

Monolayer Spreading of Polydimethylsiloxane Oil on Surfactant Solutions

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(Received 14 June 1995)

The radial spreading rate of polydimethylsiloxane oil monolayers on various surfactant solutions is measured by observing Teflon tracer particles with a video microscope. We find that a simple model, based solely on Marangoni driven surface tension gradients, accurately predicts the power-law behavior observed for these expanding monolayers. In addition, we document observations of so-called pseudopartial wetting, and discuss its connection to more classical wetting theories.

PACS numbers: 68.10.Gw, 51.20.+d

Oil spreading at the air-water interface has been studied since Phoenician navigators realized that the process can dampen sea waves. Benjamin Franklin also utilized the phenomena to provide the first conclusive proof of the ultimate indivisibility of matter and of the atomic theory [1]. More recently the focus has shifted towards containment of oil spills and liquid-phase pollutants. Other practical problems include spreading paint films, printing applications, detergency, fire extinction, and, of great industrial importance, antifoaming behavior. Apparently, in the latter case, spreading oil entrains subsurface fluid which then drains the individual foam films, causing film rupture and eventual destruction of the foam. Although this destruction hypothesis has existed for some time, a systematic experimental study on relevant systems has yet to emerge [2]. Moreover, fundamental questions centered around drop spreading in partial wetting systems and surface wetting layers have currently received renewed interest. Recent generalized spreading parameters, in the spirit of Frumkin-Derjaguin wetting theory [3], expand Harkins' classical spreading ideas [4], and, as we show, offer an alternative point of view for oil lens formation in systems displaying a positive initial spreading coefficient. In this Letter, we provide results from a systematic study, on a wide range of surfactant solutions, to test the applicability of simple monolayer spreading-rate theories on surfactant-rich subphases and document observations which support the so-called "pseudopartial" wetting behavior at a fluid interface.

The spreading action of oil monolayers on an aqueous substrate is a classic example of Marangoni-driven flow (i.e., flow driven by surface tension gradients). Landt and Volmer [5] were some of the first to outline the hydrodynamics underlying this particular problem and later Fay [6] identified the basic mechanisms using a simple one-dimensional model. Similar analytical treatments can also be found in Joos and co-workers [7]. Finally, a rigorous numerical description of the problem is given in an excellent series of papers by Di Pietro *et al.* [8].

Most of the experimental work on monolayer spreading rates are descendents of the early work by Davies and Rideal [1], who used nonwetting tracer particles to track the rapidly advancing monolayer. Since then many works

have been reported, however, most utilize systems that do not have added surface-active ingredients [7–9] or only contain surfactant in the spreading phase [7,10,11]. In Ref. [11], it is shown that spreading can be faster than surfactant adsorption and that this results in a surface tension gradient between the tip of the monolayer (almost surfactant free) and the center, where adsorption had time to take place: This produces the characteristic finger instabilities of the spreading drop. Missing is a systematic study on possibly the most relevant systems, pure oil droplets spreading on aqueous solutions that contain soluble surfactants. Outstanding questions that arise are: Does the presence of soluble surfactant in the substrate phase affect the dynamic spreading behavior, and can current theoretical developments be applied to these systems?

In summary, for spreading in the monolayer regime, the tension gradient along the monolayer must be balanced by the shear stress arising from substratum flow,

$$\nabla\sigma + \tau = 0, \quad (1)$$

where σ is the surface tension and τ represents the shear stress at the interface. Assuming that the tension is independent of monolayer film thickness and distributing the surface tension gradient over the distance traveled by the monolayer, one obtains for radially expanding monolayers, $d\sigma/dr = S_{o/w}^I/r$, where r is the radius of the leading edge of the spreading front and $S_{o/w}^I = \sigma_{aw} - \sigma_{ow} - \sigma_{oa}$ is the classical initial spreading coefficient of Harkins [4]. Here σ_{ij} corresponds to the bulk equilibrium surface or interfacial tension, and the subscripts o , w , and a signify, oil, water, and air, respectively. It should also be noted that positive values of $S_{o/w}^I$ indicate a thermodynamic preference for the oil to spread over the air-water interface, while negative values imply that oil exists as a lens on the surface. Using an exponentially decaying velocity profile into the bulk solution, $v_r = v_r(r, z = 0, t)e^{mz}$, for evaluating the shear stress induced by the bulk fluid, $\tau_0 = \eta(\partial v_r/\partial z)_{z=0}$, and applying the horizontal force balance of Eq. (1), gives

$$\frac{S_{o/w}^I}{r} = \eta \left(\frac{\partial[(dr/dt)e^{mz}]}{\partial z} \right)_{z=0}, \quad (2)$$

where η is the bulk fluid viscosity, and m is the so-called penetration depth, $m = \sqrt{\rho/\eta t}$, with ρ equal to the bulk

solution density. In Eq. (2) we have also expressed the radial velocity at the surface, $v_r|_{z=0}$, by dr/dt . Lastly, integrating Eq. (2) with respect to time at $z = 0$ yields

$$r = \left(\frac{4}{3}\right)^{1/2} \left(\frac{S_{o/w}^I}{\rho^{1/2}\eta^{1/2}}\right)^{1/2} t^{3/4}. \quad (3)$$

