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Autophobing on Liquid Subphases Driven by Interfacial Transport of Amphiphilic Molecules

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Abstract

We investigated the phenomenon of incomplete wetting of a high energy liquid subphase by drops of pure amphiphilic molecules as well as drops of amphiphile solutions which are immiscible with the subphase. We show that amphiphiles escape across the contact line of the drop, move on the subphase/vapor interface and form a submonolayer or full monolayer external to the drop. If this monolayer is sufficiently dense, it can reduce the surface tension of the subphase, raise the contact angle of the drop and prevent the drop from fully wetting the subphase. This phenomenon is called autophobing and has been extensively studied on solid substrates. For the liquid subphase studied here, we measure the surface tensions of the three relevant interfaces before and after the drop is deposited. The measured surface tension external to the drop shows that amphiphiles can move across the contact line and form a monolayer outside of the drop. In some cases, at equilibrium, the monolayer is in a sufficiently packed state to create the nonwetting condition. In other cases, at equilibrium the monolayer density is insufficient to lower the surface tension enough to achieve the nonwetting condition. Unlike on solid substrates where the formation of the monolayer external to the drop is kinetically hindered, the amphiphiles can move rapidly across the liquid subphase by Marangoni driven surface transport and local equilibrium is achieved. However, because the amphiphile inventory and subphase area are limited, the achievement of autophobing on a liquid subphase depends not only on the intrinsic subphase/amphiphile interaction but also on the total amphiphile inventory and area of the liquid subphase.

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INTRODUCTION

Zisman and co-workers observed that drops of some amphiphilic compounds do not completely wet some high energy solid surfaces as would have been expected from a simple consideration of surface energies. Rather the drops exhibit a non-zero contact angle.¹⁻³ They postulated that on the surfaces where a nonzero contact angle forms, the surface interaction with the liquid molecules is sufficiently strong that an oriented monolayer of molecules spontaneously forms on the solid surface and the liquid does not wet its own monolayer. This behavior was called autophobing.^{1,2} It has been shown that the static manifestations of autophobing could be turned on and off by changing the strength of the interaction between the solid surface and the polar group of the amphiphilic molecule.¹ Escape of amphiphilic molecules across the drop contact line and its effect on the wetting state of the drop has been the subject of many investigations, particularly for surfactant solutions.⁴⁻¹³

In general, the spreading behavior of a liquid is predicted by the spreading coefficient,

$$S = \gamma_{SV} - \gamma_{SL} - \gamma_{LV} \quad (1)$$

where, for a solid surface, the interfacial tensions γ_{SV} , γ_{SL} , γ_{LV} are for the solid/vapor, solid/liquid and liquid/vapor interfaces, respectively. If the spreading coefficient is positive ($S > 0$) then the drop will completely wet the underlying substrate. However, if the spreading coefficient is negative ($S < 0$) then a nonzero contact angle will form with the angle determined by Young's equation,

$$\gamma_{LV} \cos \theta = \gamma_{SV} - \gamma_{SL} \quad (2)$$

Figure 1(a) shows the interfaces corresponding to each interfacial tension and the contact angle.

A simple argument shows that autophobing cannot occur solely due to the formation of an oriented surface layer at the solid/liquid interface for most systems. Most autophobing systems on solid surfaces have contact angles below 90° so $\gamma_{SV} > \gamma_{SL}$. Since the orientation of amphiphilic molecules at the solid/drop interface is a spontaneous process driven by the strong interaction between the surface and the polar portion of the molecule, this orientation lowers γ_{SL} and would thus decrease, not increase, the contact angle compared to a base state of an unoriented surface layer. This process acting alone would actually increase the spreading coefficient. Autophobing requires lowering γ_{SV} with molecules from the liquid drop despite the fact that the solid/vapor interface is beyond the contact line and thus not obviously exposed to any of the molecules in the drop.

In the case of an amphiphile solution on a solid surface, oriented amphiphiles have been directly observed beyond the contact line in a region where the liquid has never reached.^{8,14,15} These molecules, even though they may not extend more than some tens of microns beyond the contact line, reduce γ_{SV} locally and cause autophobing.¹⁶ On solid substrates, the formation of a monolayer external to the drop is kinetically hindered due to limited mobility of the amphiphiles across the dry solid surface. This makes autophobing on solid substrates appear to be independent of substrate area and amphiphile inventory in the drop.

On liquid subphases, the mobility of the amphiphiles which cross the contact line can be large and in fact driven along the subphase surface by Marangoni stresses. The system can quickly reach equilibrium. This final state of the system will occur when the chemical

potential for the amphiphiles on each of the three interfaces and in the bulk liquid remaining in a drop or thin film are equal and the interfaces are in mechanical equilibrium, producing either a nonwetting drop or a thin film completely wetting across the surface. If the area of the subphase is large enough or the total amphiphile inventory is sufficiently limited, formation of the monolayer outside the drop can significantly deplete the amphiphile concentration in the deposited drop, thereby affecting surface tensions on the drop interfaces and altering the final wetting state of the system.

