

Autophilic Effect: Wetting of Hydrophobic Surfaces by Surfactant Solutions

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This paper resolves questions in the literature regarding the autophilic effect (i.e., movement of surfactant past the advancing contact line—leading to an increase in drop radius beyond that due to the advance) and its importance to quasi-static sessile drop wetting. Various systems (SDS, HTAB, and MEGA 10 surfactant solutions at three concentrations each and pure water and ethylene glycol on hydrophobic Teflon and OTS-coated silicon) are probed to determine the existence, time constant, and magnitude of the autophilic effect, using quasi-static advancing and receding sessile drops. From spreading results and advancing contact angle measurements, it is inferred that the autophilic effect does not occur for our systems (in contradiction of some literature) for the following reasons. First, no relation exists between the time constant for spreading and surfactant concentration, meaning the spreading seen is likely inertial in cause and not due to surfactants. Second, advancing contact angle decreases between tests on clean surfaces and those pre-exposed to surfactant, ruling out the possibility that the autophilic effect is faster than the advance. Third, spreading is seen after the end of the advance over both clean and pre-exposed surfaces, ruling out the possibility that the autophilic effect is slower than the advance. Finally, the pure liquids spread in a similar fashion to surfactant solutions on Teflon and similar contact angle measurements are seen for surfactant solutions and pure liquids of similar surface tension.

1. Introduction

Wetting by surfactant solutions has been investigated for scientific knowledge,^{1–9} for applications to detergency, enhanced oil recovery, etc.,^{10–22} and as simplified representations of impure liquids (since most impurities added to water will decrease surface tension, as surfactants do).^{23–26}

Though not the focus of this paper, the wetting of hydrophilic surfaces (contact angle with water less than 90°) by surfactant solutions leads to the autophobic³³ effect^{5,8,16} in which surfactants adsorb to the solid interface either through the liquid phase during or after an advance⁸ or by evaporation and condensation¹⁶ or surface diffusion⁵ onto the bare solid–vapor interface. In either case, the thermodynamic driver to decrease the energy of the interface leads to surfactant adsorption, thus leading to either a retreat of the contact line (increase in contact angle) or a halt of the spreading of the contact line. In the latter case, the spreading would halt at a contact angle higher than would be expected based on a solid–vapor interface without surfactant adsorption.

Wetting of hydrophobic surfaces by surfactant solutions has also been studied.^{1–3,6,12,14,15,17–21} Among the works is ref 1, where, analogous to the autophobic effect, the autophilic effect (later named by ref 6) has been put forward. The autophilic effect is defined as the adsorption of surfactant ahead of the advancing or advanced contact line (CL) (on dry, clean solid–vapor (s–v) interface), which would lead to one of the following two behaviors. First, the autophilic effect could be slower than the rate of forced advance. In this case, the surfactant solution would not autophilize the surface during the forced advance (caused, e.g., by volume addition) but could spread across a hydrophobic surface or penetrate into a hydrophobic capillary after the end of the forced advancing stage¹. Alternatively, if the autophilic effect were faster than the rate of forced advance, this would lead to a contact angle during the forced advance that was lower than would be expected on the basis of decrease in liquid–vapor (l–v) and solid–liquid (s–l) interfacial energies due to surfactant adsorption.^{6,11}

The existence of the autophilic effect has not been proven from a thermodynamic basis; instead, it was first put forward as an explanation for the spontaneous imbibition of surfactant solution into hydrophobic capillaries after a period of some minutes.¹¹ Later, researchers have proposed it to be in effect for sessile drops of a specific volume placed on a surface from above² and a

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(1) Churaev, N. V.; Martynov, G. A.; Starov, V. M.; Zorin, Z. M. *Colloid Polym. Sci.* **1981**, 259, 747.
(2) Starov, V. M.; Kosvintsev, S. R.; Verlarde, M. G. *J. Colloid Interface Sci.* **2000**, 227, 185.
(3) Starov, V. M. *J. Colloid Interface Sci.* **2004**, 270, 180.
(4) Johnson, B. A.; Kreuter, J.; Zograf, G. *Colloids Surf.* **1986**, 17, 325.
(5) Frank, B.; Garoff, S. *Colloids Surf., A* **1996**, 116, 31.
(6) Kumar, N.; Varanasi, K.; Tilton, R. D.; Garoff, S. *Langmuir* **2003**, 19, 5366.
(7) Varanasi, K. S.; Garoff, S. *Langmuir* **2005**, 21, 9932.
(8) Mamur, A.; Lelah, M. D. *Chem. Eng. Commun.* **1981**, 13, 133.
(9) Troian, S. M.; Wu, X. L.; Safran, S. A. *Phys. Rev. Lett.* **1989**, 62, 1496.
(10) Lee, K. S.; Ivanova, N.; Starov, V. M.; Hilal, N.; Dutschk, V. *Adv. Colloid Interface Sci.* **2008**, 144, 54.
(11) Ivanova, N.; Starov, V.; Johnson, D.; Hilal, N.; Rubio, R. *Langmuir* **2009**, 25, 3564.
(12) Starov, V. M.; Velarde, M. G.; Radke, C. J. *Wetting and Spreading Dynamics*; Surfactant Science Series; CRC Press: Boca Raton, FL, 2007; Vol. 138.
(13) Scales, P. J.; Grieser, F.; Furlong, D. N.; Healy, T. W. *Colloids Surf.* **1986**, 21, 55.
(14) Stoebe, T.; Hill, R. M.; Ward, M. D.; Davis, H. T. *Langmuir* **1997**, 13, 7276.
(15) Keurentjes, J. T. F.; Cohen Stuart, M. A.; Brinkman, D.; Schroën, C. G. P. H.; van't Riet, K. *Colloids Surf.* **1990**, 51, 189.
(16) Novotny, V. J.; Marmur, A. *J. Colloid Interface Sci.* **1991**, 145, 355.
(17) Vogler, E. A. *Langmuir* **1992**, 8, 2005.
(18) Vogler, E. A. *Langmuir* **1992**, 8, 2013.
(19) von Bahr, M.; Tiberg, F.; Yaminsky, V. *Colloids Surf., A* **2001**, 193, 85.
(20) Eriksson, J.; Tiberg, F.; Zhmud, B. *Langmuir* **2001**, 17, 7274.
(21) Dutschk, V.; Sabbatovskiy, K. G.; Stolz, M.; Grundke, K.; Rudoy, V. M. *J. Colloid Interface Sci.* **2003**, 267, 456.
(22) Chan, K. Y.; Borhan, A. *J. Colloid Interface Sci.* **2005**, 287, 233.
(23) Ferrari, M.; Ravera, F.; Rao, S.; Liggieri, L. *Appl. Phys. Lett.* **2006**, 89, 053104.
(24) Shirtcliffe, N. J.; McHale, G.; Newton, M. I.; Perry, C. C.; Roach, P. *Mater. Chem. Phys.* **2007**, 103, 112.
(25) Mohammadi, R.; Wassink, K.; Amirfazli, A. *Langmuir* **2004**, 20, 9657.
(26) Milne, A. J. B. MSc Thesis, University of Alberta, Alberta, **2008**.

