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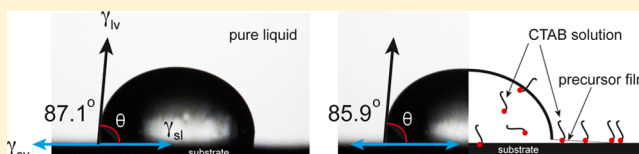
Counteracting Interfacial Energetics for Wetting of Hydrophobic Surfaces in the Presence of Surfactants

Bijoyendra Bera,^{*,†} Odile Carrier,[†] Ellen H. G. Backus,[‡] Mischa Bonn,[‡] Noushine Shahidzadeh,[†] and Daniel Bonn[†]

[†]Institute of Physics, Science Park 904, Amsterdam 1098 XH, The Netherlands

[‡]Max Planck Institute for Polymer Research, Ackermannweg 10, Mainz 55128, Germany

ABSTRACT: Surface active agents (surfactants) are commonly used to improve the wetting of aqueous solutions on hydrophobic surfaces. The improved wettability is usually quantified as a decrease of the contact angle θ of a droplet on the surface, where the contact angle θ is given by the three surface tensions involved. Surfactants are known to lower the liquid–vapor surface tension, but what they do to the two other surface tensions is less clear. We propose an improved Zisman method for quantifying the wetting behavior of surfactants at the solid surface. This allows us to show that a number of very common surfactants do not change the wettability of the solid: they give the same contact angle as a simple liquid with the same liquid–vapor surface tension. Surface-specific sum-frequency generation spectroscopy shows that nonetheless surfactants are present at the solid surface. The surfactants therefore change the solid–liquid and solid–vapor surface tensions by the same amount, leading to an unchanged contact angle.



INTRODUCTION

Surfactants are widely used as wetting agents;¹ e.g., each time one washes the dishes after a meal, one uses a detergent (surfactants) to make the hydrophobic, greasy (from oil and fat) plates water-wetting again so as to facilitate cleaning. However, what the surfactant actually does at these solid surfaces is not completely clear. Usually, the surfactant action on a solid surface is attributed to the surfactant adsorption from an aqueous phase onto the surface,^{2–4} especially for hydrophobic surfaces.^{5,6} If one places a drop of an aqueous surfactant solution on a hydrophobic surface, say a parafilm or a greasy dish, it, therefore, seems plausible that the hydrophobic tails of the surfactant molecule will adsorb onto the hydrophobic surface.^{7,8} Since the hydrophilic heads of the surfactant are then pointing into the solution, one would expect this composite surface to be more hydrophilic, and hence the contact angle of the drop to decrease compared to that of a simple liquid that has the same liquid–vapor surface tension. However, surprisingly little data exist on the presence and/or action of surfactants at solid surfaces. Here, we study the wetting of solids by aqueous surfactant solutions and the surfactant adsorption simultaneously, using contact angle measurement, sum-frequency generation (SFG) spectroscopy, and fluorescence microscopy. Using a novel way of making a Zisman plot that characterizes the wettability of any solid, we find that although the surfactants do adsorb onto the surface, surprisingly its wettability is not different from that of a liquid (without any surfactant) of the same surface tension.

The characterization of the wetting of a solid by a liquid is usually done using Young's law: $\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta$, where γ_{SV} , γ_{SL} , and γ_{LV} represent the solid–vapor, solid–liquid, and liquid–vapor surface tensions, respectively.^{9,10} Making a

Zisman plot,^{9,11} one subsequently assumes that the difference in solid interfacial tension $\Delta\gamma = \gamma_{SV} - \gamma_{SL}$ is a property of the solid surface, i.e., does not depend on the specific liquid used. In a traditional Zisman plot, the cosine of the contact angle θ is plotted as a function of the liquid–vapor surface tension (γ_{LV}), which is changed using different liquids; a linear extrapolation to $\cos \theta = 1$ then gives the “critical” surface tension (γ_c) of the surface, defined as the surface tension of the liquid that just completely wets the solid. This way of plotting with a linear extrapolation is in fact not correct, since Young's law stipulates that $\cos \theta = \frac{\Delta\gamma}{\gamma_{LV}}$ instead of $\cos \theta \propto \gamma_{LV}$. Here, we propose to plot the cosine of the contact angle versus the inverse of the liquid–vapor surface tension. In this way, the slope of the curve directly gives $\Delta\gamma$.