To date, studies of autophobing on liquid subphases have been limited to cases where transport through either the vapor phase or the bulk subphase could allow molecules originating in the drop to move to the subphase/vapor interface beyond the drop and cause autophobing.^{17–20} Motivated by research on Marangoni driven spreading of insoluble surfactants across liquid films,^{21–26} in this paper we have investigated the mechanism of autophobing on liquid subphases when the extremely low solubility and low vapor pressure of the amphiphiles make it implausible for bulk transport to cause the autophobing on short timescales. We examine the static wetting state on a finite area subphase by drops of pure amphiphilic molecules as well as solutions of amphiphiles, after the spreading event is over. Unlike drops on a solid surface, all three interfacial tensions; drop liquid/vapor, subphase/vapor and subphase/drop liquid– involve only liquid phases and can be directly measured. In this work, we deposit a drop of liquid containing amphiphiles on a subphase that is laterally confined to a finite area and simultaneously measure the subphase/vapor surface tension. We find that in some cases there is an almost immediate decrease in the subphase surface tension at centimeter scale distances beyond the contact line because of the rapid transport of the amphiphiles across the subphase/vapor interface. This decrease in surface tension supports the idea that molecules of the drop liquid cross the contact line of the drop and move centimeters across the subphase/vapor interface. We conclude that this reduction in surface tension caused by the transport of the amphiphiles along the subphase/vapor interface causes autophobing when the subphase/vapor surface tension is reduced below a threshold value. Since the amphiphiles are free to spread over large distances on the liquid subphase, we observe, whether or not autophobing occurs depends on a coupling between the total subphase area and the amphiphile inventory in the drop. Autophobing on liquid subphases is dependent on both intrinsic (e.g. amphiphile chemistry) and extrinsic (e.g. amphiphile inventory, subphase area) system properties.

MATERIALS AND METHODS

We explore the wetting of water or 75% v/v glycerol in water subphases by three different types of liquid drops composed of either: (i) pure non-amphiphiles (hexadecane), (ii) pure amphiphiles (oleic acid), or (iii) amphiphile solutions (2.2 M dodecanol in hexadecane and different concentrations of dodecanol in methyl-terminated poly(dimethylsiloxane), PDMS). The glycerol (density 1.26 g/mL) was used as received from Sigma-Aldrich (99.5%, Cat#G7893) and was maintained in a sealed bottle until use. The water (density 0.99 g/mL, pH ~6) was 18 MRcm resistivity water from a Milli-Q Academic unit with total organic content <10 ppb. The 75% v/v glycerol in water (density 1.19 g/mL) mixture was prepared and stored under nitrogen to inhibit further water uptake. The surface tensions of these liquids are provided in Table 1. The glycerol/water surface tension did not drift over the course of this study, so further uptake of water after the mixture was first prepared had no effect on the experiments.

Hexadecane (Sigma-Aldrich, 99.8%, Cat#52209, density 0.77 g/mL), oleic acid (Sigma-Aldrich, 99.0%, Cat#75090, density 0.89 g/mL, vapor pressure (25°C) $1.9 \pm 0.9 \times 10^{-6}$ Pa,²⁷ water solubility (50°C, 15MPa) 10^{-6} moles/kg water²⁸), dodecanol (Sigma-Aldrich, 98.0%, Cat# 44095, density 0.83 g/mL, vapor pressure (25°C) 0.1 Pa,²⁹ water solubility

(29.5°C) 2×10^{-3} moles/kg water³⁰), chloroform (Sigma-Aldrich, 99.0%, Cat#372978), PDMS (Gelest Inc., product code DMS-T11, viscosity 10 cSt) were used as received. The hexadecane and oleic acid bottles were opened for the minimum possible amounts of time to limit air exposure between experiments. A 0.03 M solution of oleic acid in chloroform, the spreading solvent, was used to produce oleic acid surface pressure-area isotherms. All glassware used to contain the liquids was acid-cleaned using NoChromix followed by rinsing with DI water.

All experiments were performed at a temperature of $23 \pm 1^\circ\text{C}$. Liquid drops were deposited on liquid subphases using an adjustable micropipette (Eppendorf Research Plus). Before deposition from the micropipette, the outside of the pipette tip was wiped with tissue paper (KimWipe) to avoid deposition of any adhered liquid. Petri dishes of radius 2.5, 4.5, 5.0 or 7 cm were used to contain the liquid subphase. Surface pressure-area isotherms for oleic acid were prepared by depositing 0.5 μL drops of oleic acid solution in chloroform onto the subphase using a syringe (Hamilton 600 series) attached to a repeating dispenser (Hamilton PB600-1).

Liquid/liquid interfacial tensions were measured using a Pt DuNouy ring.³¹ In these measurements, the subphase liquid was about 2 cm deep to ensure that the bottom of the container had no impact on the measurements. The layer of liquid above the subphase was at least 1.5 cm deep, large enough that the meniscus broke free from the ring before the ring approached the liquid/vapor interface. The Pt ring was cleaned using ethanol, acetone and DI water and allowed to vapor dry before each measurement. Care was taken throughout the process to avoid distorting the ring. With these procedures, we reproduced the interfacial tension of the hexadecane/water interface reported in the literature.³² The measured interfacial tensions are reported in Table 1.

All the surface tensions at liquid/vapor interfaces were measured with a Wilhelmy plate apparatus using the balance from a Kibron MicroTroughX Langmuir trough. In the apparatus, a Pt pin replaces the usual Wilhelmy plate to reduce buoyancy effects. The roughened pin was cleaned extensively to ensure complete wetting of the pin by the liquid. The cleaning process included washing the pin with DI water, ethanol, acetone and DI water and then flaming with a Bunsen burner. This cleaning procedure was performed before each new reading. Equilibrium liquid/vapor surface tensions were measured for the clean subphase/vapor interface, the liquid/vapor interface for the liquid to be deposited in the drop, and the subphase/vapor interface during pressure-area isotherm measurements. These tensions are reported in Table 1. In order to measure each surface tension, the solution was poured into a clean Petri dish (4.5 or 5 cm radius) and the pin, which was positioned away from the walls of the dish, was lowered to just touch the surface of the liquid. The Wilhelmy pin apparatus was calibrated using the known surface tension of PDMS (19.8 mN/m)³³ with the assumption that the measured and actual surface tensions were linearly proportional. Repeated measurements of this calibration factor provided a precision of $\sim 1.5\%$. In use, the calibration factor produced surface tensions for water and pure hexadecane that agreed very well with literature values.^{34,35} The uncertainties on all quantities reported henceforth represent the propagation of the standard error of the mean.