Wilhelmy plate-like system.⁶ Note that in ref 2 the autophilic effect was not considered for the initial unsteady spreading of the drop as it touched the surface but was proposed to occur after the drop was settled. The basis for proposing the autophilic effect in these cases relied on condensation figures, examination of contact angle for clean and pre-exposed surfaces, and attempts to measure solid–vapor surface energy using Young's equation.⁶ Observed spreading of surfactant solutions across surfaces after the end of an advancing stage² and some speculation that the adsorption of surfactant on the s–v interface will decrease the global energy while increasing the s–v surface energy¹¹ were also put forward. The effect has also been mentioned by other groups^{21,27} who have not provided evidence of its existence, so the idea has gained some support in recent years.

On a closer reading of the literature, however, one can become confused since the evidence for the autophilic effect as described above is sometime contradictory in terms of the time scale and magnitude and for what solution–substrate systems it is in effect. In the initial paper presenting the autophilic effect¹ a time scale of minutes was reported for imbibition of surfactant solution (Syntamide-5 in water) into hydrophobized capillaries. The same group reported² a time scale of tens of seconds (or less, decreasing with concentration) and a spreading magnitude of $\sim 50\ \mu\text{m}$ for sessile drops of SDS solution on PTFE films. More recently, the same group¹¹ reported that SDS does not spread on Teflon, though a closer study of Figure 1 in ref 11 shows a $\sim 25\ \mu\text{m}$ spread over a range of tens of seconds.

Turning to the theoretical arguments put forward by these authors in support of the autophilic effect¹² raises more issues: Without any mechanistic basis it is taken as a given that surfactants will both escape from the liquid phase and cover the hydrophobic surface leading to an increase in solid–vapor surface energy.¹² This increase is contrary to the role of surfactants at any interface (i.e., to reduce interfacial energy). Also, while Young's equation is described by the authors as baseless,^{11,12} it is nonetheless used in their theoretical base for the autophilic effect. Further, the authors¹² make arbitrary assumptions about the speed of surfactant adsorption on various interfaces, with the assertion that adsorption on the s–v interface should be slowest. There are also assumptions made about the relative energy of a surfactant molecule on a hydrophobic surface compared to the same molecule in a solution (necessary to allow construction of formulations in support of the proposed effect). Furthermore, it is also assumed (or at least not discussed) that surfactant molecules do not transfer from the s–l to the s–v interface, which would likely seem possible if transfer takes place from the l–v to the s–v as proposed by ref 12. All in all, the theoretical formulation given cannot resolve the conflicts found in the experimental literature.

Examining the experimental work by other authors, in ref 6 it was reported that the autophilic effect took place for a Wilhelmy platelike apparatus used to examine octaethylene oxide monododecyl ether solution on OTS monolayers. The contact line advanced at a rate of $10\text{--}50\ \mu\text{m/s}$. It was concluded that the autophilic effect was observed based partly on surface energy calculations. The calculation of s–v surface tension as a function of concentration could be confounded by the use of multiple different measurements as inputs and contact angle hysteresis, as pointed out in ref 6. Further, the conclusion of the autophilic effect in ref 6 was also based on condensation figures taken 5 min after the advance. However, the conclusion also relied on the observation of no change in the advancing contact angle between tests on clean substrates and that pre-exposed to surfactant

solution. This would suggest that the effect happened so rapidly that it overtook the advancing contact line. This seeming incongruity in time scales (during the advance versus 5 min after) has since been explained.³⁴

The condensation figures used in ref 6 were interpreted to gauge the region of surfactant absorption on the s–v interface to be $\sim 10\ \mu\text{m}$ in length (i.e., the autophilic effect only reached this distance away from the three-phase contact line after a 5 min wait). This length is orders of magnitude lower than the region of influence of the autophobic effect ($> 1\ \text{cm}$, as reported in ref 16 for various pure liquids on clean silicon). Further, in the condensation figures presented in ref 6, the region around the contact line appears devoid of condensed drops, suggesting it is completely wetted by the condensation. If the area around the contact line were completely wetted, one would expect a very low contact angle for the bulk liquid (near zero degrees macroscopic contact angle). This was not seen in ref 6, which suggests that the autophilic effect is perhaps at most a microscopic effect which has little effect on the macroscopic contact angle.

