

Antisurfactant (Autophobic) Behavior of Superspreader Surfactant Solutions

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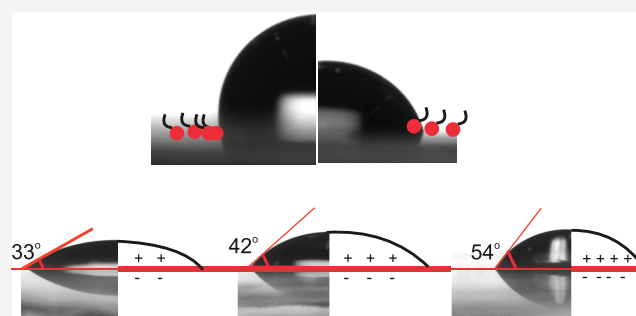
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ABSTRACT: Surfactants are often added to water to increase the wetting of hydrophobic surfaces. We previously showed that most surfactant solutions behave identically to simple liquids with the same surface tension, indicating that the surfactants do not change the wettability of the solid surface itself. Here, we show that the superspreading surfactant Silwet results in a systematically higher contact angle on a hydrophobic surface than other surfactant solutions of comparable liquid–vapor surface tension. We also experimentally observe this “antisurfactant” behavior for CTAB on hydrophilic substrates. Supported by sum-frequency generation spectroscopy results, we suggest that this effect is due to charge-binding of the surfactant with the substrate.



INTRODUCTION

Surfactants can improve the wetting of an aqueous solution on a solid substrate.¹ As a result, they are widely used in various household and industrial applications,² such as in detergents for cleaning clothes or dishes,³ in food products,⁴ and as adjuvants to help improve pesticide efficiency in crops.⁵ Because of their widespread use,^{6–9} surfactant solutions, and their wetting properties have been studied for almost two centuries. Nonetheless, there are still many surfactant-induced phenomena that remain unexplored. We have previously reported the wetting behavior of the surfactant solutions on hydrophobic substrates and showed that there is almost no difference between the behavior of a surfactant solution and that of a pure liquid of the same surface tension.¹⁰ In contrast, in this work, we report on the “antisurfactant” behavior where a surfactant induces poorer wetting on hydrophobic as well as hydrophilic surfaces than simple liquids of similar surface tensions.

Autophobic and autophilic effects are two examples of intriguing phenomena usually attributed to the adsorption of surfactant molecules on solid surfaces.^{11–15} On a hydrophilic substrate, surfactants sometimes lead to an increase in the equilibrium contact angle. This phenomenon is known as the “autophobic effect”.^{16,17} On hydrophobic surfaces, however, the adsorption of other types of surfactants in the thin film coexisting with the droplet leads to a decrease in the contact angle. This is the so-called “autophilic effect”.^{18–21} In many industrial applications, good wetting of the aqueous solution on a hydrophobic substrate is crucial and hence the autophilic effect is used extensively to achieve (near) complete wetting. It has, however, also been noticed in many cases that the

autophilic effects do not occur on hydrophobic substrates.²² Superspreading surfactants, generically known as trisiloxanes, are widely used to increase wetting on hydrophobic surfaces. They are for instance employed in agriculture where aqueous pesticide solutions are sprayed onto hydrophobic plant leaves. The specificity of the whole class of trisiloxane surfactants is that they lower the surface tension of water significantly more than almost all other types of surface-active molecules.²³ If the solid surface tensions (with liquid and vapor) are unaffected by the surfactant, this implies indeed a better wetting when trisiloxanes are added. In the present work, we show that on different types of hydrophobic surfaces, the superspreading surfactant in fact shows autophobic behavior, showing a smaller wetting efficiency compared to other liquids or surfactant solutions of the same liquid–vapor surface tension.