The surface tension of the drop liquid/vapor interface after a deposited drop of a pure liquid (amphiphilic or non-amphiphilic) had formed a static lens on the subphase was also measured using the Wilhelmy pin apparatus in order to ensure that the drop's surface tension did not change after deposition. The pin was carefully lowered to touch the drop/vapor interface after depositing a 100 μL drop and was gently pulled upwards until it reached the point of detachment from the drop. The surface tension was recorded. The larger volume drop ensured that the pin did not pierce the drop/subphase interface. All the drop/vapor

surface tensions measured by this method were found to be in agreement with surface tensions measured for corresponding bulk liquid samples with the Wilhelmy pin technique.

In addition, transient surface tension measurements were made during drop spreading experiments for the subphase/vapor interface outside of a drop as a function of time after drop placement on the subphase. In this case, the depth of the subphase in the Petri dish was at least 0.5 cm and the pin was positioned ~1 cm away from the walls of the dish.

Drops were deposited on the subphase, remotely from the pin (~3 cm) and were placed gently to minimize the disturbance of the subphase. We confirmed that the drop deposition did not affect the surface tension measurement by placing a drop of the same liquid as the subphase onto the subphase (e.g., water deposited on water). No disturbance that would change the force on the pin and masquerade as an apparent change in surface tension was produced by this deposition. To measure the surface tension of oleic acid spread on various subphases as a function of area per molecule, thereby producing a surface pressure-area isotherm, a 0.5 μL drop of a known concentration of oleic acid in chloroform was placed on the subphase surface and the surface tension was recorded when it had stabilized, on the order of a minute after drop deposition. This process was repeated until the surface tension stopped decreasing significantly upon the addition of a new drop.

Two methods were used to determine if a drop of liquid with nonzero contact angle remained as a lens on the subphase surface after drop spreading. At the same time as surface tension measurements were made with a Wilhelmy pin, the surface of the liquid in the Petri dish was viewed at a grazing angle. If a drop of liquid remained on the surface, distortions of the surface were evident to the eye. If the liquid spread completely, no distortion could be seen. In addition, on separate samples of the same materials, we used the distortion of the image of a Ronchi ruling³⁶ to detect the presence of the static lens. These two techniques were applied to separate experiments because the Ronchi ruling could not be used on the same apparatus as the Wilhelmy pin. Using the Ronchi ruling method, the diameter of the static lens at the end of the spreading process was measured. This measured diameter was compared to the theoretically predicted spread diameter, calculated as described below.

THEORY

The shape of a static liquid lens on a liquid subphase can be determined from the Young-Laplace equation, a balance of the static pressure with the capillarity of the liquid at the interface in the presence of gravity. Pujado and Scriven³⁷ found an equilibrium drop shape for a lens on an immiscible liquid that was not limited by the thickness of the subphase or the lens. This result relies heavily on numerical computation. If the lubrication approximation is implemented, where the height scale (H) of the system is much smaller than the lateral length scale (L), giving $H/L \ll 1$, then the curvatures of the interfaces can be simplified, allowing the equations for each interface to be solved analytically. Kriegsmann and Miksis³⁸ derived a system of equations that model the dynamic spreading of the drop on a thin liquid subphase using the lubrication approximation in one dimension. Following a similar derivation, a system of equations can be derived for axisymmetric spreading. In the derivation, both liquids are assumed to be Newtonian, incompressible, and immiscible. The derivation begins with the Navier-Stokes equations and is reduced to the Stokes equations by implementing the lubrication approximation. The boundary conditions are no slip along the solid wall under the subphase, continuity of tangential stress and continuity of velocity at the liquid/liquid interface, and no tangential stress at the liquid/vapor interface. As is typical of the derivation of the thin film equation, the system can then be simplified to a system of equations for the interface shape. Since we are interested in the final static shape, we can reduce the dynamic equations to the equilibrium relations

$$Bo \frac{dh}{dr} - \frac{d}{dr} \left(\frac{1}{r} \frac{d}{dr} \left(r \frac{dh}{dr} \right) \right) = 0, \quad r_0 \leq r \leq L \quad (3)$$

$$Bo(1-\beta) \frac{db}{dr} - \gamma^{DF} \frac{d}{dr} \left(\frac{1}{r} \frac{d}{dr} \left(r \frac{db}{dr} \right) \right) = 0, \quad 0 \leq r \leq r_0 \quad (4)$$

$$Bo\beta \frac{da}{dr} - \gamma^D \frac{d}{dr} \left(\frac{1}{r} \frac{d}{dr} \left(r \frac{da}{dr} \right) \right) = 0, \quad 0 \leq r \leq r_0 \quad (5)$$

where, $h(r)$ represents the final static subphase/vapor interface, $b(r)$ the final static subphase/drop interface, and $a(r)$ the final static drop/vapor interface. Note that the equation for each interface is specified on a particular domain where r_0 is the location where the three interfaces meet, i.e., the contact line, and L is the radius of the dish. The nondimensional parameters are: the Bond number, Bo , which represents the relative magnitude of gravity and surface tension forces; the density ratio of the drop to the subphase, β ; and the drop liquid/vapor surface tension and drop liquid/subphase interfacial tension, each normalized by the subphase/vapor surface tension, γ^D and γ^{DF} , respectively. The solutions to these equations are Bessel functions with