Further confounding evidence around the autophilic effect is that for similar systems to those above other researchers have not reported the autophilic effect.^{4,14,15,17–21} To clarify the work of Dutschek et al., they did not report the autophilic effect for surfactant solutions on Teflon but did suggest the autophilic effect as a mechanism for spreading on other surfaces in the time scale of tens of seconds.²¹ The reasoning in ref 21 was that a power law spreading was expected by the authors but not seen, and therefore the autophilic effect might be taking place. However, as Suo et al.²⁸ point out, a power law for spreading is not expected when the final contact angle is nonzero.

Clearly, disagreement exists between those who have suggested the existence of an autophilic effect to explain surfactant solution wetting on hydrophobic surfaces, and further there is experimental work that does not support the effect. So, the questions remain: if the autophilic effect exists, how fast it is ($\sim 10\ \text{s}$ or \sim minutes), how significant its effect is, and on what solution–substrate systems it is in effect and why. Considering our interest and past experience with sessile drop studies, and the recent works looking at SDS–Teflon,^{2,11,21} we have decided to study the system of SDS solution on Teflon-coated smooth silicon wafer, using the quasi-static sessile drop technique.

Further, tests on clean and pre-exposed substrates following the idea of⁶ were performed. By comparing this data with that in the literature,^{2,6} and that which we collected previously²⁶ for SDS, HTAB, and MEGA 10 on Teflon and OTS-coated silicon, we set out to investigate the significance and particulars of the autophilic effect, in the hope of resolving literature disputes regarding the existence for given systems and particulars (time scale/magnitude) of the autophilic effect.

2. Experimental Setup

Smooth silicon wafer was taken as received, diced, drilled with an abrasive bit (0.9 mm diameter), thoroughly rinsed with pure water and acetone, and then coated with a 5:1 v:v mixture of FC 75 and Teflon AF 1600 (DuPont Co.) on a spin-coater (model 6700, Specialty Coating Systems Inc.). The hole was drilled in the surface to allow for mounting of a syringe below the surface to create a drop on top of the surface. SEM and AFM images show the samples to be quite smooth, $R_a = 48.35\ (25.48)\ \text{nm}$ (standard deviation in parentheses).

Contact angle and contact line radius were monitored by the technique of axi-symmetric drop shape analysis (ADSA).²⁹

(27) Tang, H.; Wng, X.; Pan, M.; Wang, F. *J. Membr. Sci.* **2007**, *306*, 298.

(28) Suo, Y.; Stoev, K.; Garoff, S.; Ramé, E. *Langmuir* **2001**, *17*, 6988.

(29) Kwok, D. Y.; Neumann, A. W. *Adv. Colloid Interface Sci.* **1999**, *81*, 167.

Advancing and receding contact angles were measured for the quasi-static advancing and receding contact line. A custom-built apparatus was used for tests, in which the surface was placed on a stage that could be leveled and raised/lowered. A clean syringe filled with the surfactant solution was mounted under the surface, through the hole drilled in the surface, with the tip position just underneath the top of the hole in the leveled surface. The syringe was driven by a motor at a rate of $0.5 \mu\text{L/s}$, resulting in a rate of contact line motion (advancing and receding) of between 15 and $30 \mu\text{m/s}$. The rate of volume addition and removal for the advancing and receding contact angle measurements were the same, and the rate is low enough that inertial effects are minor. The rate of advance is on the same order as the rate of advance of ref 6 ($10\text{--}50 \mu\text{m/s}$) and slightly higher than the rate of spreading attributed to the autophilic effect by ref 2 (not listed, but approximately $2.5\text{--}25 \mu\text{m/s}$, faster for higher concentrations). Thus, if the autophilic effect occurred in our experiments, it would be expected to either manifest as spreading shortly after the stop of the advance or as an effect present during the advance. Both these possibilities will be discussed in the Results section.

Tests were run in the following way. Starting on a clean surface that had never been exposed to surfactant, it took ~ 40 s to advance a drop from a contact radius of ~ 1.7 mm to a contact radius of ~ 2.4 mm. The drop was imaged at a rate of 1 picture/s during this time and throughout the test. The quasi-static advance was followed by a 5 min wait while the motor was stopped. During this time the drop was monitored for spreading, following literature protocol.^{2,11} The 5 min period was chosen to coincide with wait times of ref 6. After the wait time, the syringe motor was reversed and volume removed from the drop over a period of ~ 40 s. After drying the surface with a nitrogen stream, tests were then immediately run again on the same surface to give measurements of contact angles and spreading on a pre-exposed surface (similar to the protocol of ref 6). This was followed by a ~ 20 s wait time, during which the motor was stopped, and finally by a second receding phase with the motor running in reverse. The contact line was seen to move uniformly and constantly during the advance/recede, without pinning or sticking on the advance, and seldom on the recede, and at a relatively constant advancing contact angle (see Figure 1). Tests were conducted at $21\text{--}22^\circ\text{C}$, and $14\text{--}17\%$ relative humidity, and so a cuvette was placed over the drop to limit evaporation. In tests, it was observed that the rate of evaporation was negligible. This low relative humidity should prevent the formation of a condensed film on the surface (which has been seen to transport surfactants on a wet hydrophilic surface).^{8,9} Surfactant transport across a wet surface could lead to a false observation of the autophilic effect, since it is thought to occur on a dry surface. Three tests were run (always on fresh samples) for each concentration of SDS. Standard deviation is calculated from the three repetitions of tests at each concentration.