EXPERIMENTAL SECTION

Measurement of Surface Tension. Pure liquids, i.e., liquids without any surfactant molecules, used in the experiments are Milli-Q water ($\gamma_{LV} \sim 72$ mN/m), glycerol (Sigma-Aldrich, $\gamma_{LV} \sim 64$ mN/m), ethylene glycol (Sigma-Aldrich, $\gamma_{LV} \sim 47$ mN/m), dodecane (Sigma-Aldrich, $\gamma_{LV} \sim 25$ mN/m), and silicon oil (Rhodorsil 47V20, Sigma-Aldrich, $\gamma_{LV} \sim 21$ mN/m). Surfactant solutions were prepared with fresh Milli-Q water. Three main surfactants were used: a cationic surfactant, cetyl trimethylammonium bromide (CTAB, Sigma-Aldrich); two anionic surfactants, sodium dodecyl sulfate and aerosol OT (SDS and AOT, both from Sigma-Aldrich); and a nonionic surfactant, Triton X-100 (TX100, Sigma-Aldrich). We did not recrystallize the SDS sample, which implies the presence of a small

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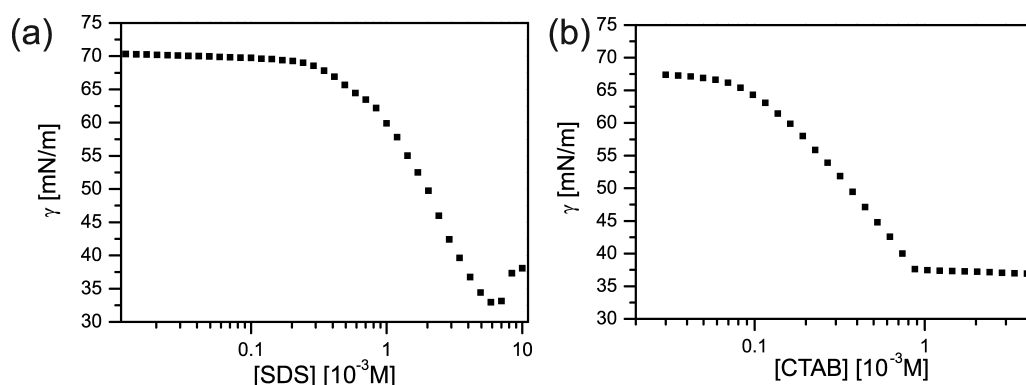


Figure 1. Example of change of liquid–air surface tension by changing the amount of surfactant in the aqueous solution: (a) anionic surfactant SDS and (b) cationic surfactant CTAB.