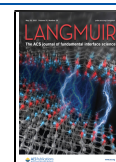
EXPERIMENTAL SECTION

Chemicals. Several surfactants are used for the measurements of the contact angles and the liquid–vapor interfacial tensions. As a typical cationic surfactant, cetyl trimethylammonium bromide (CTAB, Sigma-Aldrich, NL) is used, while sodium dodecyl sulfate (SDS, Sigma-Aldrich, NL) is used as a typical anionic surfactant. In addition, Triton X-100 (TX100, Sigma-Aldrich) is used as a nonionic surfactant, and also the charge-neutral trisiloxane Silwet (SL-77,

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Sigma-Aldrich) is used as a representative of “superspreading” surfactants. To prepare the surfactant solutions, the required amount of the surfactant is added to Milli-Q water (Merck Millipore, Germany) and gently stirred using a magnetic stirrer overnight. Besides the surfactant solutions, we also study simple liquids of different surface tensions: ultrapure water, glycerol (Sigma-Aldrich), ethylene glycol (Sigma-Aldrich), dodecane (Sigma-Aldrich), and silicon oil (Rhodorsil 47V20, Sigma-Aldrich) with liquid–vapor surface tensions γ_{LV} of ~ 72 , ~ 64 , ~ 47 , ~ 25 , and ~ 21 mN/m, respectively. We will refer to these liquids without any surfactant molecules as “pure liquids” in the remainder of the paper.

Surface Tension Measurements. A K100 force tensiometer (Krüss, Hamburg, Germany) is used to measure the liquid–air interfacial tensions with the Du–Noüy ring method. The interfacial tension in these experiments is varied by varying the concentration of the surfactant molecules. The concentration of the surfactant solution is varied during an experiment using preset automatic dilution steps. For a detailed account of the procedure, examples of surface tension data as well as discussion about the anomalies in such measurements, the reader is referred to our previous work.^{10,24–26}

Contact Angle Goniometry. An Easydrop (Krüss, Hamburg, Germany) optical contact angle goniometer is used to measure the contact angles in a closed environment of constant temperature (23 ± 2 °C) and relative humidity ($50 \pm 2\%$). All of the contact angles are measured for droplets of a constant volume of $2 \mu\text{L}$ (error in dispensing measured to be within $\pm 10\%$). There are several ways of optically measuring the equilibrium contact angle; e.g., subjecting the drop to a gravitational force and then measuring the work of adhesion from the solid–liquid contact area,²⁷ or by considering the three-phase contact line energy and coupling this with the advancing and receding contact angles.²⁸ In this work, we have adopted the latter of these two methods and extracted the equilibrium contact angles from the corresponding advancing and receding contact angles.

Silanized glass, polyethylene, and Teflon are used as hydrophobic substrates. Silanized glass is prepared using Dynasylan OCTEO (Evonik) following the protocol of Brzoska et al.²⁹ Fresh Petri dishes (VWR, The Netherlands) are used as polyethylene substrates, while Teflon bands are taped on clean glass slides (Menzel, Thermo Scientific, The Netherlands) to prepare the Teflon substrates. These Menzel glass slides are also used as hydrophilic substrates. The substrates are cleaned in ethanol and water and subsequently treated in an O_2 plasma cleaner. Through this cleaning procedure, these glass slides acquire a negative charge on their surface. The second batch of hydrophilic substrates is prepared by making these substrates positively charged where a polyelectrolyte deposition protocol is followed, as described below.

Sum-Frequency Generation Spectroscopy. Sum-frequency generation (SFG) is a surface-specific alternative to infrared (IR) and Raman spectroscopy and is used in this work for obtaining information about adsorption at the solid–liquid interface. In these experiments, we use bare (hydrophilic) silica and silanized (hydrophobic) silica substrates. In principle, the vibrational spectrum of just an interfacial layer can be obtained. More details of the setup and the measuring principle can be found in ref 10.

Modified Zisman Methodology. To study the surfactant adsorption at the solid–liquid and solid–gas interfaces, we use a modified Zisman methodology as introduced previously.¹⁰ In the traditional Zisman method, the cosine of the three-phase contact angle ($\cos \theta$) is plotted against the liquid–vapor tension (γ_{LV}) following Young’s equation

$$\cos \theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \quad (1)$$

where γ_{SV} and γ_{SL} are the solid–vapor and solid–liquid interfacial tensions, respectively. Then, one extrapolates to the point where $\cos \theta = 1$, yielding the γ_{LV} of the liquid, which would spread completely on that solid surface. We showed that plotting $\cos \theta$ against the inverse of γ_{LV} is more appropriate since (a) this is a more direct representation of Young’s equation and (b) the slope of the plotted straight line gives

an estimate of the difference in solid–vapor and solid–liquid interfacial tensions and hence of surfactant adsorption on the solid surface.

