type or 2 plateau). The isotherm is:

$$\Gamma_{xy} = \Gamma_{xy}^{\infty} \frac{K_{xy} C_s^{n_{xy}}}{1 + K_{xy} C_s^{n_{xy}}}$$
(2)

where Γ_{xy}^{∞} is the limiting surface coverage (i.e. the maximum possible interfacial concentration of surfactant). The pre-factor, K_{xy} , is the product of the equilibrium constants for the first and second adsorption steps. The exponent, n_{xy} , is an empirical fitting parameter²⁷ (though it was originally understood to represent the aggregation number of the hemimicelles²⁶). It is worth noting here that the methodology for developing the model is sufficiently general that any integrable isotherm(s) could be used in place of Equation 2, if other types of adsorption were necessary to model a given system.

Combining Equations 1 and 2 and integrating gives an expression for interfacial tension as a function of surfactant concentration.

$$\gamma_{xy}(C_{s}) = \gamma_{xy}^{0} - \frac{\Gamma_{xy}^{\infty}RT}{n_{xy}} \ln\left(1 + K_{xy}C_{s}^{n_{xy}}\right)$$
(3)

where γ_{xy}^0 is the interfacial tension for $C_s = 0$ (or more precisely, for zero adsorption to the xy interface).

The subsequent paragraphs in this section expand on the previous work⁸ which was summarized above. Due to their broad application in literature, the Cassie²⁸ and Young¹ equations are used to advance the derivation. These equations give equilibrium contact angle on heterogeneous and homogeneous surfaces, respectively. The focus of this study is on the thermodynamic equilibrium state for the drop, hence the metastable states giving rise to advancing and receding contact angles are not considered. The Young contact angle, θ_{y} , is given for a material *m* by Equation 4:

$$\cos\theta_{y}\Big|_{m} = \frac{\gamma_{sv} - \gamma_{sL}}{\gamma_{Lv}}\Big|_{m}$$
(4)

where the Young (intrinsic) contact angle is for liquid on a smooth, flat, rigid, homogeneous and chemically inert surface. The Cassie equation (5) is used to calculate the contact angle of a pure liquid on a heterogeneous, flat, rigid and chemically inert surface, made up of m different materials:

$$\cos\theta_c = \sum_m f_m \cos\theta_y \Big|_m \tag{5}$$

where θ_c is the Cassie contact angle. The weighting factors, f_m , are the actual wetted areas of each of the *m* materials under the drop, normalized by the total projected area. The use of the actual area divided by total projected area is required to account for any roughness of the material(s) under the drop. As Cassie and Baxter explained²⁸, as $f_{2..m} \rightarrow 0$ (i.e. as the heterogeneous surface approaches a homogeneous one), the Cassie equation should return the behavior of the Wenzel equation (for rough, homogeneous

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surfaces), by having $f_l \rightarrow r$, where r is defined as the total area under the drop normalized by the projected area. This nuance is commonly missed in literature, and many researchers (explicitly or implicitly) make the assumption that $\sum_{m} f_m = 1$, when in fact $\sum_{m} f_m \ge 1$, with the equality holding only for smooth heterogeneous surfaces, as recently discussed²⁹. In this paper, both rough and smooth heterogeneous surfaces will be considered by properly making use of the *f* values of various materials.

Equation 4 and Equation 5 can be combined to express the Cassie contact angle as a function of surface tensions. We make the limiting assumption here that surfactant adsorption on one material does not affect the adsorption on adjacent materials. This assumption is required to make progress, since otherwise the results of surfactant adsorption isotherms on pure materials could not be directly applied to heterogeneous surfaces of the same mixed materials. Making this assumption, taking the derivative of the result with respect to $\ln(C_s)$ and applying Equation 1, one obtains Equation 6 describing the relationship between contact angle and surfactant concentration for a heterogeneous surface.

$$\left(\frac{\gamma_{lv}}{RT}\right) \times \left(\frac{d\cos\theta_c}{d\ln(C_s)}\right) - \Gamma_{lv}\cos\theta_c + \sum_m f_m (\Gamma_{sv} - \Gamma_{sl})\Big|_m = 0$$
(6)

To allow for inclusion of the autophobic effect in the model, Γ_{sv} can be retained as a non-zero term for suitable hydrophilic materials. Substituting the isotherm model of Equation 2 into Equation 6 and rearranging terms yields:

$$\frac{d\cos\theta_c}{d\ln(C_S)} - \frac{\Gamma_{lv}^{\infty}RT}{\gamma_{lv}} \left(\frac{K_{lv}C_S^{n_{lv}}}{1 + K_{lv}C_S^{n_{lv}}}\right) \cos\theta_c = \frac{RT}{\gamma_{lv}} \sum_m f_m \left(\Gamma_{sl}^{\infty} \left(\frac{K_{sl}C_S^{n_{sl}}}{1 + K_{sl}C_S^{n_{sl}}}\right) - \Gamma_{sv}^{\infty} \left(\frac{K_{sv}C_S^{n_{sv}}}{1 + K_{sv}C_S^{n_{sv}}}\right)\right) \right|_m$$
(7)

with the γ_{lv} term in Equation 7 given by Equation 3 expressed at the liquid-vapor interface. As a reminder, if the surface is hydrophobic or slightly hydrophilic, the Γ_{sv} terms in Equation 6 and 7 (and subsequently derived equations) are set to zero^{8,22}.