amount of the hydrolysis product dodecanol. Our conclusions are independent of the presence of any dodecanol in the SDS mixture, since we are interested in relating γ_{LV} with γ_{SV} and γ_{SL} . In other words, the liquid–vapor surface tension (γ_{LV}) that we measure for a SDS solution is a specific quantity with/without the presence of dodecanol. Hence, as long as we interpret the results on the basis of a general trend of contact angle and surface tension in the presence of any surfactant, the hydrolysis product dodecanol does not affect our conclusions. All liquid vapor (air) surface tensions were measured at equilibrium using a force tensiometer with a Du–Noüy ring (Kruss K100, Germany). The surface tension data as a function of the surfactant concentration in the solution were obtained by performing automatic dilutions. In this way, the instrument allows us to measure the surface tension values for very small concentration steps of the surfactant. To ensure equilibrium, the solution is stirred for 30 s at each dilution step, and the value of the measured surface tension is registered only when the standard deviation between five consecutive measurements is within 0.1 mN/m. Consequently, the average total time taken for one measurement is around 10 min (depending on how fast the system equilibrates), which is normally long enough for equilibration. These measurements are performed in a closed chamber of constant relative humidity ($50 \pm 2\%$), to ensure that evaporation does not influence our results. Figure 1 shows two typical results for two of the surfactants used. It shows that the liquid–vapor tension can be varied between ~ 35 and ~ 70 mN/m by increasing the concentration of both the anionic and the cationic surfactant. We notice in Figure 1a, that the SDS curve has a small kink at higher concentrations at the beginning of the experiment,¹² plausibly due to the presence of dodecanol in the SDS solution.¹³ The CTAB curve shown in Figure 1b does not reach a maximum value of around 72 mN/m (interfacial tension of water–air, which the curve is expected to approach at very low CTAB concentration). This could be due to the lower surrounding temperature (20°C) during the experiments compared to the minimum temperature required for a stable CTAB solution, which is around 40°C , or perhaps due to an experimental artifact due to the Du Noüy ring method. In any case, we present an equilibrium value of surface tension very close to the surface tension of pure water, while in literature,¹⁴ often a nonequilibrium value for a diluted CTAB solution is reported.

Measurement of Contact Angle. Contact angles of various liquids (the above-mentioned surfactant solutions as well as the neutral nonpolar liquids) on three different hydrophobic surfaces (silane-coated glass, polyethylene, and Teflon) were measured using an optical contact angle goniometer (Easy Drop, Kruss, Germany). Contact angles were measured until 1 min after the droplet was deposited on the substrate to prevent any influence of the possible evaporation and spreading. One of the hydrophobic surfaces, octo-silanized glass, was prepared according to the procedure described in Brzoska et al.¹⁵ with Dynasylan OCTEO (Evonik) and showed a contact angle of $104 \pm 1^\circ$ with pure water. The other two hydrophobic substrates were polyethylene and Teflon. Polyethylene substrates were Petri dishes and gave a contact angle of $96 \pm 1^\circ$ with

pure water. A Teflon surface was prepared by placing a Teflon band on a glass slide and exhibited a contact angle of $118 \pm 2^\circ$ with pure water. The contact angle and surface tension measurements were all realized under constant laboratory conditions with a temperature of $23 \pm 2^\circ\text{C}$ and relative humidity of $50 \pm 2\%$.

Sum-Frequency Generation Spectroscopy. Also, we have performed sum-frequency generation spectroscopy to resolve the adsorption of the surfactant molecules to a hydrophobic surface. Vibrational sum-frequency generation spectroscopy (SFG) is a surface-specific alternative to infrared and Raman spectroscopies. In SFG, two short laser pulses, one in the IR regime and the other in the visible-light regime, are overlapped in space and time at the interface, which causes emission of light at the sum frequency $\omega_{\text{SFG}} = \omega_{\text{IR}} + \omega_{\text{VIS}}$. The intensity of emitted light is resonantly enhanced when ω_{IR} coincides with a vibrational mode of molecules at the surface. A spectrum is obtained using broad-band (femtosecond) IR pulses. A molecular vibration only produces SFG if it is microscopically and macroscopically in an asymmetric environment, i.e., if the molecule resides at an interface with a preferred net polar orientation of the probed ensemble. Oppositely oriented molecular groups (i.e., pointing away or toward the interface) can be distinguished by the opposite sign of their susceptibility. In intensity measurements, such as the ones presented here, the sign of the susceptibility can be inferred from the interference between the different molecular groups. More details of the setup and the measuring principle can be found in Carrier et al.¹⁶ Since these experiments require an optically transparent surface, we use the above-mentioned silane-coated Infrasil glass as a hydrophobic surface; the contact angle of water on this substrate is $\sim 120^\circ$.