RESULTS

We measure the contact angles (θ) by putting drops of aqueous surfactant solutions on a substrate for different liquid–vapor interfacial tension (γ_{LV}).

Silwet is a trisiloxane surfactant known as a superspreader, i.e., aqueous solutions of this surfactant wet most surfaces very rapidly. Surprisingly, we find (Figure 1) that drops of the

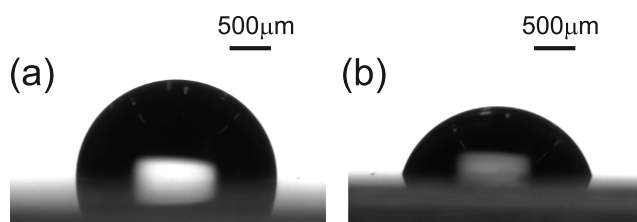


Figure 1. Screenshots from contact angle measurements: (a) a $2 \mu\text{L}$ drop of 0.001 wt % Silwet solution ($\gamma_{LV} \sim 45$ mN/m) on an octeosilanized glass and (b) a $2 \mu\text{L}$ drop of ethylene glycol ($\gamma_{LV} \sim 47$ mN/m) on an octeosilanized glass.

Silwet solution systematically exhibit a higher contact angle on a silanized glass surface than other surfactant solutions such as SDS, CTAB, etc., as well as pure liquids with the same surface tensions. The consistently higher contact angle for Silwet is also evident from the modified Zisman plot (Figure 2), where CTAB, SDS, TX100 solutions, and pure liquids show similar θ s for a given γ_{LV} , and all these angles are lower than that for Silwet.

We identify the behavior of Silwet as an antisurfactant since the addition of this surfactant makes the surface less wettable.

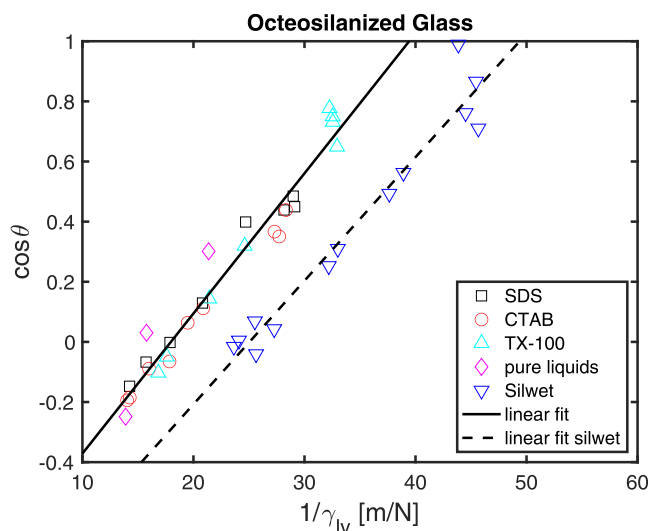


Figure 2. Modified Zisman plot of the cosine of the equilibrium contact angles θ of various surfactant solutions and pure liquids on a silanized glass surface versus the inverse of liquid–vapor interfacial tension γ_{LV} . All data points other than those belonging to Silwet are from our previous work.¹⁰ The solid line is a straight line fit for the data points belonging to all surfactants excluding Silwet and the dashed line is a straight line fit for the data points belonging (only) to Silwet.