Equation 7 is a linear, inhomogeneous, ordinary differential equation with variable coefficients. Solving Equation 7 requires applying the technique of variation of parameters, and results in Equation 8, a modified form of the Cassie equation relating changes in heterogeneous surface contact angle with surfactant concentration:

$$\cos\theta_{c}(C_{S}) = \frac{\cos\theta_{c}^{0}\gamma_{lv}^{0} - RT\sum_{m} \left[f_{m} \left(\frac{\Gamma_{sv}^{\infty}}{n_{sv}} \ln\left(1 + K_{sv}C_{S}^{n_{sv}}\right) - \frac{\Gamma_{sl}^{\infty}}{n_{sl}} \ln\left(1 + K_{sl}C_{S}^{n_{sl}}\right) \right) \right]_{m}}{\gamma_{lv}^{0} - \frac{\Gamma_{lv}^{\infty}RT}{n_{lv}} \ln\left(1 + K_{lv}C_{S}^{n_{lv}}\right)}$$
(8)

where γ_{lv}^0 is the liquid-vapor interfacial tension of the pure liquid, and θ_c^0 is the Cassie contact angle for a pure liquid on the heterogeneous surface, given by Equation 5. Equation 8 will be referred to as the modified heterogeneous Cassie equation throughout this paper (to differentiate it from a different form of the modified Cassie equation we presented previously to describe the effect of surfactant adsorption on wetting of a rough surface composed of a single solid material⁸). Equation 8 can also be derived by substituting Equation 3 directly into Equation 5 for each of the interfacial tension terms.

Equation 8 is a predictive tool to study the effect on contact angle of surfactant adsorption at the solidliquid, solid-vapor, and liquid-vapor interfaces of drops on heterogeneous surfaces. To our knowledge, no similar models have been developed to date. By varying adsorption constants, one could model any surfactant in any liquid on any solid. If the combination in question followed a different isotherm from that used in the derivation, any integrable isotherm(s) could be used in place of Equation 2. It should be noted here that the model does not attempt to explain, e.g., the specifics of molecular orientation, layer structure, etc. on the surface (so differences in surface charge and resultant changes in surfactant orientation and (hemi)micelle shape are not explained). Nor does the model specifically account for, e.g., the adsorption of water onto the solid-liquid or solid-vapor interfaces³⁰. Instead, the net effects of such specifics on the macroscopic contact angle are assumed to be captured by the smooth surface adsorption coefficients which are used in the model, and which are determined as discussed in the next section.

Studying the model, for $C_s = 0$ (no surfactants present), Equation 8 simplifies to the unmodified Cassie equation (Equation 5). As discussed earlier, by definition the Cassie equation can be simplified to either the Wenzel equation or Young equation (Equation 4) for m = 1 and $f_m \ge 1$ (with the equality for the Young equation). As a note: If a surface is rough and wetted in an unpenetrated mode (i.e. with air remaining in crevices under the drop), the air can be treated as an additional material with $\theta_y = 180^\circ$. This strategy is often employed to explain the superhydrophobicity of certain rough surfaces. It is common in such cases to let m=1 be solid, and m=2 be air, and to express f_2 as $(1-f_i)$. This presumes that the portions of the solid touched by the liquid are smooth and flat, and that any curvature/distortions of the liquid-vapor interface under the drop are negligable. We made this presumption in our previous work⁸ for simplicity, and due to its common practice in the study of superhydrophobic surfaces, but here we will consider the more general case of $\sum_m f_m \ge 1$, whether or not one of the materials under the drop is air.

Smooth heterogeneous surfaces (for which $\sum_{m} f_{m} = 1$) will be considered first. Then the model will be explored for rough heterogeneous surfaces (for which $\sum_{m} f_{m} \ge 1$), wetted either in penetrated (Wenzel) or

unpenetrated (Cassie) modes.

3.0 Model Parameters

To explore the model fully, several different sets of adsorption constants would be necessary. As an initial set, model results are presented here for heterogeneous surfaces made up of various representative 10 of 38

materials, which necessitates representative adsorption constants for each, which will be discussed below. Readers wishing for predictions of a particular system can determine adsorption constants and model predictions in a similar manner to that described here.

As a first (non-autophobing) material, previously obtained adsorption coefficients⁸ for aqueous solutions of Sodium Dodecyl Sulfate (SDS, an anionic surfactant) on Teflon will be used for all hydrophobic materials in this paper. By definition hydrophobic surfaces do not experience the autophilic effect²². These adsorption coefficients were obtained using the procedure that will be outlined later in this section. For more general non-autophobing hydrophilic materials, *ad hoc* constants will be used.

To model the autophobic effect, additional solid-vapor interface adsorption constants are required. The wide range of autophobic behaviors—e.g. the amount of increase in contact angle (~15° to ~70° above the pure water contact angle on one and the same surface^{3,16,17}), and whether the increase is to a maximum^{3,16,17} or a plateau¹¹—indicates that multiple sets of adsorption constants are possible/needed. There is a dearth of experimental data showing both surface tension and contact angle measurements versus concentration for autophobing systems. As such, in this paper one set of adsorption coefficients describing the behavior on a surface undergoing the autophobic effect is determined from experimental data as described next. Others sets of constants are chosen on an *ad hoc* basis, based on characteristics described in the literature.

The goal in the remainder of this section then is to fit the experimental data of Nedyalkov et al.¹⁶ for aqueous solutions of hydrophobically modified inulin (INUTEC[®]SP1, a non-ionic surfactant) on quartz glass, a system which displays the autophobic effect. Doing so will determine values for Γ_{xy}^{∞} , n_{xy} and K_{xy} for the *l-v*, *s-l*, and *s-v* interfaces for this system. The results of Nedyalkov et al.¹⁶ were for surfactant solutions with varying concentrations of salt. The results used in this section are for the lowest salt concentration considered (10⁻⁴ mol/l) since this data set¹⁶ includes measurements of both liquid-vapor

interfacial tension and contact angle. We acknowledge here that the Inutec system is very specific, which somewhat limits the scope of applicability of the results derived from it use. However, previous results show that our model can work for general systems (Sodium Dodecyl Sulfate in water on Teflon, and solutions of SDS, hexadecyltrimethylammonium bromide, and n-decanoyl-n-methylglucamine on several different surfaces^{8,31}), so the fact that the model works for general and specific systems shows its range of applicability.

