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Surfactant-Enhanced Spreading

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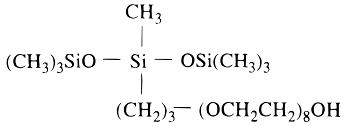
The spreading of aqueous mixtures of a number of surfactants, including "superspreading" trisiloxane surfactants, has been investigated as a function of surfactant concentration, substrate surface energy, temperature, humidity, and substrate roughness. The substrate surface energy, characterized in terms of the contact angle of water, was controlled by the deposition of mixed organosulfur monolayers with different terminal chemical functionalities. The data demonstrate a strong spreading rate dependence on both surfactant concentration and surface energy. Furthermore, they indicate that nonturbid trisiloxane surfactant solutions, which were previously believed not to promote rapid spreading, display superspreading characteristics, albeit on substrates which were less hydrophobic than those initially investigated. Moreover, both turbid dispersions and nonturbid solutions of nonionic surfactants lacking trisiloxane groups have also been found to promote greatly enhanced spreading on less hydrophobic surfaces. Cationic and anionic surfactants were not observed to exhibit enhanced spreading characteristics. These results indicate that surfactant-enhanced spreading denoted earlier as "superspreading", is not limited to turbid aqueous dispersions of trisiloxane surfactants, and this phenomenon may be more general and occur in a much more diverse class of compounds than previously thought.

Introduction

Spreading of liquids over solid substrates is an extremely important but, in many aspects, poorly understood process. Consequently, the development of effective surfactant agents to aid spreading is a priority for a number of industrial applications including coatings,[1] cosmetics,[2] and herbicides.[3] Wetting is also a critical factor in many other complex processes and a more thorough understanding of this subject would provide insight into effects as diverse as phase transitions[4] and the adsorption of medicinal aerosols into the lungs.[5] In general, a liquid is expected to spread and cover (or wet) a solid−vapor interface only if the spreading coefficient S ($=\gamma_{SV} - \gamma_{SL} - \gamma_{LV}$) is positive.[6] The symbols γ_{SV}, γ_{SL}, and γ_{LV} refer to the solid−vapor, solid−liquid, and liquid−vapor interfacial tensions, respectively. For example, water has a relatively high surface tension ($\gamma_{LV} \approx 70$ mN m^{-1}) and spreading is inhibited over lower energy (hydrophobic) surfaces. The addition of surfactants can lower the surface tension by as much as 50 mN m^{-1} and so these water−surfactant mixtures are much more likely to wet low-energy surfaces. This simple thermodynamic treatment does not describe wetting kinetics however. Indeed, the spreading rate, which is often of great practical importance, is not always directly related to the magnitude of the spreading coefficient.[7] Despite theoretical progress,[8] the dynamics of a spreading droplet are complex and present models are far from adequate. This has prompted our investigation of the spreading dynamics of a number of aqueous surfactant solutions and dispersions.

Recently, a class of siloxane-based surfactants that greatly enhance the ability of aqueous mixtures to rapidly spread over and wet even highly hydrophobic substrates has been systematically investigated. These low molecular weight nonionic surfactants share similar structural elements, namely a trisiloxane hydrophobic head group coupled to a poly(oxyethylene) hydrophilic tail. For example, the surfactant denoted as M(D′E$_8$OH)M



$$\begin{array}{c} CH_3 \\ | \\ (CH_3)_3SiO - Si - OSi(CH_3)_3 \\ | \\ (CH_2)_3 - (OCH_2CH_2)_8OH \end{array}$$

where M = $(CH_3)_3SiO$, $E_n = (OCH_2CH_2)_n$, and D′ = $-SiCH_3R$, substantially enhances the spreading rate of aqueous mixtures over very hydrophobic surfaces such as Parafilm. Although the trisiloxane hydrophobe is roughly comparable in hydrophobicity to a $C_{12}H_{25}$ group, the molecular structure is very different.[9] The trisiloxane hydrophobe is shorter (9.7 Å versus 15 Å for a linear dodecyl group) and much wider (the molecular volume of the trisiloxane hydrophobe is approximately 530 Å^3 compared with 350 Å^3 for a linear dodecyl group). Ananthapadmanabhan et al.[10] postulated that this unusual structure and the peculiar character of the trisi-

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loxane moiety may be critical to the rapid spreading (termed "superspreading") displayed by dilute (<1.0 wt %) aqueous dispersions of these surfactants. The turbidity of these mixtures has also been correlated with their spreading properties. In fact, Zhu et al.[11] noted a linear relationship between turbidity and the spreading rate. Spreading was accelerated when the dispersed aggregates were made smaller by sonication. Moreover, Zhu et al.[11] also reported that nonturbid micellar solutions did not spread over very hydrophobic surfaces such as Parafilm and polyethylene. This work suggested that the microstructure of the dispersed droplets was essential to superspreading. However, despite extensive investigation of the phase behavior of aqueous surfactant mixtures,[12,13] the mechanism responsible for the rapid spreading has not been elucidated.