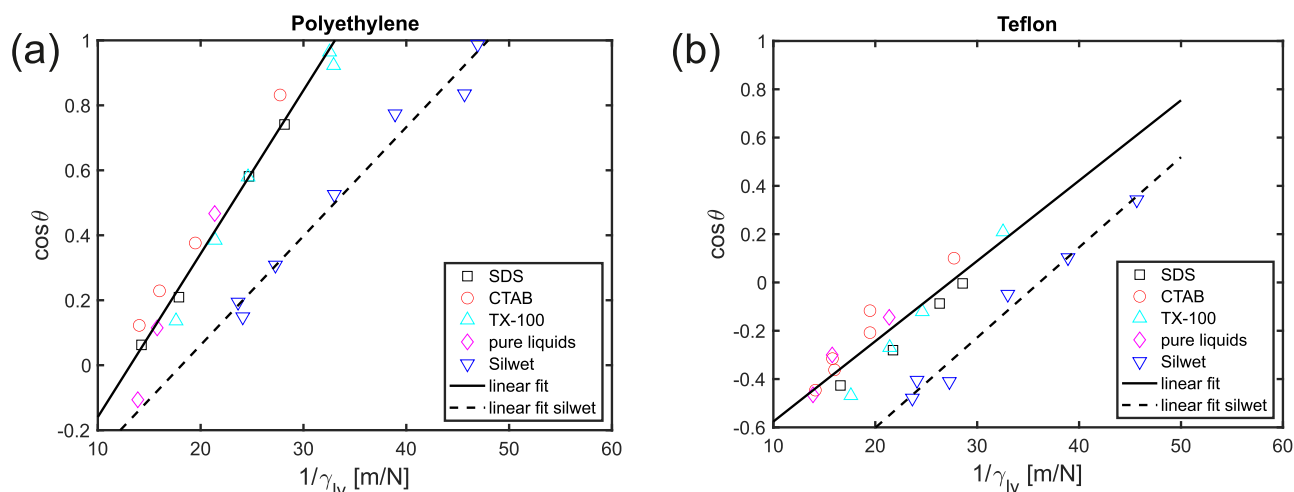


Figure 3. Modified Zisman plot of the cosine of the equilibrium contact angle θ of various surfactant solutions and pure liquids on polyethylene (a) and Teflon (b) substrates versus the inverse of the liquid–vapor interfacial tension γ_{LV} . Both in (a) and (b), the solid line is a straight line fit for the data points belonging to all surfactants excluding Silwet and the dashed line is a straight line fit for the data points belonging (only) to Silwet.

This antisurfactant behavior is also seen for Silwet on the other hydrophobic surfaces: polyethylene (Figure 3a) and Teflon (Figure 3b).

To understand this phenomenon, we turn to the Gibbs adsorption equation: $\frac{d\gamma}{d \ln C} = -mk_B T \Gamma$, where $d\gamma$ is the change in surface tension, C is the bulk surfactant concentration, $k_B T$ is the thermal energy, m is a prefactor for distinguishing ionic from nonionic surfactants, and Γ is the surface coverage due to the adsorption of molecules on a surface. This implies that the adsorption of surfactants at the solid–liquid interface decreases the solid–liquid interfacial tension (γ_{SL}). Hence, following Young’s equation (eq 1), a smaller γ_{SL} should lead to a higher $\cos \theta$ (and hence, a lower contact angle), provided the solid–vapor and liquid–vapor interfacial tensions (γ_{SV} and γ_{LV} , respectively) remain constant. However, in our previous work,¹⁰ we have shown that the reason why various surfactants behave similarly to pure liquids is that the solid–vapor interfacial tension (γ_{SV}) actually decreases as much as γ_{SL} so that the contact angle does not decrease. This was demonstrated to be the consequence of the formation of a precursor film in an equilibrium with a macroscopic droplet. Extrapolating this conclusion to the current results for Silwet, the antisurfactant behavior would require the solid–liquid tension to decrease less than the solid–vapor one. Adsorption of the surfactant molecules both at solid–liquid and liquid–vapor interfaces on each side of a nanoscopically thin precursor film is a very plausible scenario as demonstrated by literature where researchers have investigated the retraction of the triple line,^{16,30} or one part of the contact line propelling itself and by doing so dragging the other part of the contact line.^{31,32} Usually, the fluctuations of the triple line leading to the “leakage” of surfactant molecules is considered the reason behind such behavior of the droplets.³³