$$h(r) = C_h + C_{hh} I_0(\sqrt{Bo}r) + C_{hhh} K_0(\sqrt{Bo}r), \quad r_0 \leq r \leq L \quad (6)$$

$$b(r) = C_b + C_{bb} I_0\left(\sqrt{\frac{Bo(1-\beta)}{\gamma^{DF}}}r\right) + C_{bbb} K_0\left(\sqrt{\frac{Bo(1-\beta)}{\gamma^{DF}}}r\right), \quad 0 \leq r \leq r_0 \quad (7)$$

$$a(r) = C_a + C_{aa} I_0\left(\sqrt{\frac{Bo\beta}{\gamma^D}}r\right) + C_{aaa} K_0\left(\sqrt{\frac{Bo\beta}{\gamma^D}}r\right), \quad 0 \leq r \leq r_0 \quad (8)$$

where, the coefficients $C_h, C_{hh}, C_{hhh}, C_a, C_{aa}, C_{aaa}, C_b, C_{bb}, C_{bbb}$ are dependent on the location of the leading edge of the drop, r_0 , which is determined by conservation of mass of the drop liquid. As $r \rightarrow 0$ the Bessel function $K_0 \rightarrow \infty$ which is unphysical behavior which implies the $C_{aaa} = C_{bbb} = 0$; C_{hhh} remains as $h(r)$ is calculated in the outer domain ($r_0 < r < L$). Similarly we take $C_{hh} = 0$ when r becomes large ($r \rightarrow L$). The remaining coefficients are found by applying the boundary conditions of continuity of interfaces at r_0 ,

$$h(r_0) = a(r_0) \quad (9)$$

$$h(r_0) = b(r_0); \quad (10)$$

the balance of contact angle and surface tensions at r_0 using Newton's equations relating the horizontal and vertical forces separately and only keeping terms up to $O(\epsilon^2)$

$$\frac{db}{dr} = \frac{dh}{dr} + \sqrt{-2S \frac{\gamma^D}{\gamma^{DF}}} \text{ and} \quad (11)$$

$$\frac{da}{dr} = \frac{dh}{dr} - \sqrt{-2S \frac{\gamma^{DF}}{\gamma^D}} \quad (12)$$

where, S is the spreading coefficient; continuity of pressure

$$\Delta h - \gamma^D \Delta a - \gamma^{DF} \Delta b = 0; \quad (13)$$

axisymmetry at the origin; the height at the edge of the domain as determined by the mass of the underlying liquid; and a flat profile at the outer edge such that the first derivative of the profile is zero. Here, Δ represents the Laplacian in axisymmetric coordinates. These equations are numerically solved to find the final static radius of the axisymmetric lens.

RESULTS AND DISCUSSION

Drops of Non-amphiphiles

We first examine the case where the drop is not composed of amphiphiles. We place a 1 μL hexadecane drop on a water subphase about 0.5 cm in depth in a 4.5 cm radius dish (area, 63.6 cm^2). The corresponding surface tensions prior to spreading for subphase/vapor, drop liquid/vapor and drop liquid/subphase are shown in Table 1. From these measured surface tensions, the expected spreading coefficient would be -5.4 ± 0.7 mN/m, and therefore the drop would be expected to have a nonzero contact angle. Both visual observation and Ronchi ruling imaging clearly show that the final static state is a lens of hexadecane on the water surface as expected. We observe no detectable change in the surface tension (i.e., <0.05 mN/m) on the subphase/vapor interface beyond the contact line after the drop is deposited, which suggests that no molecular layer or thin film has moved beyond the drop across the subphase surface. Thus, as predicted by the spreading coefficient, the drop does not fully wet the subphase. The measured diameter of the static lens is 1.93 ± 0.02 mm, in relatively good agreement with the calculated diameter of 2.19 to 2.47 mm, where the range in the calculated diameter comes from the uncertainties in the surface tensions, densities and volume.

When a 1 μL drop of hexadecane is deposited on a 75% v/v glycerol in water solution in the same size dish, the spreading coefficient calculated from the surface tension values listed in Table 1 is 8.2 ± 0.8 mN/m, and therefore the drop should completely wet the subphase and exhibit a zero degree contact angle. The drop is visually observed to spread across the subphase and engulf the Wilhelmy pin positioned about 3 cm from the drop deposition point, and no static lens can be observed at the end of the spreading event. Thus on both subphases, the non-amphiphilic hexadecane wets the subphase simply as predicted by the spreading coefficient; no molecules move across the interface in advance of the macroscopic hexadecane body. Autophobicity is not observed in this case.

Drops of Pure Amphiphiles

We next examine the case of a pure liquid drop composed of amphiphiles. In the case of pure oleic acid on water, the expected spreading coefficient based on the pre-spreading surface tensions in Table 1 is 24.2 ± 0.7 mN/m. Thus, the drop is expected to wet the subphase as a thin film with zero degree contact angle. Nevertheless, a static lens of oleic acid with nonzero contact angle is observed on the water subphase using the Ronchi ruling technique after spreading has stopped, as shown in Figure 2(a). Figure 2(b) shows a representative graph from replicate experiments in which the subphase/vapor surface tension far from the drop falls by 32.1 ± 0.6 mN/m after drop deposition. This demonstrates that oleic

acid molecules have escaped from the drop and moved across the surface to the position of the Wilhelmy pin, a distance of more than 3 cm from the drop edge. The spreading pressure measured in this case, 32.1 ± 0.6 mN/m, matches the collapse pressure of an oleic acid monolayer deposited on a water subphase at pH 6,³⁹ suggesting that a monolayer of oleic acid has spread beyond the contact line in a close-packed state near collapse on the subphase surface. This is further confirmed by the surface pressure-area isotherm that we have measured for oleic acid on water, which gives evidence for collapse at areas less than $20\text{--}25$ Å²/molecule, corresponding well with the cross-sectional area of an alkyl tail. If we now replace the pure water/vapor surface tension in the spreading coefficient with the monolayer-covered water/vapor surface tension measured after spreading, we obtain a spreading coefficient of -7.9 ± 0.9 mN/m, which predicts that the drop should not wet completely, in agreement with observation. Clearly, the monolayer that has spontaneously moved ahead of the drop across the subphase is responsible for the autophobic behavior. For a 1 µL drop, we observe a diameter of 1.67 ± 0.02 mm, in reasonable agreement with the range of 1.8 to 2.1 mm calculated using the monolayer-covered subphase/vapor surface tension.