RESULTS AND DISCUSSION

Figure 2 shows, in a modified Zisman plot, the measured contact angles as a function of the measured liquid–vapor surface tension for the pure liquids and various surfactant solutions. Surprisingly, the data for the different surfactant solutions and the pure liquids lie on the same straight line (Figure 2). Similar surprising result has been shown by Milne and Amirfazli,¹⁷ who also reported a complete absence of “autophilic” effect of surfactants on hydrophobic substrates. However, they have not provided any concrete thermodynamic argument leading to their results, rather pointing to possible vibration and gravitational effects on the spreading of the droplet. We, however, would like to try and find a reasoning that complies with thermodynamics using our modified Zisman plots.

That all the data points lie on a straight line in our results implies that the surfactants do not change $\Delta\gamma$. Since $\Delta\gamma = \gamma_{SV} - \gamma_{SL}$ is only a function of the wetting properties of the solid, this means that only the liquid–vapor tension determines the

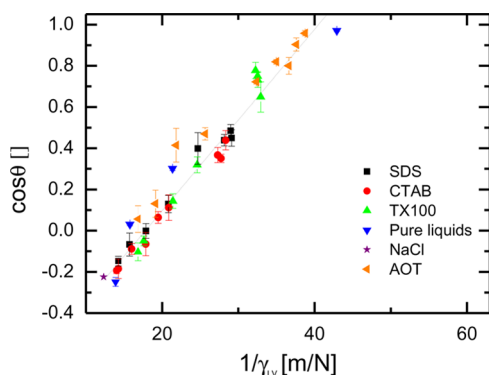


Figure 2. Modified Zisman plot on a silanized glass surface: cosine of equilibrium contact angle θ of pure liquids and various surfactant solutions wrt the inverse of liquid vapor interfacial tension for the corresponding solution. Pure liquids include Milli-Q water ($\gamma_{LV} \sim 72$ mN/m), glycerol ($\gamma_{LV} \sim 64$ mN/m), dodecane ($\gamma_{LV} \sim 25$ mN/m), ethylene glycol ($\gamma_{LV} \sim 47$ mN/m), and silicon oil ($\gamma_{LV} \sim 21$ mN/m), while the surfactant solutions are of SDS, CTAB, AOT, and TX100 at different concentrations. The slope of the fitted line ($\Delta\gamma$) is 45 mN/m.

contact angle, regardless of the presence of surfactants in bulk, which presumably interact with the solid surface. The value of $\Delta\gamma$ is given by the slope of the fitted line, which in this case is 45 mN/m. The behavior of the surfactant solutions is exactly the same on other hydrophobic substrates (polyethylene, Figure 3a and Teflon, Figure 3b) as well. The values of $\Delta\gamma$ for these substrates are 51 and 32.5 mN/m, respectively. It is worth noting that this slope varies from one substrate to another but is constant for a specific hydrophobic substrate. Hence, a given hydrophobic substrate has a unique slope (or $\Delta\gamma$) in a modified Zisman plot.

There are two possible explanations for the observation that $\Delta\gamma = \gamma_{SV} - \gamma_{SL}$ remains unchanged in the presence of surfactants: either the solid–liquid tension changes very little or the solid–vapor interfacial tension changes as much as the solid–liquid tension,^{8,9} so that the two contributions cancel out. The above statements actually do not imply that γ_{SV} or γ_{SL} are independent of the surfactant concentration. Rather, it means that instead of focusing the attention on the solid properties as an indicator of the critical surface tension, one requires knowledge about the surfactant concentration as well as the nature of surfactant adsorption to explain the

microscopic mechanism of the critical surface tension. To differentiate between the two explanations, we have performed SFG^{18–20} on the silanized glass–surfactant solution interface. The SFG measurements have been performed at a specific representative surfactant concentration for each of these above-mentioned surfactants: at approximately 0.3 critical micellar concentration. Figure 4 depicts the SFG signals for Millipore