Surfactant solutions were made by measuring set masses of SDS (Fisher Scientific) on a microbalance and dissolving the SDS in known volumes of deionized water (resistivity $18.2 \text{ M}\Omega\cdot\text{cm}$) in a flask. Surface tension of the solutions was measured by pendant drop analysis (First Ten Angstroms), and the surfactant concentrations and their surface tensions are listed in Table 1 and match literature results²¹ relatively well. The critical micelle concentration (cmc) of SDS is ~ 8.3 mM.

3. Results and Discussion

Advancing and receding contact angle measurements for SDS solutions on Teflon-coated silicon are shown in Figure 2 (top). Results for both clean and pre-exposed surfaces are shown on the same graph. The low contact angle hysteresis (CAH, advancing contact angle minus receding contact angle) shows that the surfactant molecules are not significantly changing the topo-

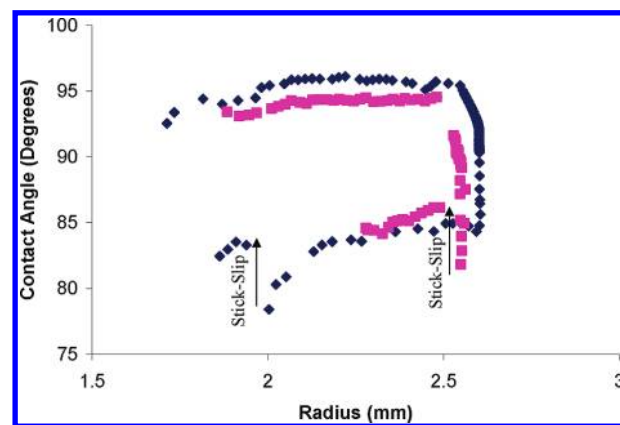


Figure 1. Representative result (8 mM SDS on Teflon-coated silicon) showing advancing and receding behavior for clean (diamond symbols) and pre-exposed (square symbols) surface.

Table 1. SDS Surfactant Concentration and Surface Tension (Standard Deviation in Parentheses)

concentration (mM)	surface tension (mJ/m^2)
2	58.19 (1.1)
4	47.70 (0.5)
8	39.54 (0.4)

graphy of the surface between the advancing and receding stages and has been seen before in the literature.^{4,30–32} Similar levels of CAH are seen for water on the same surface.²⁶

As stated above, the rate of contact line advance, $\sim 15\text{--}30 \mu\text{m/s}$, was on the same order of magnitude as the expected rate of spreading due to the autophilic effect.^{2,6} Thus, if the autophilic effect occurred for some concentration of SDS solution on Teflon, it would either manifest during the advance (if it were faster than the rate of advance) or shortly after the end of the advance (if it were slower). To clarify the second case, after the end of the forced advance, the slower autophilic effect could take place, hydrophilizing the up until now “pure” s–v interface and leading to spreading of the drop without a forced advance (this spreading being the definition of the autophilic effect). By examining the results of the clean and pre-exposed tests, one can rule out both possibilities.

For the sake of argument, consider first the possibility that the autophilic effect were faster than the rate of advance. This would mean that on the first advance there should be surfactant ahead of the contact line as it is proposed to “jump ahead” faster than the rate of advance. On the second advance (over an area already exposed to surfactant solution and stopping within this area) there is surfactant ahead of the contact line (independent of the existence of the autophilic effect), as suggested in the literature.^{6,7} Solid–liquid and liquid–vapor surface tensions are the same between tests (as both are simple functions of surfactant concentration, which is constant). Thus, the difference in advancing contact angles between tests (lower on the second advance, as seen

(31) Nedyalkov, M.; Alexandrova, L.; Platikanov, D.; Levecke, B.; Tadros, T. F. *Colloid Polym. Sci.* **2008**, *286*, 713.

(32) Graca, M.; Bongaerts, J. H. H.; Stokes, J. R.; Granick, S. J. *Colloid Interface Sci.* **2007**, *315*, 662.

(33) The term “autophobic” or “autophobic” was first coined by Zisman to describe the wetting behavior of pure liquids on solid surfaces that they should wet well, but which they instead wet more poorly due to an adsorbed layer of the pure liquid’s vapor on the solid surface. The phrase has been extended to surfactant solutions on hydrophilic surfaces.

(34) In personal communication, S. Garoff has stated that the 5 min pause was to allow sufficient time for the autophilic effect to bring surfactant to a distance of $10 \mu\text{m}$ from the contact line, allowing imaging.

(30) Soboleva, O. A.; Badun, G. A.; Korobkov, V. I.; Ivanova, N. I. *Colloid J.* **2007**, *69*, 506.