The onset of the decrease in surface tension at the pin occurs within a second of depositing the drop at a distance 3 cm away, reaching its final value 2.0 ± 0.1 s after the onset of the surface tension change. The time of this onset suggests that the front of oleic acid molecules advances rapidly across the subphase with a speed greater than 3 cm/s. This agrees with previous measurements where the speed of the front of surfactant molecules moving ahead of an aqueous surfactant solution drop is on the order of 5 to 10 cm/s.⁴⁰ This rapid surface transport is in contrast to previous reports of other autophobic systems on liquid subphases.^{17–20} In those cases the autophobic is observed only when the two liquids have enough time to become mutually saturated by the diffusion of molecules between the drop and the subphase or by vapor transport of molecules to the subphase/vapor. The speed of the monolayer formation strongly suggests that it is formed by a convective interfacial process rather than bulk diffusional transport. The amphiphiles only have to diffuse to a point just beyond the contact line where the Marangoni stresses, produced by the amphiphile concentration gradient on the subphase/vapor interface, sweep the molecules across the subphase.

We repeated the measurements for a drop of pure oleic acid on a subphase of a 75% v/v glycerol in water mixture in the same size dish. Again, we observe that the drop never fully wets the subphase (Figure 2(c)) despite the positive value of the spreading coefficient calculated using the 75% v/v glycerol in water surface tension (19.5 ± 0.8 mN/m). The drop assumes the form of a static lens. The surface tension of the subphase starts decreasing within a second after depositing the drop ~3 cm from the pin, ultimately decreasing by 25.5 ± 0.3 mN/m as shown in Figure 2(d). As on the water subphase, the subphase surface tension 3 cm from the drop begins to decrease within a second of drop deposition, again suggesting that the autophobic is caused by surface transport of oleic acid across the subphase/vapor interface.

The surface pressure-area isotherm in the inset of Figure 2(d) suggests that the monolayer on the subphase surface outside of the drop, at ~25 mN/m surface pressure, is in a packed state near collapse, similar to the behavior on water. If one had ignored the presence of the monolayer, the spreading coefficient would have been positive in contradiction to the observation of a drop with nonzero contact angle; but with the 37.0 ± 0.7 mN/m surface tension for the monolayer covered subphase, the spreading coefficient becomes negative, -6.0 ± 0.8 mN/m, now in agreement with the observation. For a 1 µL drop, we observe a diameter of 1.66 ± 0.06 mm, in reasonable agreement with the calculated range of 1.9 to 2.2 mm using the monolayer-covered subphase surface tension.

In addition to the measurements showing static manifestations of autophobing of oleic acid on a 75% v/v glycerol in water subphase, we observe movement of the capillary ridge and contact line which have been investigated by others.^{21–25,41–45} Figure 3 shows images of the spreading event. In Figure 3(a), the drop has just been deposited, and movement of air bubbles trapped in the subphase shows that there is subphase flow after drop deposition at and ahead of the Marangoni-driven capillary ridge. At the same time, we also observe a lens of the oleic acid left behind the capillary ridge. We focus on the behavior of this lens: In Figure 3(b) the lens continues to spread, reaching a maximum spread area in Figure 3(c), and then retracts in Figures 3(d) and 3(e). It is evident in Figure 3(c) that the oleic acid drop does not spread completely to zero degree contact angle but stops and retracts after reaching a maximum spread area. The bubbles in the subphase are not seen in any frame except Figure 3(a) as they are pushed away towards the edge of the Petri dish by the expanding capillary ridge. Again, the formation of the capillary ridge suggests that the amphiphiles must transport along the subphase interface, driven by Marangoni flow.

Drops of Surfactant Solutions

Next we examine autophobing for surfactant solutions by depositing a 1 μL drop of a 2.2 M dodecanol in hexadecane solution on a water subphase in a 63.6 cm^2 dish (4.5 cm radius). The high concentration of dodecanol surfactant in the solution ensured that the monolayer forming on a subphase/air interface is dominated by solute molecules with little, if any, solvent.¹ The results are similar to the results for pure oleic acid on both pure water and glycerol-water subphases. The spreading coefficient calculated from the interfacial tension for 2.2 M dodecanol in hexadecane on water and the pure water subphase surface tension, assuming it is unaffected by the deposited solution, is positive, 34.9 ± 0.7 mN/m, and would predict complete spreading. Yet, the solution drop does not fully wet the subphase, as seen in Figure 2(e). Multiple lenses are formed due to complex dewetting phenomena. We again attribute the decrease in surface tension of the subphase to amphiphiles, in this case dodecanol molecules leaving the lens of dodecanol in hexadecane solution and crossing the three phase contact line. In contrast, recall that although pure hexadecane also did not spread on water, it failed to decrease the subphase surface tension because no molecules were drawn out of the drop and across the subphase.