Liquid-vapor interfacial tension data (read from Table 1 of Nedyalkov et al.¹⁶) are presented in Table 1 and Figure 1, and show a gradual decrease in liquid-vapor interfacial tension with increasing INUTEC concentration. The best fit of Equation 3 to the data is also shown in Figure 1. The fit was obtained using Matlab's curve fitting 'cftool' GUI, with Γ_{lv}^{∞} , n_{lv} , K_{lv} and γ_{lv}^{0} varied; the first three parameters were constrained to have positive signs. Pure water interfacial tension (γ_{lv}^{0}) was not given in Nedyalkov et al.¹⁶; it was therefore allowed to vary between ~72.0 mN/m and ~72.7 mN/m (based on previous work⁸). The best fit parameters were $\Gamma_{lv}^{\infty} = 1.629 \times 10^{-6} \text{ mol/m}^2$, $n_{lv} = 1.155$, $K_{lv} = 453.0$ and $\gamma_{lv}^{0} = 72.11 \times 10^{-3}$ J/m², with goodness-of-fit parameters: SSE: $1.368 \times 10^{-5} \text{ J}^2/\text{m}^4$, R²: 0.94, Adjusted R²: 0.84 and RMSE: $2.615 \times 10^{-3} \text{ J/m}^2$.

Table 1 also shows contact angle results (read from Figure 8 of Nedyalkov et al.¹⁶) for the same modified inulin solutions on smooth, hydrophilic, quartz glass. Only single measurements of contact angle were given¹⁶, without indication of whether the measurements were of advancing, receding, or equilibrium contact angles. To make progress, the measurement will be assumed to approximate the equilibrium contact angle modelled in Equation 8. The contact angle data is shown in Figure 2, along with the best fit of Equation 8 to the data for m = 1 and $f_m = 1$ (i.e. for a smooth homogeneous surface). The fit was obtained in a similar way as for the interfacial tension data, with the values of Γ_{lv}^{∞} , n_{lv} , K_{lv} and γ_{lv}^{0} as found above entered as constants into Equation 8, which was then fit for Γ_{sl}^{∞} , n_{sl} , K_{sl} , Γ_{sv}^{∞} , n_{sv} , K_{sv}

and θ_y^0 . The six solid-liquid and solid-vapor parameters were constrained to ensure their positive signs. The cosine of the pure water contact angle, $\cos(\theta_y^0)$, was allowed to vary near 0° (Nedyalkov et al. indicated¹⁶ that the pure water contact angle was 0° on the surfaces they tested). The best fit gave the parameters to be $\Gamma_{sl}^{\infty} = 2.984 \times 10^{-6} \text{ mol/m}^2$, $n_{sl} = 0.9337$, $K_{sl} = 649.1$, $\Gamma_{sv}^{\infty} = 4.465 \times 10^{-6} \text{ mol/m}^2$, $n_{sv} = 0.917$, $K_{sv} = 417.6$ and $\theta_y^0 = 0^\circ$, with goodness-of-fit parameters: SSE: 5.018×10^{-5} , R²: 0.92, Adjusted R²: 0.83 and RMSE: 0.003542.

The good fit of Equation 8 to the contact angle data of Nedyalkov et al.¹⁶ shows that the form of the developed model can capture the important features of the autophobic effect, validating its use for this purpose. Further, the model gives details of the autophobic effect, showing that solid-vapor adsorption is more favorable than solid-liquid adsorption in this case (i.e. $\Gamma_{sv}^{\infty} > \Gamma_{sl}^{\infty}$). This supports the observation made by Frank and Garoff¹¹ that the autophobic effect occurs for surfactant solutions that have a low affinity for the (solid-liquid) surface that they wet, and a higher affinity for the unwetted (solid-vapor) surface. In the case of the INUTEC[®]SP1, water, glass system, it is further seen that liquid-vapor adsorption is the least favorable (i.e. $\Gamma_{sv}^{\infty} > \Gamma_{sl}^{\infty}$).

It should be noted that equal weighting was given to data points at all concentrations in the fits discussed above. Higher weighting on data points at high concentration may give a better estimate³² of the limiting surfactant coverage Γ_{xy}^{∞} , but our interest in predicting behaviors over the entire range of concentration led to the decision to use equal weighting for the fit.

4.0 Results and Discussion

As stated at the start of Section 3.0, this paper uses adsorption constants that are both found through fits of experimental data, and also chosen on an *ad hoc* basis. The adsorption coefficients for each surface

considered in this section are given in Table 2, and the rationale behind each *ad hoc* choice will be outlined where it is made.

In this section, several scenarios will be considered in terms of heterogeneous surface wetting. First, the case of slightly heterogeneous surface chemistries will be considered (i.e. surfaces for which one material predominates, with small amounts of another material). Next, rough heterogeneous surfaces will be modeled. Finally, the full range of behaviors seen as solid fractions range from zero to their maximum values (i.e. wetting on more equally partitioned heterogeneous surfaces) will be investigated.

4.1 Two-Material Smooth Surface with Slight Heterogeneity

Consider first a simple two-material smooth heterogeneous surface. One material is perfectly wet by water $\theta_y^0|_1 = 0^\circ$, and undergoes the autophobic effect in a manner such that contact angle rises with surfactant concentration up to a plateau. The other material is hydrophobic $\theta_y^0|_2 = 120^\circ$, and does not experience the autophobic effect. Adsorption constants for both materials are listed in Table 2. The constants for material 1 were chosen on an *ad hoc* basis, using the *l*-*v* constants for SDS in water as a basis and then following the observations in Section 3.0 that for materials undergoing the autophobic effect, $\Gamma_{sv}^{\infty} > \Gamma_{sl}^{\infty} > \Gamma_{lv}^{\infty}$, $n_{sv} \approx n_{sl} \approx n_{lv}$ and $K_{sv} \approx K_{sl} \approx K_{lv}$. The end result for material 1 is an autophobic effect that causes contact angle to rise with concentration to a plateau value, similar to that seen in literature¹¹, though to a different maximum value of contact angle and at a different value of concentration. The adsorption constants for material 2 are taken from experiments for aqueous solutions of SDS on Teflon⁸ following the same procedure as outlined in Section 3.0. The wetting behavior of aqueous SDS solutions on Teflon is a monotonic decrease in contact angle with concentration.