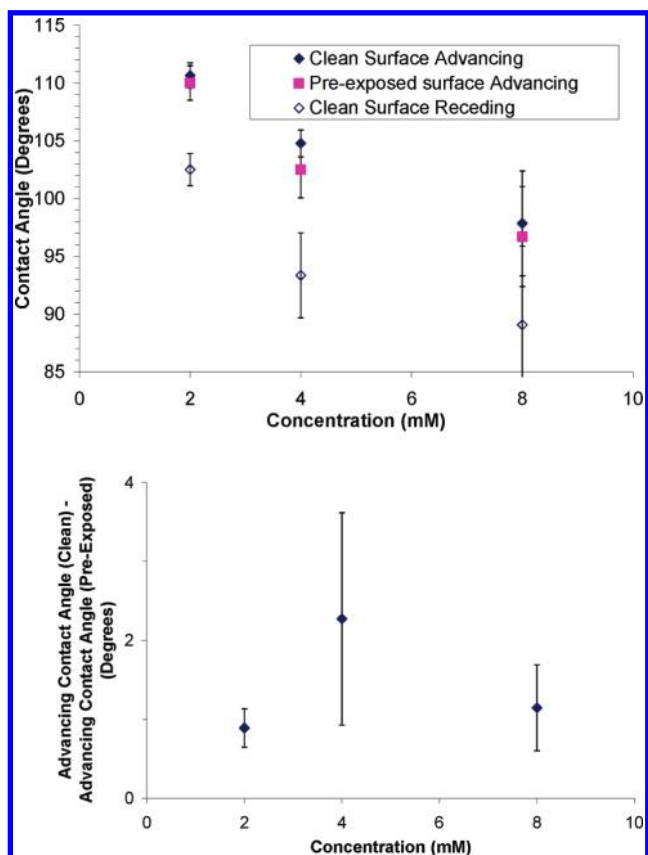


Figure 2. Top: Advancing and receding contact angles versus concentration for aqueous SDS solution on Teflon-coated silicon. Tests for both clean and pre-exposed surfaces are shown. The low contact angle hysteresis shows that surfactant molecules are not significantly changing the topography of the surface between the advancing and receding stages. Bottom: Average of advancing contact angle on each clean surface minus advancing contact angle on the same pre-exposed surface versus concentration for the same aqueous solutions as top. Error bars denote ± 1 standard deviation.

in Figure 2) is due to a difference in $s-v$ surface energy for the pre-exposed surface. The contact angle change between two runs is reflective of a change in the $s-v$ surface energy on the order of 1 mJ/m^2 , applying, e.g., the approach in ref 29. This means there is no surfactant adsorption on the solid–vapor interface ahead of the contact line on the first advance over the clean surface, ruling out the possibility that the autophilic effect is faster than the rate of advance.

It is important to note that in the top of Figure 2, while the standard deviations of the two advancing traces overlap each other, this is due to test-to-test variability in contact angle. In each case, the advancing contact angle on the pre-exposed surface was noticeably lower than the value for the clean surface (see Figure 1 or Figure 2, bottom), showing the trend that disproves the autophilic effect is occurring during the advance. In support of this, t tests have been performed comparing advancing contact angle measurements on clean and pre-exposed surfaces. For 2, 4, and 8 mM concentrations, the extremely low average t test values (6.0×10^{-5} , 2.6×10^{-9} , and 1.7×10^{-8} , respectively) show that advancing contact angle is statistically lower on pre-exposed surfaces. Student t tests can also be performed comparing the contact angle difference (Figure 2, bottom) to zero difference (i.e., examining if the difference is significant). This gives values of 0.003, 0.043, and 0.022 for 2, 4, and 8 mM concentrations, respectively, showing that the difference in contact angle is

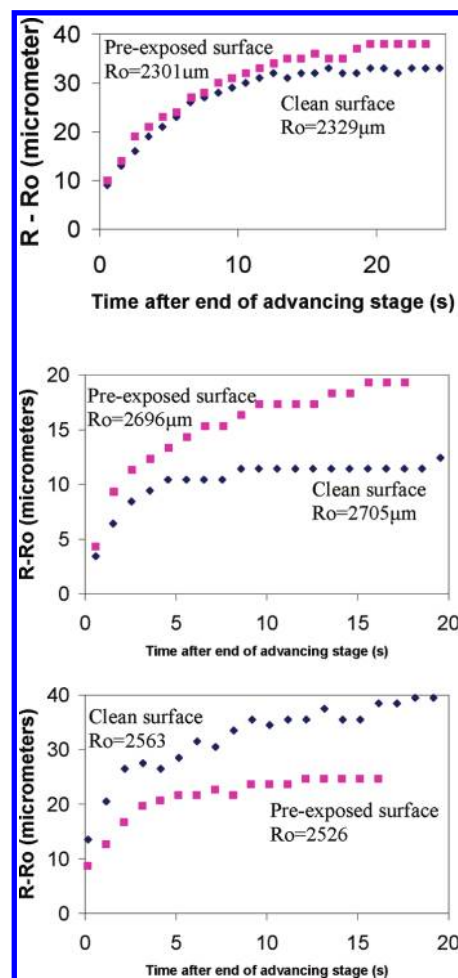


Figure 3. Representative graph of spreading of 2 mM (top), 4 mM (middle), and 8 mM (bottom) SDS solution after advance over clean (diamond symbols) and pre-exposed (square symbols) Teflon-coated smooth silicon. Pixel resolution is $\sim 12 \mu\text{m}/\text{pixel}$, but the ADSA technique²⁹ uses subpixel interpolation to increase accuracy. Spreading is given as $R - R_0$, where R_0 is the radius at the end of the advance and R is the radius at time t . R_0 values for clean and pre-exposed surfaces are given on each graph.

statistically different from zero. Such findings further support the conclusion that the advance over a pre-exposed surface has a lower value than the advance over a clean surface and undermining the idea that the autophilic effect is occurring during the advance.