When the drop is deposited, we observe a rapid decrease in the surface tension of the subphase well outside the drop by 46.1 ± 0.8 mN/m as shown in Figure 2(f). Subsequent addition of more drops of dodecanol solution (outside of the original lenses) onto the subphase does not cause any further reduction in the surface tension of the subphase. Further the observed surface tension reduction is the same as that observed if a drop of pure dodecanol is placed on a clean water subphase (45.2 ± 0.5 mN/m). These observations strongly suggest that a packed monolayer of dodecanol has formed external to the drop of original solution.

This packed monolayer on the 63.6 cm^2 surface contains 4.2×10^{16} molecules, assuming an area/molecule of $\sim 15 \text{ \AA}^2/\text{molecule}$ ^{46,47} and the formation of the monolayer does not remove a significant fraction of the 1.3×10^{18} molecules in the original drop. Thus, the concentration of the dodecanol before and after spreading is essentially the same and we may use the surface tension measured for the bulk solution and listed in Table 1 to calculate the spreading coefficient. We obtain a value of $S = -11.2 \pm 1.1$ mN/m more negative than that of the pure hexadecane solvent (-5.4 ± 0.7 mN/m as discussed above), justifying our observation of nonwetting by the drop. Using Neumann's Triangle,⁴⁸ we calculate the interior contact angle of the lens on the subphase (see Figure 1(b)) from our measured surface tensions. We find that the addition of the dodecanol surfactant to the hexadecane raises the angle from 44.8° for the pure hexadecane solvent to 99.5° for the solution. Thus, the lens of a surfactant solution drop has the higher contact angle than the lens formed by the

pure solvent drop. This is due to the surface pressure exerted by the monolayer of surfactant molecules formed outside of the drop.

Extrinsic Effects

We next discuss the effect of the extrinsic factors: amphiphile inventory in the deposited drop and subphase/vapor area on autophobing by depositing drops of different concentrations and volumes of dodecanol in PDMS solution on water subphases and by changing the size of petri dish containing the subphase. Since the subphase is bounded, there are limits on the amount of amphiphile that can spread to the monolayer and be depleted from the lens. Below, we describe how a drop of pure PDMS completely wets the water subphase by forming a thin film ($S = 9.9 \pm 0.9$ mN/m), but a drop of dodecanol in PDMS solution with a sufficiently large dodecanol inventory autophobes when deposited on the same subphase, due to dodecanol monolayer formation outside the drop. We chose this system because the very different molecular structures of PDMS and dodecanol minimize the amount of PDMS drawn into the external monolayer even when the monolayer is not tightly packed with dodecanol.¹

When a lens forms, amphiphilic molecules will partition among the drop and all three interfaces: subphase/vapor, lens/vapor and lens/subphase. The material balance is:

$$C_i V = \Gamma_{\text{Subphase/vapor}} (1-f) A + \Gamma_{\text{Lens/vapor}} (f) A + \Gamma_{\text{Lens/subphase}} (f) A + C_f V \quad (14)$$

where, C_i is the initial dodecanol concentration in the deposited drop, V is the drop volume, $\Gamma_{\text{Subphase/vapor}}$, $\Gamma_{\text{Lens/vapor}}$, $\Gamma_{\text{Lens/subphase}}$ are the surface concentrations of dodecanol on subphase/vapor, lens/vapor and lens/subphase interface respectively; f is the fraction of subphase area covered by lenses; A is the area of the subphase; and C_f is final concentration of dodecanol left in the bulk lenses after equilibrium is established. Therefore, $C_i V$ is the number of dodecanol molecules deposited; $\Gamma_{\text{Subphase/vapor}} (1-f) A$, $\Gamma_{\text{Lens/vapor}} (f) A$, $\Gamma_{\text{Lens/subphase}} (f) A$ are the number of dodecanol molecules at the subphase/vapor, lens/vapor and lens/subphase respectively; and $C_f V$ is number of dodecanol molecules in the bulk lens. In our calculations, we make the simplifying assumption that the areas of the lens/subphase and lens/vapor interfaces are the projected areas of the interfaces onto the plane of the subphase and that the amphiphiles occupy a negligible volume of the drop so the final and initial volumes of the drop are identical.

Our measurements show that the liquid/vapor surface tensions for all the concentrations of dodecanol in PDMS solution used here were the same as that of pure PDMS ($\gamma = 19.8$ mN/m)³³ as expected. The replacement of PDMS molecules at liquid/vapor interface by dodecanol molecules ($\gamma = 29.4$ mN/m)³⁵ is energetically unfavorable. In eqn. (14), $\Gamma_{\text{Lens/vapor}}$ can therefore be set to zero. Figure 4 shows the surface tension isotherm for the dodecanol in PDMS solution interface with pure water. We calculate $\Gamma_{\text{Lens/subphase}}$ as a function of the bulk dodecanol concentration using the Gibbs adsorption equation and assuming the solution is ideal.⁴⁹

$$\Gamma_{\text{Lens/subphase}} = -\frac{C}{RT} \frac{d\gamma}{dC} = -\frac{1}{RT} \frac{d\gamma}{d \ln C} \quad (15)$$

where, R is the universal gas constant, T is the temperature and C the concentration of dodecanol. From a least squares fit to our data we find, $\frac{d\gamma}{d \ln C}$ is -11.64 ± 0.16 mN/m.