To probe the effects of slight heterogeneity, we consider the case of $f_1=0.1$, $f_2=0.9$ (a predominantly hydrophobic surface), and $f_1=0.9$, $f_2=0.1$ (a predominantly hydrophilic surface). Such mixtures are

possible, either unintentionally (say, by an imperfect Teflon coating on a glass surface) or through purposeful modification of a surface³³. Regardless, these situations are illustrated in Figure 3, which shows the modified Cassie model predictions (based on Equation 8) for these two heterogeneous surfaces. Also shown for comparison on Figure 3 are predictions for each material as a smooth homogeneous surface.

In Figure 3, the inclusion of $f_1=0.1$ of material 1 ($\theta_y^0|_1=0^\circ$) on the predominantly hydrophobic surface $(f_2=0.9, |\theta_y^0|_2=120^\circ)$ is seen to decrease contact angle compared to a surface composed entirely of material 2. Likewise, the inclusion of $f_2=0.1$ of material 2 on the predominantly hydrophilic surface is seen to increase contact angle compared to a surface composed entirely of material 1. In this way, the f_1 and f_2 parameters can be thought of as weighting factors, determining how to mix the effect of surfactant adsorption on each material to model the effect of surfactant adsorption on contact angle of surfactant solution drops on heterogeneous surfaces.

It is interesting to note the non-linear nature of the mixing/weighting of contact angles shown in Figure 3. For the same ratio of materials (1:9), the inclusion of a small amount of material 2 has a greater effect on material 1 (i.e. f_1 =0.9, f_2 =0.1) than vice versa (i.e. on a surface for which f_1 =0.1, f_2 =0.9). This is because the f_1 and f_2 parameters act on the cosine of the contact angles for surfactant solutions on each material. As a result, a small change in the cosine at low contact angles results in a large change in contact angle. Conversely, an identical small change in the cosine at contact angles closer to 90° results in a relatively small change in contact angle. This indicates that in experiments, a small amount of hydrophobic contamination (for example, oil or grease from ones fingers) would significantly increase contact angle on a hydrophilic surface.

The large change on the $f_1=0.9$, $f_2=0.1$ surface in Figure 3 affects the shape of the curve, flattening it to a nearly horizontal line, while the $f_1=0.1$, $f_2=0.9$ surface largely maintains the same curve shape, though

shifted to lower contact angles. This could affect the interpretation of experimental data, since the change on the $f_1=0.9$, $f_2=0.1$ surface could lead to incorrect conclusions about surfactant adsorption if the surface were wrongly assumed to be homogeneous.

As a second example, consider another smooth, two-material heterogeneous surface. Figure 4 shows the predictions for both of these materials in their pure state, and for surfaces with $f_i=0.1$, $f_2=0.9$ and $f_i=0.9$, $f_2=0.1$. The adsorption constants for each material are given in Table 2. The constants for material 1 correspond to the data for aqueous solutions of modified inulin on glass¹⁶ that were fit in Section 3.0; they result in an autophobic effect on material 1 that causes contact angle to first increase and then decrease with concentration. The adsorption constants for material 2 are chosen on an *ad hoc* basis, taking the *l-v* constants for modified inulin in water as a starting point. Solid-vapor adsorption is set to zero to give a surface that does not autophobe with the modified inulin solution. Solid-liquid adsorption coefficients are set following the observation⁸ that for surfaces not undergoing the autophobic effect (i.e. surfaces displaying a monotonic decrease in contact angle with concentration), $\Gamma_{st}^{\infty} \leq \Gamma_{hv}^{\infty}$, $n_{st} \approx n_{hv}$ and $K_{st} \approx 10K_{hv}$. The end result is a material with pure water contact angle of 60°, displaying a smooth decrease in contact angle with concentration.

It can again be seen that the f_1 and f_2 parameters act to weight the behavior of each material on the surface, determining how they are mixed to model the behavior of the heterogeneous surface. In Figure 4, it is interesting to note that the four predictions all cross at the same point. Specifically, the four curves cross at $\ln(C/C_{CMC}) \approx -1.75$. At this concentration the contact angle for material 1 in its pure state is equal to the contact angle for material 2 in its pure state (i.e. at $\ln(C/C_{CMC}) \approx -1.75$, $\theta_y(C_s)|_1 = \theta_y(C_s)|_2 \approx 9.5^\circ$). At this concentration then, mixing the behavior of both materials has no effect due to the identical concentration dependent contact angle. The curves therefore intersect at this point regardless of the f_1 and f_2 parameters, since the surface is smooth (i.e. since $f_1 + f_2 = 1$).

The crossing of the curves emphasizes and expands the point made in discussing Figure 3 regarding the non-linear mixing of material behaviors. In Figure 4 it is again seen, at low concentrations, that the inclusion of a small amount of (hydrophobic) material 2 on a surface predominantly composed of (hydrophilic) material 1 has a large effect on heterogeneous surface contact angle. In the opposite case (material 1 contaminating material 2), the effect is smaller. However, once the curves have crossed at $\ln(C/C_{CMC}) \ge -1.75$, the effects are reversed, and now the contamination of material 1 by material 2 results in a decreased effect. This emphasizes that it is the pure material contact angles *at a given concentration* that must be considered when judging the relative effect of small amounts of contamination on surfaces. Due to this additional complexity, both the $f_i=0.1, f_2=0.9$ and $f_i=0.9, f_2=0.1$ surfaces behave noticeably differently than the $f_2=1$ and $f_i=1$ surfaces, respectively. The $f_i=0.1, f_2=0.9$ has a different shape than the $f_2=1$ surface at low concentrations, while the $f_i=0.9, f_2=0.1$ surface has a high concentration 'tail' that is not present for the $f_i=1$ surface. This further illustrates the importance of knowing the degree of heterogeneity in order to make accurate assessments of experimental results.