To investigate the origins of the unexpected behavior of Silwet, we carry out SFG spectroscopy on silanized glass in contact with pure water and with Silwet solutions. The signals in the spectrum of pure water (Figure 4) between 2800 and 3000 cm^{-1} are due to the C–H groups in the silane layer of the substrate. The broader signal between 3000 and 3600 cm^{-1} originates from water in the vicinity of the surface. For the Silwet solutions compared to pure water, an increase in the

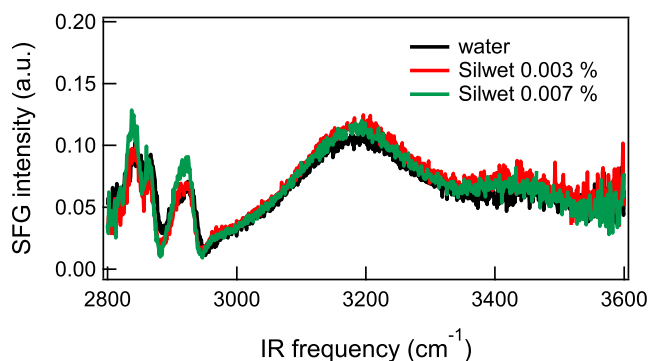


Figure 4. SFG spectra for Silwet solutions in contact with silanized glass. The corresponding $1/\gamma_{LV}$ values for 0.003 and 0.007% Silwet solutions are 25.53 and 37.64 m/N , respectively, as can be seen in Figure 2.

SFG signal of the CH modes is observed. This indicates that Silwet is present at the solid–liquid interface for the silanized glass like CTAB, SDS, and Triton,¹⁰ and thus decreases γ_{SL} according to the Gibbs’ adsorption equation. We previously concluded that for the surfactants CTAB, SDS, and Triton, the solid–vapor and solid–liquid surface tensions decrease by the same amount, as the wettability for these surfactants is the same as that for pure liquids of the same surface tension.¹⁰ For Silwet, however, the contact angles are larger than those for CTAB, SDS, and TX100, which implies that for Silwet γ_{SV} decreases more than γ_{SL} likely due to the formation of the precursor film, as was observed in our earlier work.¹⁰

Antisurfactant Effect on a Hydrophilic Substrate. The observed antisurfactant effect should not necessarily be limited to hydrophobic surfaces; we would expect it to be present for any system, for which the surfactant modifies the solid–liquid surface tension. One might expect that the electrostatic attraction between the surface and the surfactant would give rise to antisurfactant effects. To explore this possibility, we investigate the effect of the surfactants on a clean glass substrate, which is hydrophilic, i.e., (slightly) negatively charged when cleaned. Negatively charged or neutral surfactants such as SDS, TX100, and Silwet show very low contact angles, between 5 and 15°. This is expected because of

these aqueous solutions' low liquid–vapor tensions and the low tension of the hydrophilic surface. CTAB, however, shows a reproducibly larger contact angle, as seen in Figure 5. We also observe that when the pH of the CTAB solution is changed, the corresponding contact angles change.

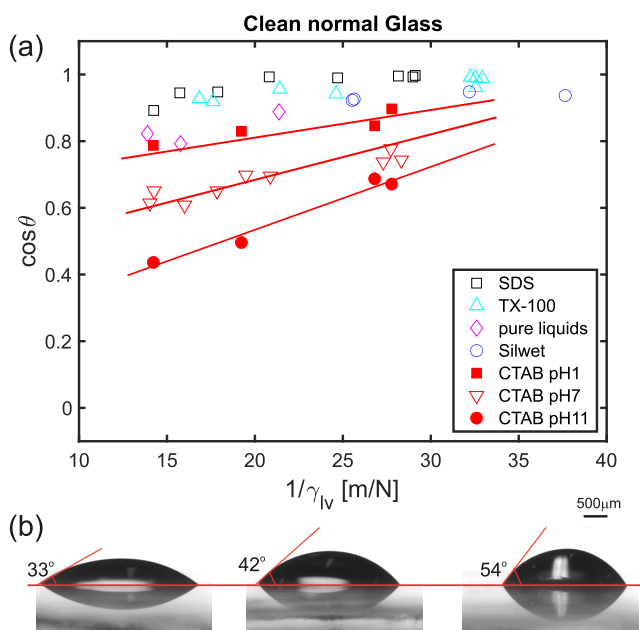


Figure 5. (a) Modified Zisman plot of the cosine of the equilibrium contact angle θ of various surfactant solutions and pure liquids on clean glass. The solid red lines are fits to a straight line for CTAB solutions (pH 1, pH 7, and pH 11) mainly to distinguish these data points from each other and from other surfactants. (b) Screenshots of contact angle measurement for drops (2 μL volume) of CTAB solutions on clean glass slides with (left) pH 1; (center) pH 7; and (right) pH 11.