The effect of amphiphile inventory in the deposited drop on autophobing was first studied by varying amphiphile concentration (C_i) in the deposited drop at fixed volume V (1 μL) and fixed subphase area A (19.6 cm^2). The results are presented for C_i ranging from 0 to 0.2 M in Table 2. If spreading coefficients are calculated using the bulk surface tensions (Table 1) before drop deposition, they are all positive suggesting that all of the examined concentrations should result in complete wetting of the subphase. Nevertheless, the final wetting state changes from a wetting film to lenses as the amphiphile concentration is increased in the drop. Lens formation was observed for $C_i \geq 0.075$ M. At the highest amphiphile concentration of 0.2 M, the surface tension of the subphase/vapor interface decreases by 46.2 ± 0.7 mN/m when the drop is deposited. This reduction in surface tension matches: our measurement of the surface tension reduction when a pure dodecanol drop is deposited on a water subphase, our measurement of the surface tension reduction when depositing a drop of 2.2 M dodecanol in hexadecane solution on water, and the literature value of equilibrium spreading pressure of dodecanol on water at 25 $^\circ\text{C}$.⁵⁰ Thus, at this highest concentration a densely packed monolayer forms external to the lenses, and the monolayer appears to be the same regardless of the solvent in the drop from which it came.

The spreading coefficients now calculated with the proper subphase/vapor surface tension measured after spreading, aided by the measured solution/subphase surface tension isotherm (Figure 4), the material balance eqn. (14) and Gibbs adsorption eqn. (15) to account for amphiphiles at the lens/subphase interface and the bulk of the lens, are negative, in agreement with the observation of the lenses at equilibrium for $C_i \geq 0.075$ M. The subphase surface tension reduction caused by monolayer formation decreases as the concentration of amphiphile is reduced in the drop. As the amphiphile concentration is decreased to the point where partitioning does not deliver enough amphiphiles to the subphase interface to cause the spreading coefficient to become negative, the final wetting state changes from lenses to a fully wetting film.

The detailed dodecanol partitioning calculations for the concentrations where lenses form are shown in Table 3.⁵¹ The total area of the lenses is determined from Ronchi ruling images. Lenses cover around 3.5% of the dish area in the case of 0.075 M drop deposition and 4% when the concentration is 0.2 M. The area covered by the lenses for other concentrations is estimated by interpolating the data between these points. We estimate an uncertainty of 10–20% in the area which does not have any effect on our basic conclusions.

As seen Table 3, in every case that yielded lens formation, the passage of amphiphiles across the contact line has depleted the concentration in the drop by $\sim 10\%$ for the higher concentration and $> 25\%$ for the lowest. The values of the spreading coefficient (S_{Mono}) shown in Table 3 are found by: using the directly measured subphase/vapor surface tension, determining the final dodecanol concentration in the lens after the monolayer formation has depleted the initial concentration and then finding the corresponding lens/subphase interfacial tension from the interfacial tension isotherm (Figure 4), and setting $\Gamma_{\text{Lens/vapor}}$ to zero as discussed above. These spreading coefficients are all negative, in agreement with the observed lens formation.

The effect of surfactant inventory on autophobing can also be observed by changing the volume of drop deposited at fixed amphiphile concentration and subphase area. Two cases of change in final wetting state with changes in deposition volume are shown in Table 4. In the first case, it is seen that a decrease in deposition volume from 1 to 0.1 μL of a 0.1 M solution at the same subphase area (19.6 cm^2) changes the wetting state from lenses to a film. Thus in this case, the partitioning of the amphiphile inventory in 0.1 μL drop does not deliver enough amphiphiles to the subphase/vapor interface to change the subphase surface tension and the sign of the spreading coefficient. Hence, no autophobing is observed and the

drop completely wets the underlying subphase. When the 1 μL volume is used, the inventory is high enough to cause autophobing. In the second case shown in the table, we induce the film-to-lens transition by increasing the deposition volume for a second case of amphiphile concentration (0.075 M) and subphase area (153.8 cm^2).

Likewise, the inventory effect is also demonstrated by changing the subphase area at fixed amphiphile concentration and drop volume. Drops having the same amphiphile inventory can autophobe on a smaller subphase area but form a wetting film on a larger subphase area. Two cases of such a change in final wetting state with changes in subphase area are shown in Table 5. In both the cases, a drop forming lenses on a subphase of 19.6 cm^2 completely wets the subphase when deposited on a larger subphase (153.8 cm^2). Again, this can be attributed to the insufficient amphiphile inventory which cannot produce a monolayer on the large area subphase that is dense enough to cause autophobing.

SUMMARY

We have examined the mechanism of autophobing of drops of pure amphiphiles and of amphiphile solutions on high energy liquid subphases in terms of the independently measured surface tensions. We observe that amphiphiles form a monolayer external to the drop immediately after the drop is deposited on the subphase, reducing the subphase surface tension beyond the lens, resulting in autophobing. Further, the extremely low solubility and the low vapor pressure of the amphiphiles examined here plus the immediacy of monolayer formation clearly lead to the conclusion that interfacial amphiphile transport, rather than bulk amphiphile transport, is responsible for autophobing. Monolayer formation on the subphase and the attendant surface tension reduction is the key. Although amphiphile adsorption or reorientation at the drop/subphase interface may decrease that interfacial tension, this alone cannot produce autophobing. In contrast to autophobing on solid substrates, the extent of monolayer formation on liquid subphases is not kinetically hindered, allowing the system to reach an equilibrium state. That final state is dictated by the partitioning of the amphiphiles to the three interfaces and the bulk liquid that remains as a lens or a film and the capillary balance achieved with those final surface tensions. These are in turn affected by the total amphiphile inventory available to the system and the area of the subphase. Therefore, the phenomenon of autophobing on a liquid subphase is dependent not only on the material properties of the system but also on the amphiphile inventory in the deposited drop and on the subphase area.

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Figure 1. Force balance on the three phase boundary and contact angle made by a liquid drop on (a) solid substrate and (b) liquid subphase.