4.2 Rough Heterogeneous Surfaces

The wetting of rough heterogeneous surfaces will now be considered briefly, following ideas presented previously⁸. Figure 5a shows predictions (made using Equation 8, with the same adsorption constants as for Figure 3) of contact angle on a rough surface being wetted by a surfactant solution in an unpenetrated (composite Cassie) mode. Unpenetrated wetting means that air remains in the crevices/pores under the drop (and is treated as another material making up the surface under the drop), and is more commonly seen for intrinsically hydrophobic materials such as those considered in Figure 3 and Figure 5a. Figure 5a considers a smooth surface ($f_1 = 0.1, f_2 = 0.9$), allowing progressively more of the heterogeneous surface to be taken up with an (assumed flat) air-liquid interface. Physically speaking, this is equivalent to creating non-wetted holes in the heterogeneous flat surface (as such, the precise value of roughness depends on the depth of the holes, but since the holes are non-wetted their depth does not factor into the calculation). The

air fraction decreases the effect of the remaining wetted heterogeneous surface. For example, when $f_{air} = 0.75$, $f_1 = (1 - f_{air}) * 0.1 = 0.025$, $f_2 = (1 - f_{air}) * 0.9 = 0.225$. One could perform a similar analysis with a more rough surface²⁹ (i.e. for $f_1 + f_2 + f_{air} > 1$), but a smooth topped surface is considered here for the sake of simplicity.

On unpenetrated surfaces (Figure 5a), it is seen (similar to before⁸) that increasing air fraction (decreasing solid fraction) attenuates the effect of surfactant adsorption on contact angle on heterogeneous surfaces. Specifically, as f_{air} increases, contact angle increases (due to the increased weighting of the 180° contact angle associated with the air). Further, the magnitude of the change in contact angle with respect to concentration decreases. This can be seen in Figure 5a by comparing the 'air free' surface to surfaces with increasing values of f_{air} .

It is interesting to note that the behavior on the unpenetrated surfaces can be modeled in either of two equivalent ways. First, the effect of surfactants on each material (including the air) can be weighted by each material's f factor and then combined. Equivalently, the effect of surfactants on each solid material can be combined as on a smooth surface, using f values that sum to one and account for the relative amounts of each solid material. The model predictions for the smooth heterogeneous surface can then be adjusted by the air fraction of the actual surface. Physically, this means that roughening a heterogeneous surface has the same result as applying a heterogeneous coating to a rough surface. This equivalency means, in effect, that roughness and heterogeneity are decoupled during modeling, a conclusion that will be expanded on below in considering penetrated wetting.

In comparison to unpenetrated wetting, Figure 5b shows predictions of contact angle on a rough surface being wetted by a surfactant solution in a penetrated (Wenzel) mode (made using Equation 8, with the same adsorption constants as for Figure 4). Penetrated wetting means that the liquid fills in the crevices/pores under the drop, which is more commonly seen for hydrophilic surfaces (meaning it is more likely to be seen for the materials considered in Figure 4 and Figure 5b). The roughness results in an

increased wetted area under the drop. The effect on contact angle of the increased area can be accounted for by specifying f_1 and f_2 for Figure 5b in such a way that they sum to a value greater than 1 ($f_1 + f_2 > 1$) since for a rough surface, the total surface area is larger than the projected area. The individual f values still represent the relative contribution of each material on the surface. As discussed near the end of Section 2.0, and in more detail elsewhere²⁹, this is the original technique proposed by Cassie and Baxter²⁸.

Similar to before⁸, it is seen that the effect of roughness is to amplify the effect of surfactant adsorption. For hydrophilic surfaces then, as roughness increases the contact angle versus concentration curve decreases to lower values (amplifying the intrinsic hydrophilicity). Further, the magnitude of the change in contact angle with respect to concentration increases, resulting in a 'faster' decrease in contact angle with surfactant concentration. This can be seen in Figure 5b by comparing the $f_1 = 0.1$, $f_2 = 0.9$ (smooth) surface prediction, to the progressively more rough $f_1 = 0.11$, $f_2 = 0.99$; $f_1 = 0.12$, $f_2 = 1.08$; and $f_1 = 0.13$, $f_2 = 1.17$ surface predictions. The total roughness of these surfaces (in terms of the Wenzel roughness which is total area divided by projected area) is $r = f_1 + f_2 = 1.1$, 1.2, and 1.3 for the three surfaces considered.

As with unpenetrated wetting, it is seen that the behaviors can be predicted by first considering the heterogeneity of the surface and then the overall roughness, or by considering the roughness of each material in the heterogeneous surface and then combining the results. This indicates again that, in effect, roughness and heterogeneity are decoupled during modeling. Combining these similar findings for unpentrated and penetrated wetting indicates that predictions for fully rough, heterogeneous surfaces wet in the unpenetrated composite Cassie mode (and/or the penetrated Wenzel mode) are made possible by choosing suitable *f* values that do not sum to one^{8,29}.

4.3 Equally Mixed and Three-material Heterogeneous Surfaces

More complex heterogeneous surfaces (those with approximately equal weighting of each material, and those with three materials) are now considered. Much more rich and varied effects are possible on such surfaces. Consider Figure 6a, which shows a surface plot of contact angle predictions for two-material smooth heterogeneous surfaces, with the *f* parameters being varied over their entire ranges. The adsorption constants were chosen in an *ad hoc* fashion for both materials. In Figure 6a, $\theta_y^0|_1 = 70^\circ$, and material 1 does not experience the autophobic effect, while $\theta_y^0|_2 = 0^\circ$ with material 2 experiencing an autophobic effect similar to the surface/surfactant solution combination studied by El Ghzaoui³, though the constants should not be taken as an optimized fit. Adsorption constants are outlined in Table 2.