Much of the previous work was limited to a small number of compounds and only a few select substrates, most experiments being performed on either Parafilm or polyethylene, which are very hydrophobic and similar in chemical composition. Studies involving substrates with different surface composition and surface energy might, therefore, be expected to be highly revealing. Well-defined substrates with adjustable surface energies can be prepared by the deposition of organosulfur monolayers having various chemical functionalities onto gold surfaces.[14] To further investigate surfactant-enhanced spreading, we have studied the spreading of surfactant solutions and dispersions on such substrates with varying monolayer compositions and substrate surface energies. The latter having been shown to strongly influence the spreading rates of aqueous surfactant dispersions.[15] We have also investigated the spreading rate dependence on surfactant structure and concentration as well as temperature, substrate roughness, and relative humidity. While the results obtained are consistent with the previously reported data acquired on very hydrophobic surfaces, they indicate that surfactant-enhanced spreading (rapid spreading over lower energy surfaces than could be wet by a test mixture not containing the surfactant) is a much more general phenomenon than previously considered. Furthermore, these results also demonstrate that many previously reported conclusions, based on the somewhat limited data obtained using Parafilm and polyethylene substrates, are not applicable to higher energy (more hydrophilic) surfaces. For example, nonturbid trisiloxane solutions have been found to spread rapidly over sufficiently hydrophilic surfaces. These results, coupled with spreading rate measurements performed at different temperatures and for different surfactants, suggest that there is no particular aggregate microstructure (that can be identified from the reported phase diagram) responsible for the greatly enhanced wetting ability of the trisiloxane mixtures. Moreover, nonionic ethoxylated dodecyl surfactants, $C_{12}E_n$ ($C_{12} = CH_3(CH_2)_{11}$, $E_n = (OCH_2CH_2)_nOH$), were also found to enhance spreading in aqueous mixtures, demonstrating that the trisiloxane moiety is not critical to the observation of significantly increased spreading rates. The previously reported "superspreading" of the trisiloxane surfactant mixtures on Parafilm and polyethylene therefore appears to be simply a particular case describing surfactant-enhanced spreading on unusually low energy surfaces. Two conventional ionic surfactant solutions were also studied and found not to enhance spreading over any of the substrates tested, however. These new results provide insight into the mechanism of surfactant-enhanced spreading and may provide the basis for the development of even more effective spreading agents.

Experimental Section

Apparatus. The substrates for the spreading measurements were supported horizontally in a Plexiglas enclosure into which a variable mixture of wet and dry nitrogen could be introduced for humidity control. The humidity was monitored continuously using a digital hygrometer (Fisher Scientific, Pittsburgh, PA) and, once stabilized, varied by less than 2% over the course of the experiments. Unless otherwise noted, the experiments were performed under saturated (>95% relative humidity) conditions. The temperature within the housing could be adjusted using a resistive wire heater surrounding the substrates. The temperature was measured using a YSI44005 thermistor (Yellow Springs Instrument Co., Inc., Yellow Springs, OH) mounted within 2 mm of the substrate and was sufficiently stable for our purposes (<1 °C variation). Unless otherwise stated, the data were taken at room temperature (≈22 °C). The substrates comprised 25 mm diameter single crystal quartz disks onto which 12 mm diameter gold surfaces (≈2000 Å thick) were deposited by e-beam evaporation onto titanium underlayers (≈200 Å thick). The surface energy of these substrates was controlled by the deposition of mixed organosulfur monolayers onto the gold surfaces.[14] The surface energies of the substrates were characterized by measuring the sessile contact angles of 3.0 μL 18 MΩ water drops using an NRL contact angle goniometer (Rame-Hart, Inc., Mountain Lakes, NJ) (see Figure 1).[16] The contact angles were periodically checked between the spreading rate measurements and did not vary appreciably (±5°). The droplets for the contact angle measurement and the spreading experiments were introduced with a precision micrometer syringe (Model no. S-3100-S, Gilmount Instruments, Barrington, IL) modified with a custom-made delivery tip.

Materials. Quartz substrates were obtained from Valpey-Fisher (Hopkinton, MA). Organosulfur monolayers were deposited by immersing the gold-coated substrates in 1 mM ethanol solutions with different relative concentrations of $HS(CH_2)_{11}CH_2OH$ and $HS(CH_2)_{11}CH_3$.[14,15] The crystals were thoroughly rinsed successively with EtOH and with 18 MΩ deionized water and dried with compressed nitrogen between rinses and prior to use. Two types of quartz crystals were used to determine the effects of surface roughness. Unpolished crystals (roughness ≈ $0.30 \pm 0.10\ \mu$m by stylus profilometry) were used for the majority of the measurements while polished crystals (roughness ≈ 80 Å by atomic force microscopy) were used for comparison.