Except for the numerical prefactor, the power-law behavior in Eq. (3) was obtained by Fay [6] using a dimensional analysis. Di Pietro *et al.* [8] conclude that this prefactor depends on the constitutive equations that relate the surface tension to the monolayer thickness. Equation (3) represents the simplest case which assumes constant values of the surface tension (i.e., constant driving force) independent of the monolayer thickness, and therefore treats the monolayer as an advancing flat plate that generates a Blasius boundary layer in the subsurface fluid. If nonequilibrium adsorption of surfactant at the advancing oil monolayer boundary occurs, the surface tension governing the spreading rate will not be the equilibrium values and the power-law behavior predicted by Eq. (3) will no longer be valid.

Although most experimental works report that monolayer spreading follows power-law behavior, there is a large discrepancy in the power-law exponents reported. These values range from 0.25 to 0.75 [8]. Joos and co-workers [7] quote work that apparently agrees with Eq. (3) but then show that when surfactant is present in the spreading phase, strong deviations from the theory occur. They attribute the disagreement to dynamic surface tension effects that arise when equilibrium adsorption of surfactant to the interface is slower than the time scale associated with monolayer expansion. It is suggested that the rate limiting step may be demicellization and release of the surfactant monomers. Our experiments probe whether or not similar behavior is observed in the inverted situation of pure oil drops spreading on surfactant-laden fluid substrates.

Because of its industrial importance in antifoaming formulations, we use polydimethylsiloxane (PDMS) oil as the spreading agent. The oil in this study, 47v100, $M_w = 10\,000$ ($M_w/M_n = 1.8$) was supplied by Rhône Poulenc and has been treated to remove low molecular weight oligomers. We also utilize a wide variety of different surfactants; anionic aerosol-OT (AOT), purchased from Sigma, nonionic penta(ethylene glycol)-mono-*n*-decyl ether ($C_{10}E_5$) received from Nikko and cationic alkyltrimethylammonium bromide surfactants (C_n TAB with $n = 12, 14, 16$) obtained from Kodak. AOT and $C_{10}E_5$ are used as received, while the alkyltrimethylammonium bromides are two or three times recrystallized from 50:50 acetone:methanol mixtures. Every solution is prepared with water taken from a Millipore MilliQ ultrapure water system. The hydrophobic Teflon tracer particles used were manufactured by grinding off fresh flakes from clean Teflon stock and subsequently washing them with Millipore water, followed by baking for several hours to drive off surface active impurities.

All experiments were performed at ambient temperature, $21 \pm 1^\circ\text{C}$, and surfactant solutions were used at 3 times the critical micelle concentration (CMC). Radial spreading rates of the precursor monolayer film emanating from a bulk oil source are measured by tracking hydrophobic particles on the surface. A high resolution video recorder is focused from above onto a flat-bottomed, 20 cm diameter, glass Petri dish. The dish is filled with surfactant solution to a height of 2 cm, and after aspirating the surface, hydrophobic particles are lightly sprinkled near the center. Carefully prepared Teflon particles were used at different, yet always low, surface concentrations to ensure negligible interference on the spreading dynamics. To minimize disturbances to the surface the oil spread was started by carefully lowering an oil-soaked glass rod to the surface with a micrometer drive system and holding it there until the leading edge of the monolayer reached the sidewall of the dish. The entire event, which lasts less than a second, is recorded for later digital analysis. Surface tension measurements at the air-solution interface are made via the Wilhelmy method using a rectangular (20 mm \times 10 mm), open-frame probe made from 0.19 mm platinum wire, while the drop-weight method is used to determine the interfacial tensions between PDMS oil and the aqueous solutions. These techniques provided surface tensions accurate to ± 0.2 mN/m and interfacial tensions to ± 0.5 mN/m.