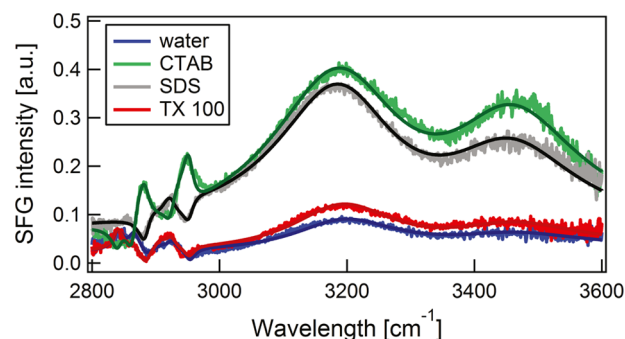


Figure 4. SFG spectra under SSP polarization of (a) SDS (at 2 mM concentration), (b) CTAB (at 0.2 mM concentration), and (c) TX100 (at 0.07 mM concentration) solutions on a silanized glass substrate in comparison to pure water in contact with the same substrate. For the SFG experiment, the silanization of the glass is performed on 2 mm thick Infrasil (International Crystal Laboratories) windows. The signal is normalized to gold-coated Infrasil. The dark lines represent fits with a Lorentzian line shape model. The data are not corrected for the Fresnel coefficients, as the Fresnel coefficient is identical for all samples and we are interested in the difference between the surfactant solutions and pure water.

water, CTAB (0.2 mM), SDS (2 mM), and Triton X-100 (0.07 mM) solutions. In the spectrum of pure water, the signals between 2800 and 3000 cm^{-1} originate from C–H vibrations in the silane layer, while the broad signal between 3000 and 3600 cm^{-1} originates from hydrogen-bonded water near the surface. For aqueous SDS and CTAB solutions, the water signal increases compared to that of the pure water sample. This indicates more ordered water owing to the presence of charged surfactants at the surface, since the intensity of the signal is a measure of the symmetry breaking at the surface. Also, the observation of peaks instead of dips in the CH region for the CTAB solution indicates that the water molecules flipped their orientation because of the positive charge of CTAB, apparently overcompensating residual negative charge

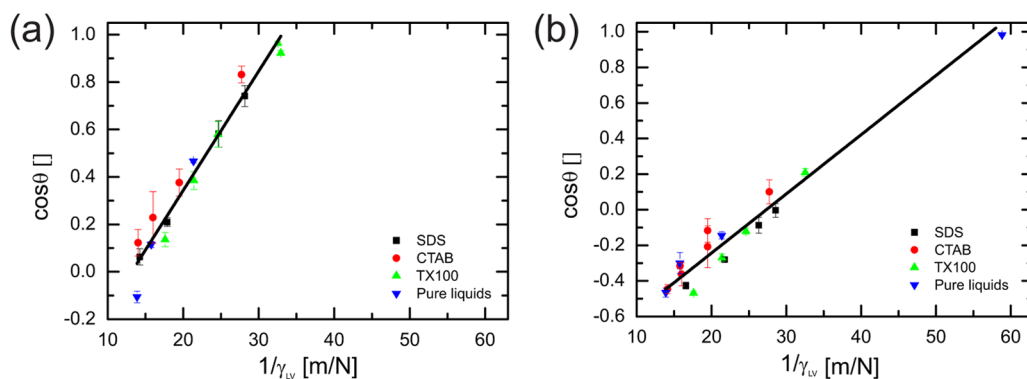


Figure 3. Modified Zisman plot on a (a) polyethylene and (b) Teflon substrate: cosine of equilibrium contact angles of various surfactant solutions wrt the inverse of liquid vapor interfacial tension for the particular surfactant solution. The liquids are the same as described in Figure 2. The slopes ($\Delta\gamma$) of the fitted lines in (a) and (b) are 51 and 32.5 mN/m, respectively.