For the surfaces with mild heterogeneity considered in Figure 3 – Figure 5, the f_1 and f_2 parameters were seen to weight the behavior of each material. This is again seen in Figure 6a, but since the f_1 and f_2 parameters vary across a wider range, there is a greater variation in the range of model predictions. The non-linear effects of the combination of contact angles (due to the cosine terms in Equation 8) can be seen in Figure 6a as a curvature of the surface plot of Figure 6b at any given concentration plane. This curvature can be seen most clearly on the plane of zero concentration.

As a result of the non-linear weighting, the contact angles predicted by the modified Cassie model for intermediate ranges of the *f* values are more complex than for each material in its pure state. Specifically, as concentration ranges from 0 to the CMC, multiple maxima and minima, inflection points, and 'kinks' (abrupt changes in slope) in the graph are seen as the *f* values vary. To illustrate this, five traces across the surface plot of Figure 6a (at $f_1 = 0, f_1 = 0.1, f_1 = 0.5, f_1 = 0.9$ and $f_1 = 1$) are shown in Figure 6b. The curves all intersect at $C/C_{CMC} \approx 0.1$, since (as was seen in Figure 4) at this concentration $\theta_y(C_s)|_1 = \theta_y(C_s)|_2$ and any weighted combination of the contact angles will return the same result.

As in Section 4.1, it is seen in Figure 6b that even a heterogeneous surface that is a 9:1 or 1:9 combination of two materials can display complex behaviors compared to $f_1=1$ and $f_1=0$. As an example, while the pure 20 of 38 water wetting of the $f_1 = 0.9$, $f_2 = 0.1$ surface would barely show a difference in contact angle compared to the $f_1 = 1$, $f_2 = 0$ surface, surfactant solutions with concentration above $C/C_{CMC} \approx 0.25$ would behave very differently on the two surfaces. Conversely, the $f_1 = 0.1$, $f_2 = 0.9$ surface shows deviation from the f_1 = 0, $f_2 = 1$ surface at low concentrations, as was seen in Figure 4. Looking at the $f_1 = f_2 = 0.5$ plot in Figure 6b, the behaviors are the most complex, showing local minima and maxima, inflection points, and abrupt changes in slope. The great variations possible in surfactant solution wetting of heterogeneous surfaces point to the extreme importance in experimental work to either ensure the homogeneity of a surface, or to characterize the heterogeneity fully.

Consider now a heterogeneous surface composed of three materials. Two of the materials are the same as those modeled in Figure 6, the third material is hydrophilic $(\theta_y^0|_3 = 45^\circ)$, with adsorption constants chosen on an *ad hoc* basis. Surfactant adsorption to material 3 results in an autophobic effect at high concentrations, with a slight decrease in contact angle at extremely low concentrations followed by a monotonic rise in contact angle with concentration. The predicted trace of contact angle with respect to concentration is shown for each material separately in Figure 7, along with the model predictions (based on Equation 8) for a heterogeneous surface composed of equal fractions of each material (i.e. $f_1 = f_2 = f_3 = 1/3$).

The predicted contact angles for the heterogeneous surface (solid line on Figure 7) are still the result of the weighted predictions of the three materials. To illustrate this, consider all four predictions as concentration increases. Starting from zero, as concentration increases, $\theta_y(C_s)|_1$ and $\theta_y(C_s)|_3$ both decrease while $\theta_y(C_s)|_2$ remains at the limit of zero degrees. The adsorption on materials 1 and 3 results in a decrease in contact angle on the heterogeneous surface. At a certain concentration $(\ln(C_s) \approx -4.25)$, $\theta_y(C_s)|_2$ begins to quickly increase, overwhelming the decrease of $\theta_y(C_s)|_1$ and $\theta_y(C_s)|_3$. Material 2

now dominates the behavior of the heterogeneous surface, leading to an increase in contact angle. Near the maximum of $\theta_y(C_s)|_2$, contact angle on the heterogeneous surface also reaches a maximum and begins to decrease again with increasing concentration. Finally, once $\theta_y(C_s)|_1$ and $\theta_y(C_s)|_2$ have reached the limiting value of zero degrees, the still increasing $\theta_y(C_s)|_3$ causes the contact angle on the heterogeneous surface to increase once more. The concept of limiting values of contact angle raises a related idea of limiting surfactant adsorption, in that the adsorption to a given material/interface may saturate before the critical micelle concentration is reached. This can be accounted for in the model by fixing the effect on that material/interface at its limiting value for higher values of concentration, though this has not been performed in the present study.

Further considering three-material surfaces, Figure 8a and 8b each show other predictions for heterogeneous surfaces made up of the same three materials considered in Figure 7. In Figure 8a, three curves show predictions for which one *f* value is set to 0.5, while the *f* values for the other two materials are set to 0.25. Comparing these three to the curve for the $f_1 = f_2 = f_3 = 1/3$ surface, it is seen that broadly similar behavior is repeated. For each set of *f* values, there is a decrease in contact angles at low concentrations, an increase at very high concentrations, and a maximum (absolute or local) at intermediate values of concentration. However, the specifics (i.e. magnitude of contact angle, location of maximum, etc.), vary widely as the weighting of each material changes, indicating that even a relatively minor change from $f_1 = f_2 = f_3 = 1/3$ can lead to very different behaviors.

In Figure 8b, the *f* value for one material is set to 0.8, while the *f* values for the other two materials are both set to 0.1. Comparing these three predictions to the prediction for the $f_1 = f_2 = f_3 = 1/3$ surface, very dissimilar behaviors are seen. This can be understood by considering that the heavier weighting (*f*=0.8) for one of the materials in each curve will tend to overwhelm the influence of the other materials (just as a weighting of *f*=0.9 largely overwhelmed the behavior on a two-material surface). Indeed, it can be seen

that each of the dotted and/or dashed curves in Figure 8b bears a close resemblance to the corresponding curve for the pure material in Figure 7. It is clear from Figure 7 and Figure 8 that a wide range of behaviors are possible on smooth heterogeneous surfaces wet by surfactant solutions. Including the effects on roughness on such a surface would further increase the range of possible behaviors. Regardless of this complexity, the newly developed model presented in this paper should help to predict and explain the wide variety of possible results and behaviors.