Table I contains both the individual tension values and the calculated classical spreading coefficients for each system studied. We have distinguished the coefficients by superscripts *I*, to indicate initial fresh surfactant-solution interfaces and *eq*, to denote surfactant-solution interfaces equilibrated with bulk PDMS oil drops. Table I reveals that all $S_{o/w}^{eq}$ values are zero within the limits of our experimental accuracy and the initial spreading coefficients are positive, indicating that it is thermodynamically favorable for the PDMS oil to spread on our solution-air interfaces. However, there may exist force barriers that prevent this from happening, in which case the system can be trapped in a metastable configuration.

A more complete description of equilibrium drop spreading behavior can be found by considering a generalized form of the spreading parameters. Within this framework the film thickness (i.e., PDMS oil-layer thickness) becomes a variable. The generalized form of the spreading coefficient can subsequently be derived from force balance considerations [12,13] or from a general free energy minimization [14]. Both methods yield the same result,

$$S_{o/w}^g = \int_{\Pi(h_z)=0}^{\Pi(h)} h d\Pi, \quad (4)$$

which is simply a consequence of the work pioneered by Frumkin and Derjaguin [3]. In Eq. (4) the superscript *g* on the spreading coefficient identifies it as the generalized form, Π corresponds to the disjoining pressure for the

TABLE I. Surface and interfacial tensions with calculated classical spreading coefficients.

Solution	σ_{aw}	σ_{ow}	σ_{aw}^a	$S_{o/w}^I$ ^b	$S_{o/w}^{eq}$	k_{theory}	$k_{experiment}$
Water	72.8	39.1	60.6	13.1	1.0	13.2	13.0
AOT	28.0	4.7	25.5	2.7	0.2	5.9	5.5
C ₁₀ E ₅	31.5	3.5	25.1	7.4	1.1	10	10.3
C ₁₂ TAB	38.8	9.8	31.3	8.4	0.9	10.6	10.5
C ₁₄ TAB	37.3	9.4	30.7	7.3	0.7	9.9	10.1
C ₁₆ TAB	37.7	9.8	30.6	7.3	0.2	9.9	10.3

^aEquilibrated film value.

^bIn all cases the air-oil tension, $\sigma_{oa} = 20.6$ mN/m.

spreading phase sandwiched between the two bulk phases, and h is the film thickness of the spreading phase. h_∞ represents a thick film, not influenced by disjoining forces, $\Pi(h_\infty) = 0$ (i.e., duplex film). The classical expressions for the spreading coefficients are subsets of Eq. (4) and can be arrived at by proper choice of the integration limits. In particular, the initial spreading coefficients, $S_{o/w}^I$ in Table I, correspond to $h = 0$, while $S_{o/w}^{eq}$ values are for $h = h_\infty$. Equation (4) implies that while $S_{o/w}^I$ predicts the final thermodynamic outcome, how a system evolves to this state will be determined by the thickness dependent surface-force interactions between the spreading phase and the substrate. Moreover, if local energy minima in these surface forces exist and are large enough, spreading can stop and a bulk droplet will remain on the surface and in contact with the initially spread molecular layer. This latter condition has been termed "pseudopartial" wetting, and Kellay, Meunier, and Binks [15] have recently provided experimental evidence for this behavior with alkane monolayers on brine solutions of AOT.

Figures 1 and 2 display radial spreading rate data for PDMS monolayers expanding on the surface of the aqueous solutions reported in Table I. Symbols indentifying each solution are labeled directly on the figures and, as suggested by Eq. (3), the curves represent power-law fits utilizing $R = kt^{3/4}$. Experimentally determined values of

k are listed in the last column of Table I, where they can be compared to the theoretical predictions calculated from Eq. (3), using our measurements of $S_{o/w}^I$, and the density and viscosity of water at 21 °C. Figures 1 and 2 indicate excellent agreement between our monolayer spreading data and the simple theory of Eq. (3).

These results show that equilibrium adsorption of a surfactant is faster than the time scale of spreading. Indeed, the surface convection produced by the advancing monolayer depletes surfactant coverage; without a replenishment from the bulk reservoir, huge surface tension gradients would occur and invalidate Eq. (3). Recall that the depleted situation does occur when surfactant is present in the spreading phase [11]. In the present case, equilibrium adsorption is diffusion controlled and this diffusion is fast when the surfactant comes from below the surface. To the contrary, when the surfactant is confined in the spreading drop, the distance between the reservoir drop and the tip of the spreading layer is large and diffusion is much slower than convection. This is at the origin of the fingering instability described in [11], and also explains why a liquid film thins more slowly when the surfactant is present in the plateau borders [16].