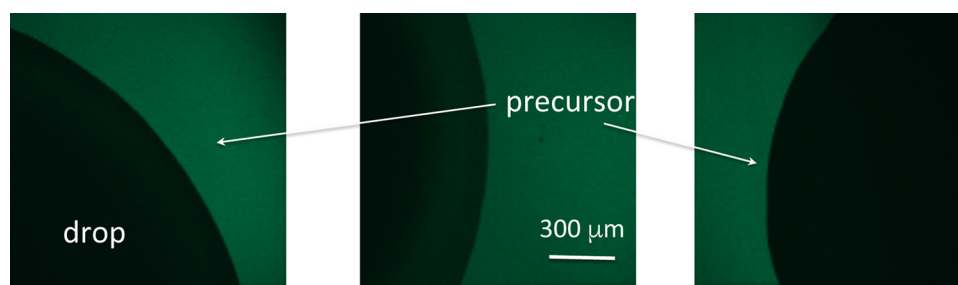


Figure 5. Fluorescent images of a droplet and its precursor film of 1 mM CTAB solution containing 1 μ M DASPI dye. The dark droplet and the green precursor film affirm our hypothesis of a co-existing nanometric film in our experiments.

of the silane-coated window. The SFG spectra can be well described using the standard line shape model¹⁶ consisting of a nonresonant signal and a sum of Lorentzian line shapes for each resonance (see dark lines in Figure 4). As the C–H vibrations of the silane layer and the surfactants are very similar we, unfortunately, cannot specify the origin of the vibrations. We fit the C–H region with the common signals for the symmetric and asymmetric CH₂ and CH₃ vibrations as well as Fermi resonances. The fits reveal that the CH spectral area between 2800 and 3000 cm⁻¹ changes upon adding surfactant solutions, indicating the presence of surfactant alkyl chains at the interface and/or a restructuring of the silane layer. In addition to the CH changes, the water signal also increases substantially. This indicates charge-induced enhanced alignment of interfacial water. From the change in both the C–H stretch signals and water signals, we therefore conclude that the quantity of the SDS and CTAB adsorption is substantial. The silanized substrate contains an alkyl chain density of ~ 50 – 100 Å²/molecule. After surfactant adsorption, the changes in the CH spectrum seem to be of the same order of magnitude as that of the surface in pure water. Hence, the silane and the surfactant density must be comparable. Here, it is important to note that the presence of the byproduct dodecanol in the case of SDS does not affect our interpretation. This is because dodecanol is charge neutral and water molecules mainly align themselves in the presence of charge. Moreover, Triton is also present at the surface since here we also observe significant spectral changes, relative to pure water, more pronounced at higher Triton concentrations. The changes are less pronounced for the charge-neutral Triton X-100,^{21–23} compared to SDS or CTAB, whose charge efficiently orients the dipoles of the water molecules.

Hence, SFG measurements clearly show (Figure 4) that for the surfactant solutions, surfactant molecules are adsorbed at the surface. Especially for the charged surfactants, the marked changes in SFG spectra show that a substantial amount of the surfactant is present at the solid–liquid interface. To obtain these marked changes, one needs at least one surfactant per 100 Å² (based on the SFG experiment reported for lipid monolayers). This is clearly a surface excess for surfactant concentration of <2 mM. According to the Gibbs adsorption equation, $\frac{d\gamma}{d\ln C} = -mk_{\text{B}}T\Gamma$ (with C the bulk concentration and $k_{\text{B}}T$ the thermal energy and m the prefactor related to ionic or nonionic surfactants; $m = 1$ for nonionic surfactants while $m \neq 1$ for ionic surfactants), surface excess Γ should change the surface tension of that surface. Thus, from the SFG spectra, comparing the solid–liquid interface without and with surfactants, we can conclude that surfactants adsorb at the solid–liquid interface, changing the interfacial tension

substantially. A monolayer of the surfactant, when present at the solid–liquid interface, should change the solid–liquid tension roughly by the same amount as the liquid–vapor tension, since a monolayer of surfactants is also present at that interface and the Gibbs equation of adsorption isotherm^{8,9} holds for both. Since the Zisman plots reveal that $\Delta\gamma = \gamma_{\text{SV}} - \gamma_{\text{SL}}$ is constant, we must conclude that γ_{SV} , the solid–vapor tension, changes in the same way as γ_{SL} , the solid–liquid tension. This is, in fact, possible since the equilibrium contact angle occurs for a droplet in equilibrium with a microscopically thin water film on the solid surface, known as the precursor film.^{9,10} This film might also contain surfactants that adsorb in the same way at the vapor interface as at the solid interface under the droplet.