The second option (that the autophilic effect is slower than the advance) is ruled out by considering Figure 3 and Table 2. The observations for an individual run depicting the spreading behaviors seen after the advance for the three SDS solution concentrations on Teflon-coated silicon is shown in Figure 3. The average results for each system are given in Table 2. Zero time on the graphs is the end of the advance (when the motor was stopped). At first glance, the fact that spreading is seen after the end of the advance would seem to support the second option for the speed of the autophilic effect as suggested in ref 2. However, it does not. It is seen in Figure 3 and Table 2 that a similar amount of spreading is seen for both the first advance (over a clean substrate) and for the second advance (over a pre-exposed substrate). Sometimes (2 mM) the spreading is practically identical between clean and pre-exposed. Other times (4 mM) there is more spreading on pre-exposed, while alternatively (8 mM) there can be more spreading on the clean surface. Performing statistical

Table 2. Average Values of Spreading of SDS Solution after Advance over Clean and Pre-exposed Teflon-Coated Smooth Silicon (Standard Deviations in Parentheses)

SDS concentration (mM)	spreading after advance over clean (μm)	spreading after advance over pre-exposed (μm)	<i>t</i> test value for hypothesis that spreading for clean and pre-exposed are same
2	21.3 (3.1)	24.7 (4);	0.48
4	13.0 (5.3)	9 (8.5);	0.66
8	44.7 (11.7)	18 (5.3);	0.07

analysis of the average values (Table 2), one can do a *t* test to determine whether the spreading seen on clean and pre-exposed surfaces is the “same” (i.e., has the same mean). The high values of the *t* test result, and the average values from Table 2, suggest that the spreading is the same.

The fact that the spreading is the same is important because if the autophilic effect were occurring slower than the rate of advance, it would be expected to take place shortly after the first advance, causing spreading. However, it would not be expected to take place after the second advance, since there would already be surfactant ahead of the contact line (note that R_0 for pre-exposed surfaces is always less than for clean surfaces). As similar spreading for both clean and pre-exposed substrates has been observed, the autophilic effect cannot be the cause of the spreading. The two options presented above were that, if the autophilic effect existed, it would be expected^{2,6} to either manifest during the advance or shortly afterward. With the above arguments, we have shown that neither is the case in the present study and so propose that the autophilic effect is not taking place for SDS on Teflon-coated silicon, contrary to the findings in the literature.^{2,6} Work presented later in this paper will expand this analysis to systems of SDS, HTAB, and MEGA 10 solutions on Teflon- and OTS-coated silicon.

The question remains: what is causing the spreading observed in Figure 3. One can think that the same mechanism suggested by ref 6, i.e., vibration/inertial based spreading after the end of the advance, is at work. As stated in the Experimental Setup, the contact line was advanced slowly, but according to Suo et al.,²⁸ even at this slow speed some inertial spreading would be expected after the end of the advance. This spreading is not due to the autophilic effect, and this argument will be expanded on later in this work. In support of the idea that the spreading is not caused by surfactants, Figure 4 shows the time constant for spreading (calculated in the manner of eq 10 from ref 2) versus surfactant concentration. In the previous literature,^{2,11} an argument in support of the autophilic effect was that the time constant decayed monotonically with concentration, which is not seen in our data. It is clear that the time for spreading is independent of surfactant concentration, meaning that the spreading is not influenced by the presence of surfactants in the manner suggested for the autophilic effect.^{2,10,11} This independence on surfactant concentration is in direct contradiction of one of the basic assumptions made in ref 12 to construct the theoretical formulation of the autophilic effect. That the time constant is independent of concentration is supported by *t* tests of the time constant values for each test, which show *t* test values of 0.15–0.84, supporting the idea that time constant values are not independent values and not decreasing with concentration. The spreading seen (not the effect of surfactants) could instead be due to inertial/vibration factors. This would also be an explanation for the data presented in ref 2 and possibly also that in ref 11.

As further support for the argument that the autophilic effect is not taking place, the present results can be compared to data taken previously by us.²⁶ Only individual tests were performed with the long wait times (~ 5 min) between advancing and receding stages since the work was performed for another

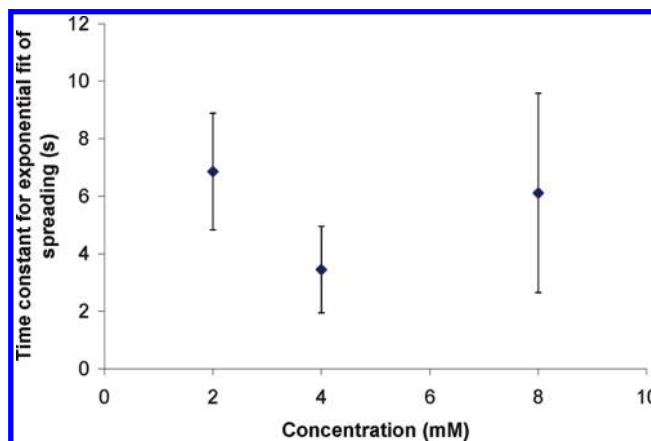


Figure 4. Time coefficient for exponential fit of spreading for the three concentrations of SDS. Error bars denote ± 1 standard deviation and, combined with the lack of downward trend, show that the time coefficient is not a function of surfactant concentration (i.e., spreading is not due to presence of surfactant).

purpose. However, single tests were conducted for three concentrations each of SDS, HTAB, and MEGA 10 solutions, and various pure liquid, on both Teflon-coated and OTS-coated silicon (see ref 26 for details).

For the tests performed, spreading was again seen to occur after the end of the advance on the fresh surface. Tests were conducted at the same motor speeds and using the same apparatus, with the same methodology as in this paper. Examining Figure 5 and Figure 6, one can see that there is no noticeable trend with respect to concentration for the time constant for spreading; again, they do not follow the monotonic decrease with concentration suggested in the literature.^{2,11} Similar to Figure 4, this suggests that the spreading seen (for five other separate systems) is not influenced by the presence of surfactants and not due to surfactant adsorption ahead of the contact line.