5.0 Conclusion

A model has been derived from first principles, modelling smooth and rough heterogeneous surface equilibrium contact angles for surfactant solutions with surfactant adsorption at the liquid-vapor, solid-liquid, and solid-vapor interface. The inclusion of solid-vapor adsorption allows the model to successfully predict experimental data for the contact angle on hydrophilic surfaces undergoing the autophobic effect with surfactant solutions.

It is seen that the f_m parameters serve as weighting factors determining how to combine the effects of surfactant adsorption on each material to predict the behavior on the heterogeneous surface. The combination leads to more complicated predictions of contact angle versus concentration for surfactant solutions wetting a heterogeneous surface compared to a perfectly homogeneous surface. Specifically, it is seen that, at a given concentration, the inclusion of a small amount of material that is hydrophobic at that concentration has a greater effect on a hydrophilic material than vice versa, due to the *f* factors acting on the *concentration dependent* cosine of the contact angles for the surfactant solution on each material. The level of complexity in model predictions increases rapidly with the number of differently behaving materials present on the surface and with more equal weighting of different materials.

Rough heterogeneous surfaces are seen to either amplify or attenuate the effects of surfactant adsorption, depending on the wetting mode (for penetrated or unpenetrated wetting, respectively, due to increased or

decreased solid areas for surfactant adsorption). The inclusion of roughness in the model adds an additional variable, indicating that the contact angle of surfactant solutions on rough heterogeneous surfaces can take even richer varieties of behaviors compared to smooth heterogeneous surfaces.

The possible complexity of surfactant solution contact angle behavior on heterogeneous surfaces points to the importance of characterizing the heterogeneities of any surface under consideration. The potentially large effects of even slight heterogeneities indicate that incorrect conclusions about the effect of surfactant adsorption could be made if surfaces are assumed to be homogeneous when they in fact contain slight heterogeneity due to, e.g., an imperfect coating or environmental contamination by oils/greases. With proper characterization, the models described in this paper will allow for prediction of contact angles on all types of heterogeneous surfaces, and design of surfaces for specific interactions with surfactant solutions.

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Table 1: Liquid-vapor interfacial tensions and contact angles (read from literature¹⁶) for various concentrations of aqueous solutions of hydrophobically modified inulin (INUTEC[®]SP1) on quartz glass. Reported accuracy is ± 0.2 mN/m for interfacial tension, and $\pm 0.3^{\circ}$ for contact angles in the range of 1°-5° and $\pm 1.0^{\circ}$ in the range of 5°-20°. Standard deviation was not reported.

$\frac{C}{C_{CAC}}$	Liquid-vapor interfacial tension ¹⁶ (mJ/m ²)	Contact angle on Quartz Glass ¹⁶ (degrees)
0.0005	N/A	2.6
0.001	N/A	8.0
0.002	N/A	10.0
0.005	N/A	11.3
0.01	67.0	12.5
0.05	61.1	11.9
0.2	56.1	8.5
0.5	52.5	6.2
1.0	50.5	3.5
2.0	50.8	3.1

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Table 2: Adsorption constants for each surface used in the model for contact angles of surfactant
solution on heterogeneous surfaces, $\gamma_{lv}^0 = 72.21$ (mJ/m ²) for water in all cases.

	Material and contact angle	Adsorption Coefficient	Liquid-Vapor Interface	Solid-Liquid Interface	Solid-Vapor Interface
Figure 3 and Figure	$1\left(\theta^{0}\right = 0^{\circ}$	Γ_{xy}^{∞} (mol/m ²)	6.013×10 ⁻⁶	1.200×10 ⁻⁵	1.790×10 ⁻⁵
5a	$1 \left(O_{y} \right)_{1} = 0$	n _{xy}	1.407	1.300	1.300
		K _{xy}	22.89	23.00	22.00
	2	Γ_{xy}^{∞} (mol/m ²)	6.013×10 ⁻⁶	4.279×10 ⁻⁶	0
	$\left(\theta_{y}^{0}\right _{2}=120^{\circ}\right)$	n _{xy}	1.407	1.990	N/A
		K _{xy}	22.89	296.2	N/A
Figure 4 and Figure	$1\left(\theta^{0}\right = 0^{\circ}$	Γ^{∞}_{xy} (mol/m ²)	1.629×10 ⁻⁶	2.984×10 ⁻⁶	4.465×10^{-6}
5b	$ _{y_{1}} = 0$	n_{xy}	1.115	0.934	0.917
		K _{xy}	453	649.1	417.6
	$2\left(\theta^{0}\right - 60^{\circ}$	Γ^{∞}_{xy} (mol/m ²)	1.629×10 ⁻⁶	1.160×10 ⁻⁶	0
	$2 \left(O_{y} \right)_{2} = 00 $	n _{xy}	1.115	0.934	N/A
		K _{xy}	453.0	4500	N/A
Figure 6,	$1 \left(\theta_{y}^{0} \right _{1} = 70^{\circ} \right)$	Γ_{xy}^{∞} (mol/m ²)	2.890×10 ⁻⁶	4.279×10 ⁻⁶	0
and		n _{xy}	1.066	1.990	N/A
Figure 8		K _{xy}	501.0	296.2	N/A
		Γ_{xy}^{∞} (mol/m ²)	2.890×10^{-6}	1.326×10 ⁻⁵	7.270×10 ⁻⁶
	$2\left.\left(\theta_{y}^{0}\right _{2}=0^{\circ}\right)$	n _{xy}	1.066	3.582	1.390
		K _{xy}	501.0	296.2	600.0
		Γ^{∞}_{xy} (mol/m ²)	2.890×10 ⁻⁶	3.640×10 ⁻⁶	7.270×10 ⁻⁶
	$3 \left \left \theta_{y}^{o} \right _{3} = 45^{\circ} \right)$	n _{xy}	1.066	1.390	1.390
	(only used in Figure 7 and Figure 8)	K _{xy}	501.0	600.0	600.0