This adsorption of a surfactant to the vapor interface actually does not influence the liquid–vapor tension. Rather, this adsorption is due to the surfactant molecules moving past the three-phase contact line into the precursor film and contributing to the changes in both solid–liquid as well as solid–vapor tension. This deposition beyond the three-phase contact line has been termed as the “carryover” of the surfactant molecules. For a hydrophilic substrate, the carryover of ionic or nonionic surfactants resulting in unusual wetting behavior (known as the “autophobic effect”) is evident and has been studied in detail.^{24–27} In comparison to that of hydrophilic substrates, the carryover of surfactants on a hydrophobic substrate has been investigated less frequently.^{17,28} Churaev et al. carried out one of the first investigations of the spreading of a surfactant solution on a hydrophobic substrate.²⁹ It was subsequently shown that different types of structures in different surfactants lead to different carryover rates into the precursor film during the spreading of the aqueous surfactant solution, which leads to varying rates of adsorption on a (hydrophobic) substrate.³⁰ Furthermore, Kumar et al. have shown that carryover of several types of surfactants can occur on a hydrophobic substrate, thereby changing the solid–vapor surface tension γ_{SV} .³¹ Various regimes in this droplet spreading/surfactant carryover dynamics on a hydrophobic substrate have been identified³² and theoretically investigated.³³ On the basis of these investigations, it became clear that the myriad spreading phenomenon on a hydrophobic substrate depends on a number of relevant things, namely, the concentration of the surfactant and the degree of hydrophobicity of the substrate as well as the specific nature of the surfactant.³⁴ Hence, it logically follows that in our experiments we observe the effect of surfactant carryover on the hydrophobic substrates leading to the reported wetting phenomenon. At the same time, using different surfactant solutions and different hydrophobic substrates clearly contributes to the amount of adsorption

and ultimately to different slopes of the modified Zisman curves.

To confirm the presence of the precursor film on our hydrophobic substrates in a relatively new manner, we carried out fluorescence microscopy with *trans*-4-[4-(dimethylamino)-styryl]-1-methylpyridiniumiodide (DASPI) as a dye. DASPI is a unique dye that fluoresces only when confined in a (sub)nanometric film.^{35,36} As a result, with a DASPI-dyed solution, the precursor film is indeed visible. We observe that for our surfactant solutions, there is always a precursor film next to the droplets. Figure 5 shows representative fluorescent images for a droplet of aqueous CTAB (at 1 mM concentration) and DASPI (1 μ M) solution on a silanized glass. The green part outside the contact line of the droplet (that shows no fluorescence) confirms the existence of the precursor film. The presence of this film will, again through the Gibbs adsorption equation, change the solid–vapor tension, irrespective of the presence or absence of surfactant molecules in the precursor film. It is, therefore, the presence of this film that makes the γ_{SV} change, which, according to our experiments, results in a constant $\Delta\gamma$: both γ_{SV} and γ_{SL} change when adding surfactants to a solution, but the two energetic contributions cancel out almost perfectly for all surfactants reported here.

CONCLUSIONS

In conclusion, for a hydrophobic surface, one might have anticipated that the surfactant simply adsorbs onto the surface with its hydrophobic part, making the hydrophilic heads sticking out into the solution and consequently rendering the surface hydrophilic. However, we find here that the surfactants do not change the Zisman critical tension of the surface, in spite of the fact that they are adsorbed. This may have important consequences, e.g., detergency, inkjet printing, or pesticide spraying, for which surfactants are commonly used to improve the sticking or the coverage of liquids on solids.

AUTHOR INFORMATION

Corresponding Author

*E-mail: b.bera@uva.nl

ORCID

Bijoyendra Bera: 0000-0002-8626-3682

Ellen H. G. Backus: 0000-0002-6202-0280

Mischa Bonn: 0000-0001-6851-8453

Noushine Shahidzadeh: 0000-0003-2692-0764

Daniel Bonn: 0000-0001-8925-1997

Notes

The authors declare no competing financial interest.

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