Further analysis of the results show that pure liquids show similar spreading behavior after the end of the advance. This can be seen in a comparison of Figures 7 and 3. This spreading, and its rate, is similar in order of magnitude to what is seen with surfactant solutions but occurs with pure liquids (water and ethylene glycol) on a clean Teflon-coated surface. The fact that the small spreading occurs for a system with the complete absence of surfactants further suggests that the similar small spreading seen for surfactant solutions (by us or as reported in the literature) is not due to surfactant adsorption on the s–v interface and instead can be due to vibration/inertial effects. Regarding this, Suo et al.²⁸ have reported that liquids show an exponential type spreading after a switch from a forced advance at a given speed to a different given speed. Further, they report that more viscous liquids take a longer time to spread. Both these statements support our data for the pure liquids, and by extension, our data for surfactant solutions, reinforcing the idea that the spreading seen for surfactant solutions is due to inertia and that the autophilic effect is not taking place. One must note that the

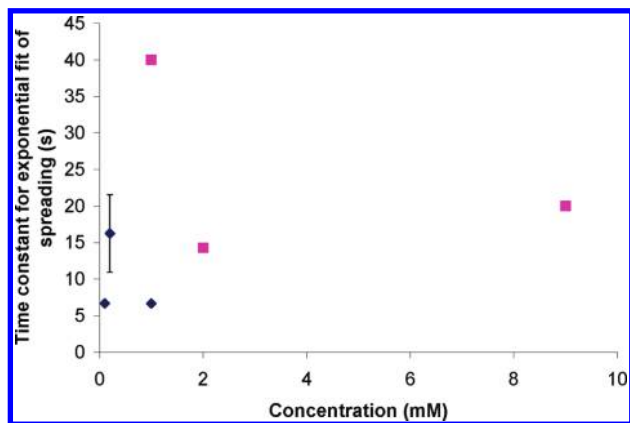


Figure 5. Time coefficient for exponential fit of spreading for three concentrations of HTAB (diamonds, cmc ~ 1 mM) and MEGA 10 (squares, cmc ~ 9 mM) on Teflon-coated smooth silicon. Error bars denote ± 1 standard deviation when more than one test was performed.

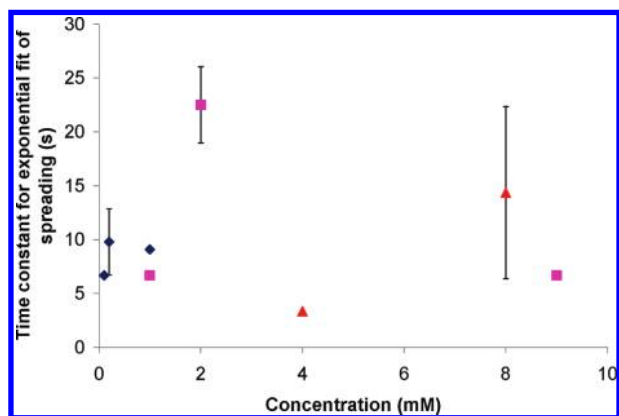


Figure 6. Time coefficient for exponential fit of spreading for three concentrations of HTAB (diamonds, cmc ~ 1 mM) MEGA 10 (squares, cmc ~ 9 mM), and SDS (triangles, cmc ~ 8.3 mM) on OTS-coated smooth silicon. Error bars denote ± 1 standard deviation when more than one test was performed.

PDMS liquids used in ref 28 had a much higher viscosity (~ 1000 times) and much lower contact angle ($< 3^\circ$ static contact angle) than the pure liquids and surfactant solutions considering in this paper but showed a similar time constant for spreading as our data (while they should differ by a similar factor of ~ 1000). Further, Suo et al.²⁸ did report slightly different behavior from ours for liquids spreading after the stop of the forced advance (they saw neither a power law nor an exponential spreading). It is not our intent therefore to make a direct comparison of our results to those of Suo et al.²⁸ (since there are differences in geometry, contact angle, and viscosity), but instead to point out that there are other causes of spreading besides the autophilic effect.

One can also consider contact angle measurements for pure liquids and surfactant solutions on OTS-coated smooth silicon. In Figure 8, results are plotted versus surface tension to allow for comparison between nonaqueous pure liquids and surfactant solutions. As a corroborating point to the above arguments against the autophilic effect, one can see in Figure 8 that pure liquids and surfactant solutions show similar contact angles for similar γ_{lv} surface energy (again similar results were seen on Teflon-coated smooth silicon). A study of Young's wetting equation suggests that the difference between $s-v$ and $s-l$ surface energies is therefore constant for a given surfactant solution concentration compared to a pure liquid of similar γ_{lv} surface