Figure Captions

Figure 1: Liquid-vapor interfacial tension versus the natural logarithm of concentration of aqueous hydrophobically modified inulin (INUTEC[®]SP1), ($C_s = C/C_{CAC}$). The points are experimental data¹⁶. The line is the best fit of Equation 3 to the data. Fit parameters are $\Gamma_{lv}^{\infty} = 1.629 \times 10^{-6} \text{ mol/m}^2$, $n_{lv} = 1.155$, $K_{lv} = 453$ and $\gamma_{lv}^0 = 72.11 \times 10^{-3} \text{ J/m}^2$, with goodness-of-fit parameters SSE: $1.368 \times 10^{-5} \text{ J}^2/\text{m}^4$, R²: 0.94, Adjusted R²: 0.84 and RMSE: $2.615 \times 10^{-3} \text{ J/m}^2$.

Figure 2: Cosine of contact angle on quartz glass versus the natural logarithm of concentration of aqueous hydrophobically modified inulin (INUTEC[®]SP1), ($C_s = C/C_{CAC}$). The points are experimental data¹⁶. The line is the best fit of Equation 8 to the data for m = 1, $f_m = 1$. Fit parameters are $\Gamma_{sl}^{\infty} = 2.984 \times 10^{-6}$ mol/m², $n_{sl} = 0.9337$, $K_{sl} = 649.1$, $\Gamma_{sv}^{\infty} = 4.465 \times 10^{-6}$ mol/m², $n_{sv} = 0.917$, $K_{sv} = 417.6$ and $\theta_v^0 = 0^\circ$, with goodness-of-fit parameters SSE: 5.018×10^{-5} , R²: 0.92, Adjusted R²: 0.83 and RMSE: 3.542×10^{-3} .

Figure 3: Predicted contact angle (from Equation 8) versus natural logarithm of surfactant concentration for smooth, two-material heterogeneous surfaces with various values of f_1 and f_2 . Material 1 is hydrophilic $(\theta_y^0|_1 = 0^\circ)$ with solid-liquid and solid-vapor adsorption constants chosen on an *ad hoc* basis as described in the text. Material 2 is hydrophobic $(\theta_y^0|_2 = 120^\circ)$ with adsorption parameters taken for SDS on Teflon⁸. See Table 2 for the values of the adsorption constants.

Figure 4: Predicted contact angle (from Equation 8) versus natural logarithm of surfactant concentration for smooth, two-material heterogeneous surfaces with various values of f_1 and f_2 . Material 1 is hydrophilic 28 of 38

 $(\theta_y^0|_1 = 0^\circ)$ with adsorption parameters based on the fit for modified inulin on glass (Figure 1, Figure 2). Material 2 is less hydrophilic $(\theta_y^0|_2 = 60^\circ)$, with solid-liquid and solid-vapor adsorption constants chosen on an *ad hoc* basis as described in the text. See Table 2 for the values of the adsorption constants.

Figure 5: Predicted contact angle (from Equation 8) versus natural logarithm of surfactant concentration for rough, two-material heterogeneous surfaces. In (a) the materials are the same as for Figure 3. In (b) the materials are the same as for Figure 4. Adsorption constants are given in Table 2. (a) Shows the predictions for unepentrated (composite Cassie) mode wetting on three porous (rough) surfaces compared to a smooth surface. (b) Shows the predicted behavior for penetrated (Wenzel) mode wetting for three different rough surfaces ($\sum_{m} f_m > 1$) compared to a smooth surface.

Figure 6: (a) Surface plot of predicted contact angle for Cassie mode wetting (using Equation 8) on a twomaterial smooth heterogeneous surface for various values of f_1 and f_2 and concentrations of surfactant solution from 0-1 C_{CMC} . Material 1 is hydrophilic ($\theta_y^0|_1 = 70^\circ$) with no solid-vapor adsorption. Material 2 is hydrophilic ($\theta_y^0|_2 = 0^\circ$) with solid-vapor adsorption modeling an autophobic effect similar to that described by El Ghzaoui³. Adsorption coefficients for both surfaces (chosen on an *ad hoc* basis) are given in Table 2. (b) Traces from the surface plot for $f_1=0$ and $f_2=1$; $f_1=0.1$ and $f_2=0.9$; $f_1=f_2=0.5$; $f_1=0.9$ and $f_2=0.1$; and $f_1=0$ and $f_2=1$.

Figure 7: Predicted contact angle (solid line) versus natural logarithm of surfactant concentration for a smooth ($f_1=f_2=f_3=1/3$) heterogeneous surface made up of equal portions of three materials. Predicted 29 of 38

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contact angle traces of each material alone are also shown as dashed/dotted lines. Predictions were made using Equation 8. Material 1 (dash-dot line, $\theta_y^0|_1 = 70^\circ$) does not demonstrate the autophobic effect (i.e. there is no solid-vapor adsorption). Material 2 (dotted line, $\theta_y^0|_2 = 0^\circ$) demonstrates the autophobic effect resulting in a maximum in contact angle. Material 3 (dashed line, $\theta_y^0|_3 = 45^\circ$) has solid-vapor adsorption, resulting in a decrease, and then an increase in contact angle as concentration increases. Adsorption constants for each material are given in Table 2. All are chosen on an ad hoc basis, with materials 1 and 2 identical to those in Figure 6.

Figure 8: Predicted contact angle (from Equation 8) versus natural logarithm of surfactant concentration for smooth, three-material heterogeneous surfaces with various values of f_1 , f_2 and f_3 . Materials are the same as for Figure 7 and adsorption constants for each material are given in Table 2. (a) shows heterogeneous surfaces of roughly equal amounts of each material. (b) shows heterogeneous surfaces for which one material is predominant.





Figure 2



Figure 3



Figure 4







Figure 7