Figure 2 shows that increasing the carbon chain length of the surfactant tail does not influence the dynamic

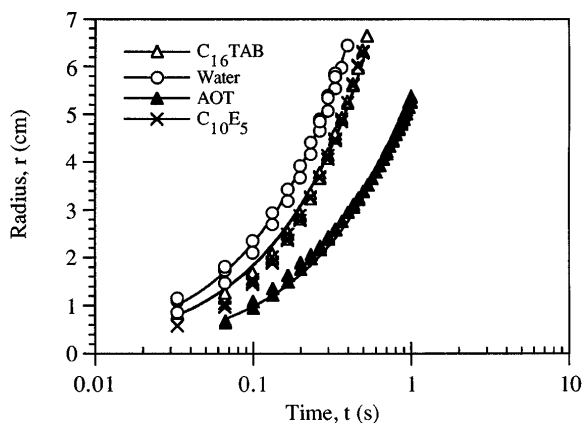


FIG. 1. Radius of PDMS monolayers versus time for spreading on water and on various surfactant solutions.

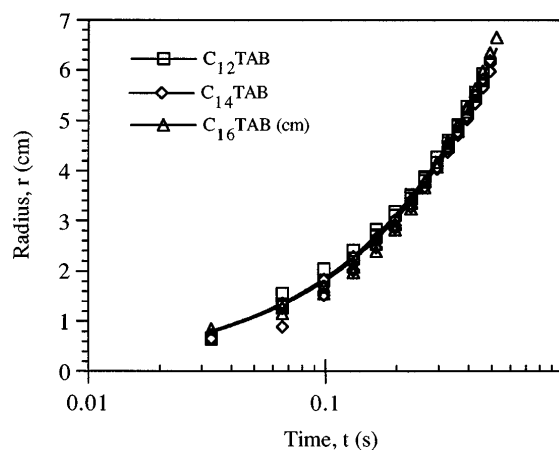


FIG. 2. Radius of PDMS monolayers versus time for spreading on cationic surfactant solutions.

expansion of the monolayer. This is somewhat unexpected, because recent measurements of the PDMS surface pressure isotherms reveal rather pronounced differences between the various C_n TAB surfactants [17]. Evidently, the magnitude of the forces that create these differences is small compared to the driving force for spreading, $S_{o/w}^I$, which is very similar for all of the C_n TAB's tested.

It does appear, however, that in some cases the intermolecular forces can indeed influence macroscopic drop spreading behavior. This conclusion derives from our thick-film spreading observations. After spreading the PDMS monolayers a 5 ml drop was carefully placed on the surface to observe the subsequent thick-film spreading. In this case the spreading can be monitored with the same equipment by following the thin-film interference colors produced. Except for the AOT solutions, in a matter of minutes the PDMS drops spread to form thick oil films on the surface (note that the Petri dish required a lid to prevent disturbances caused by air currents). To the contrary, after spreading a monolayer over the AOT solutions, a PDMS drop produces a stable lens that remains for periods in excess of seven days. In this case, although the $S_{o/w}^I$ is positive and direct observations of the advancing monolayer front confirm initial PDMS spreading, an oil lens resides on the surface in contact with a thin oil film. This condition corresponds to the partial wetting condition outlined by Brochard-Wyart *et al.* for solid surfaces [14].

Within the framework of Harkins' spreading theory, lens formation for systems displaying $S_{o/w}^I > 0$ can arise after the phases have been mutually saturated. That is, once saturated the tensions change and hence so do the spreading coefficients, with the possibility of changing sign. Therefore Harkins' coefficients are typically labeled, as in Table I, to identify the measurement conditions. The pseudopartial wetting concept is in essence the same idea and should not be viewed as completely independent from the classical interpretation. Classical coefficients simply correspond to a specific choice of the integration limits in Eq. (4). Essentially, Harkins accounts for the presence of the film by measuring the change in tension it creates, while the general view explicitly recognizes the film thickness as a variable. Combining these approaches and defining a generalized spreading coefficient clearly demonstrate the relationship between film stability and wetting behavior and strengthens the connection between past and current wetting theories.

We have also showed that simple spreading-rate theories can be used to predict the dynamics of PDMS monolayers on surfactant solutions above the CMC. In this case there is no interference from dynamic surface tension effects (which would lead to a variable driving force), and these monolayers behave as ideal, Marangoni driven, flat

plates gliding over the surface. This has important consequences for foam destruction mechanisms [2]. Extensions of this work include investigating the behavior below the CMC to determine if and when surfactant dynamics to the interface influences the spreading-rate behavior.

The authors are grateful to Rhône Poulenc for partial financial support and for the polymer samples they donated.

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