To determine if CTAB is adsorbed at the solid–liquid interface on a clean glass slide, we performed SFG experiments (Figure 6). The SFG spectrum for pure water in contact with substrate shows the broad water response between 3200 and 3400 cm^{-1} . Since the surface is negatively charged for the pure water case, the SFG signal is relatively large, as the water molecules align their dipole to the negative surface potential.

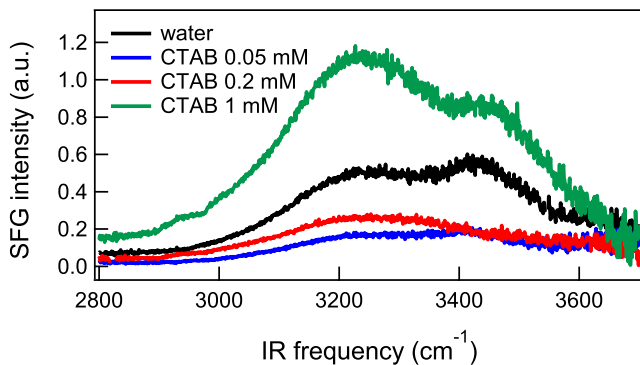


Figure 6. SFG spectra for the silica–aqueous interface for different concentrations of CTAB. With increasing concentration, the water signal initially decreases due to the neutralization of the negative surface charge. Following further adsorption of CTAB, the surface becomes substantially positively charged.

Upon the addition of 0.05 mM CTAB, the spectral intensity decreases significantly, as the positive charge of CTAB partly cancels out the negative charge of the surface. Upon further increasing the CTAB concentration, the SFG signal strongly increases due to the CTAB adsorption overcompensating the substrate's negative charge. A similar observation has been reported in ref 34. The previous argument that the existence of a precursor film would lead to the decrease of γ_{SV} , preventing a lowering of the contact angle, could be responsible for the observed changes. Ellipsometry measurements on the glass surface confirm the existence of a precursor film of ~ 10 nm thickness. On a hydrophilic surface, the electrostatic interaction is a plausible mechanism for the CTAB's behavior since the positively charged headgroups of CTAB can interact with the negatively charged glass. The latter also explains the behavior of CTAB with increasing pH. The point of zero charge (pzc) for SiO_2 of glass is around pH 2.3; hence, the glass surface becomes increasingly charged with increasing pH. This leads to more adsorption of CTAB at the solid–liquid interface, making the substrate more hydrophobic, resulting in the observed increase in the contact angle (Figure 5). As such, CTAB functions as an antisurfactant on the negatively charged silica surface.

CONCLUSIONS

We have experimentally demonstrated the antisurfactant behavior of a superspreader surfactant on a variety of hydrophobic surfaces. The antisurfactant behavior of the surfactant Silwet has been explained by considering the adsorption of the surfactant molecules on the solid–liquid as well as the solid–air interface. This is an important conclusion, since there are many applications in which trisiloxane surfactants are used to improve the wetting of aqueous solutions on hydrophobic surfaces, such as the deposition of aqueous pesticide solutions on plant leaves. A similar antisurfactant behavior is observed for the charged surfactant CTAB in contact with the oppositely charged silica. The adsorption of CTAB to the surface modifies the solid–air interfacial free energy, thereby affecting the wetting properties of the solution. Our results here show that the spectacular lowering of the liquid–vapor surface tension by these types of surfactants does not necessarily guarantee a smaller contact angle (and hence better coverage) of the surfaces: the change in solid wetting properties induced by the surfactant also has to be taken into account.

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Notes

The authors declare no competing financial interest.

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