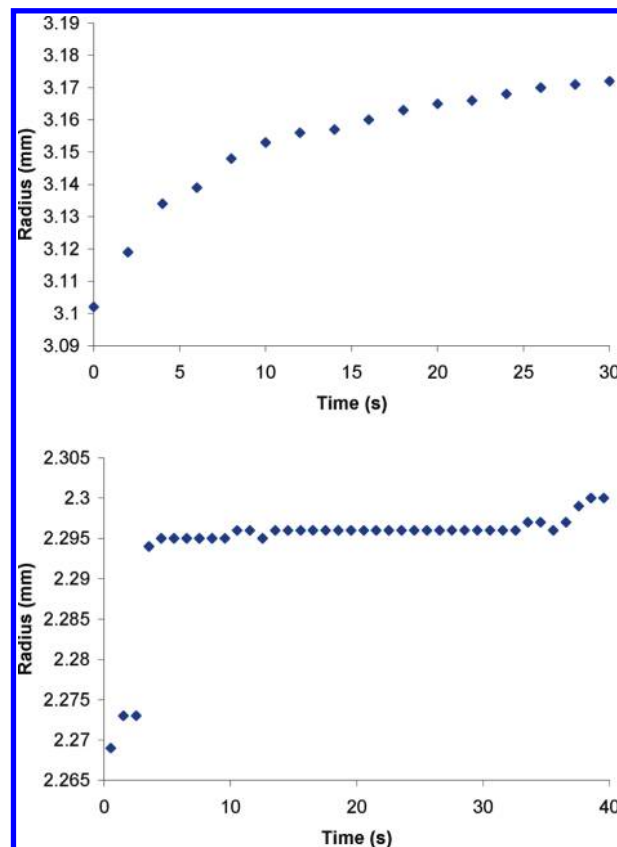


Figure 7. Representative graph of spreading of pure ethylene glycol (top) and pure water (bottom) after advance over clean Teflon-coated smooth silicon. Spreading in the case of pure liquids (without the presence of surfactants) suggests that the spreading seen for surfactant solutions is not due to adsorption of surfactants ahead of the contact line.

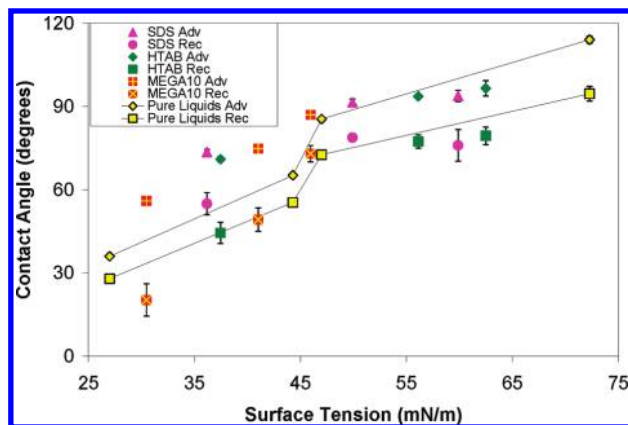


Figure 8. Surfactant solution and pure liquid contact angles for OTS-coated silicon control surface. Pure liquids are (in order of decreasing surface tension) water, ethylene glycol, bromonaphthalene, and hexadecane. Error bars denote ± 1 standard deviation (sometimes small enough to be within the symbol). Lines are to guide the eye.

energy, that is:

$$(\gamma_{sv} - \gamma_{sl})_{\text{surfactant solution}} = \gamma_{lv} \cos \theta_Y = (\gamma_{sv} - \gamma_{sl})_{\text{pure liquid}} \quad (1)$$

since $\gamma_{lv} \cos \theta_Y$ is similar for both the pure liquid and surfactant solution.

Solid–vapor surface energy does not change for the pure liquid, which combined with eq 1 leads to three possibilities:

(1) The autophilic effect could be increasing $s-v$ surface energy compared to the $s-v$ surface energy for a pure liquid wetting a surface; this would require that the $s-l$ surface energy also increase for the surfactant solution to maintain eq 1. This would be against the thermodynamic potential.

(2) Alternatively, $s-v$ and $s-l$ surface energy could decrease, but this would be against the idea of the autophilic effect.

(3) Finally, $s-v$ surface energy could remain the same for surfactant solution wetting compared to pure liquid wetting; this would mean that the autophilic effect was not occurring, supporting the other arguments we have made in this paper. Since the first two options are contradictory to the ideas of either thermodynamic potentials or the autophilic effect, the data in Figure 8 give a final piece of supporting evidence that the autophilic effect is not occurring in the systems under test.

Summarizing the above, the theoretical basis for the autophilic effect has several unresolved issues, specifically, the assumption *a priori* that the effect takes place, the use of Young's equation as a base by authors^{11,12} who consider it baseless, and numerous compounding assumptions, as discussed earlier. Further, there is contradiction in the experimental evidence for the theoretical assertion as well as a lack of a mechanism to allow/explain surfactant adsorption ahead of the contact line.^{6,11,12} Considering then the above arguments, we conclude that for quasi-static wetting of surfaces by sessile drops of sub-cmc surfactant solutions, the autophilic effect does not exist at the magnitude or time scales suggested in the literature^{2,6} and is of negligible importance in the cases we studied.

4. Conclusions

In order to resolve questions in the literature regarding the autophilic effect and its importance to sessile drop wetting, the existence, time constant, and magnitude of the autophilic effect

have been investigated for aqueous solutions of SDS, HTAB, or MEGA 10 on Teflon- or OTS-coated smooth silicon in air, using quasi-static advancing and receding sessile drops. It is concluded (contradicting some literature) that the effect does not exist for these systems. For the five systems tested, no relation exists between the time constant for spreading and surfactant concentration, contradicting results from literature and suggesting that spreading ($\sim 20\text{--}40\ \mu\text{m}$) is not controlled by the autophilic effect. Further, with more detailed tests of SDS on Teflon two observations rule out the possibility that the speed of the effect is faster than, equal to, or slower than the rate of advance. First, advancing contact angle decreases between tests on clean surfaces and those pre-exposed to surfactant. Second, spreading is seen after the end of the advance over both clean and pre-exposed surfaces. Further, pure water and ethylene glycol spread in a similar fashion to surfactant solutions on Teflon. Finally, similar contact angle measurements for surfactant solutions and pure liquids of similar surface tension further supports the idea that the autophilic effect is not taking place for sessile drops of surfactant solution on smooth Teflon- or OTS-coated silicon. Considering then the lack of experimental support for the theoretical assertion, and the lack of a mechanism to allow/explain surfactant adsorption ahead of the contact line, we conclude that for quasi-static wetting of surfaces by sessile drops of sub-cmc surfactant solutions the autophilic effect does not exist at the magnitude or time scales suggested in the literature^{2,6} and is of negligible importance in the cases we studied.

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