Figure 2.

Ronchi ruling images showing lens formation after deposition of 1 μL drops of (a) oleic acid on water, (c) oleic acid on 75 % v/v glycerol in water and (e) 2.2 M dodecanol in hexadecane solution on water. Multiple lenses are seen for (e). The period of the Ronchi rulings is 0.17 mm. The corresponding change in the surface tension of the subphase after the drop deposition ~ 3 cm from the Wilhelmy pin for figures (a), (c) and (e) is shown in (b), (d) and (f), respectively. Time $t = 0$ denotes the time of drop deposition on a subphase. The inset in (d) represents the measured surface pressure-area isotherm of oleic acid on 75 % v/v glycerol in water subphase.

Figure 3.

Capillary ridge and contact line of a 1 μL oleic acid drop on 75% v/v glycerol in water subphase. Images (a) through (e) are at <0.3 s, 2.45 s, 3.48 s, 3.74 s, and 4.04 s after drop deposition respectively. The yellow arrow in (a) points to the capillary ridge. The period of the Ronchi ruling is 0.17 mm.

Figure 4. Semi-log plot of dodecanol-in-PDMS solution/water interfacial tension versus concentration of dodecanol. The solid line represents $d\gamma/d \ln C$ which is used in eq. 15.

Table 1

Interfacial tensions

Interface	Interfacial Tension (mN/m)
water/vapor	72.7 $\pm$ 0.6
75% v/v glycerol-in-water/vapor	65.1 $\pm$ 0.6
hexadecane/vapor	27.3 $\pm$ 0.2
hexadecane/water	50.8 $\pm$ 0.3
hexadecane/75% v/v glycerol-in-water	29.5 $\pm$ 0.4
oleic acid/vapor	32.4 $\pm$ 0.3
oleic acid/water	16.1 $\pm$ 0.1
oleic acid/75% v/v glycerol-in-water	13.1 $\pm$ 0.1
2.2 M dodecanol in hexadecane/vapor	25.8 $\pm$ 0.3
2.2 M dodecanol in hexadecane/water	12.0 $\pm$ 0.3
PDMS/vapor	19.8 ^a

^a as reported in ref. 33.

Table 2

Effect of amphiphile inventory on autophobing by changing the concentration. 1 μL drop volume and 19.6 cm^2 subphase area. The uncertainty on the surface tension values is ± 0.7 mN/m.

Dodecanol Concentration (M)	Dodecanol molecules in deposited drop	$\Delta\gamma$ (mN/m)	Final Wetting State
0 (neat PDMS)	0	-11.0	Film
0.01	6.0×10^{15}	-15.9	Film
0.05	3.0×10^{16}	-28.4	Film
0.075	4.5×10^{16}	-36.8	Lenses
0.1	6.0×10^{16}	-40.0	Lenses
0.15	9.0×10^{16}	-44.5	Lenses
0.2	1.2×10^{17}	-46.2	Lenses

Table 3

Partitioning of dodecanol molecules and spreading coefficients in the cases of lens formation. 1 μL (V) deposition of a dodecanol-in-PDMS solution drop, on a 19.6 cm^2 (A) water subphase. C_i is the dodecanol concentration in deposited solution drop; $C_i V$ is the number of dodecanol molecules deposited; f is the fraction area of the dish covered by lenses; $\Gamma_{\text{Subphase/vapor}}(1-f)A$, $\Gamma_{\text{Lens/subphase}}(f)A$ are the number of dodecanol molecules at subphase/vapor, lens/subphase respectively; C_f is final concentration of dodecanol left in the bulk lenses after equilibrium is established; $C_f V$ is number of dodecanol molecules in bulk lens; S_{Mono} is spreading coefficient calculated after accounting for the monolayer covered subphase/vapor interface.

C_i (M)	$C_i V$ (molecules)	f	$\Gamma_{\text{Subphase/vapor}}(1-f) A$ (molecules)	$\Gamma_{\text{Lens/subphase}}(f) A$ (molecules)	C_f (M)	$C_f V$ (molecules)	S_{Mono} (mN/m)
0.075	4.5×10^{16}	0.035	1.17×10^{16}	2.71×10^{14}	0.055	3.31×10^{16}	-6.6 ± 0.6
0.1	6.0×10^{16}	0.036	1.25×10^{16}	4.00×10^{14}	0.079	4.75×10^{16}	-2.5 ± 0.7
0.15	9.0×10^{16}	0.038	1.25×10^{16}	6.88×10^{14}	0.129	7.76×10^{16}	-2.0 ± 0.7
0.2	1.2×10^{17}	0.04	1.25×10^{16}	1.00×10^{15}	0.178	1.07×10^{17}	-1.9 ± 0.6

Table 4

Effect of amphiphile inventory on autophobing by changing the deposition volume of dodecanol in PDMS solutions. The uncertainty on the surface tension values is ± 0.7 mN/m.

Dish Area (cm ²)	Concentration (M)	Volume Deposited (μ L)	$\Delta\gamma$ (mN/m)	Final state
19.6	0.1	0.1	-24.2	Film
19.6	0.1	1	-40.0	Lenses
153.8	0.075	1	-18.0	Film
153.8	0.075	4	-30.0	Lenses

Table 5

Effect of subphase area on autophobing. 1 μL drop of dodecanol in PDMS solutions. The uncertainty on the surface tension values is ± 0.7 mN/m.

Dish Area (cm^2)	Concentration (M)	$\Delta\gamma$ (mN/m)	Final state
19.6	0.1	-40.0	Lenses
153.8	0.1	-20.6	Film
19.6	0.075	-36.8	Lenses
153.8	0.075	-18.0	Film