The surfactants studied were obtained from a variety of sources. All were used as obtained without further purification. Table 1 describes the structure and origin of the compounds studied. The poly(oxyethylene) tails of the trisiloxane compounds are polydisperse, and the number given represents only the average tail length. The aqueous dispersions were prepared using Milli-Q reagent water (18 MΩ) (Millipore Co., Bedford, WA). The mixtures were vigorously hand shaken to disperse the surfactant and allowed to stand, typically overnight, so that any foam had dissipated before the experiments were performed.

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[16] The contact angles were measured immediately after placing the droplet onto the substrate, disturbing the system as little as possible. Because the substrates were fairly rough, substantial contact angle hysteresis was expected and observed. The absolute error in this measurement is therefore significantly larger than the relative error and the resulting surface energy scale should be regarded as somewhat qualitative. Time-dependent variations in adsorption kinetics prevent simply using the solution ratio of alcohol to methyl-terminated thiol to set this scale.

Table 1. Surfactant Nomenclature and Structure[a]

name	supplier	structure
$M(D'E_4OH)M$	DCC	$(Me_3SiO)_2Si(Me)(CH_2)_3(OCH_2CH_2)_4OH$
$M(D'E_8OH)M$	DCC	$(Me_3SiO)_2Si(Me)(CH_2)_3(OCH_2CH_2)_8OH$
$M(D'E_8OMe)M$	OSi	$(Me_3SiO)_2Si(Me)(CH_2)_3(OCH_2CH_2)_8OMe$
$M(D'E_8OAc)M$	DCC	$(Me_3SiO)_2Si(Me)(CH_2)_3(OCH_2CH_2)_8OAc$
$M(D'E_{12}OH)M$	DCC	$(Me_3SiO)_2Si(Me)(CH_2)_3(OCH_2CH_2)_{12}OH$
SDS	Fisher	$CH_3(CH_2)_{11}OSO_3Na$
DTAB	Kodak	$CH_3(CH_2)_{11}N(CH_3)_3Br$
$C_{12}E_3$	Nikkol	$CH_3(CH_2)_{11}(OCH_2CH_2)_3OH$
$C_{12}E_4$	Nikkol	$CH_3(CH_2)_{11}(OCH_2CH_2)_4OH$
$C_{12}E_5$	Nikkol	$CH_3(CH_2)_{11}(OCH_2CH_2)_5OH$

[a] Me = $-CH_3$, M = Me_3SiO-, D′ = $-Si(Me)(CH_2)_3$, E = $-(OCH_2CH_2)_nOH$, Ac = $-C(=O)CH_3$. DCC = Dow Corning Co., OSi = OSi Specialties, Inc. While the poly(oxyethylene) chains of the siloxane compounds are polydisperse, the dodecyl surfactants are monodisperse.

Procedure. After the system had been allowed to equilibrate for at least 10 min at each new temperature/humidity point, the 2.0 ± 0.1 μL test droplets formed at the tip of the syringe were further lowered through a small hole in the Plexiglas enclosure until contact with the substrate occurred. The syringe tip was then quickly retracted and the resulting spreading event was captured on videotape at roughly 7× magnification so that the 12 mm diameter gold region filled the monitor screen. The spreading usually was radially uniform; any fingering occurred over length scales generally less than 10% of the dynamic drop radius. Using a personal-computer based frame grabber (Apple Computer, Inc., Cupertino, CA), the videotape record could then be digitized in real time for data analysis. A digitization rate of 10 frames/s at 120 × 160 pixel resolution was sufficient to capture even the fastest spreading events. The frame rate was adjusted so that ≈15−50 frames were used in the determination of the spreading rate. A macro written for NIH Image[17] was used to obtain the area of the spreading droplet on successive frames. A simple linear regression fit was then used to find the slope of the area (converted from pixels^2 to mm^2) vs time (determined from the frame number times the frame rate) curve and hence the spreading rate (in mm^2/s). The area vs time data generally were highly linear with a regression coefficient, $R > 0.995$. However, there were instances, particularly involving the ionic surfactants, when the data exhibited significant curvature, thereby complicating analysis. By use of multiple measurements under similar conditions, the reproducibility is estimated to be roughly ±10%. The substrates could be used several times, rinsing with 18 MΩ water and drying with nitrogen between measurements, periodically checking for substrate degradation by measuring the contact angle between spreading measurements. All spreading rate data presented in this paper were obtained using the video-based technique introduced above. An alternative technique utilizing the resonant properties of the quartz crystals has also been developed and is further described in the companion paper. The two approaches yield quantitatively similar results.

Results and Discussion

As a preliminary study, much of the previous work using Parafilm as the substrate was repeated. The results are summarized in Table 2. The very rapid spreading of turbid trisiloxane dispersions was verified. None of the more conventional test surfactant mixtures, whether anionic (SDS), cationic (DTAB), or nonionic ($C_{12}E_n$, $n = 3,4,5$), turbid or nonturbid, spread rapidly at any concentration of Parafilm. On the basis of these results alone, the trisiloxane moiety appears to be necessary to promote rapid spreading on Parafilm. The mere presence of the trisiloxane head group is not sufficient, however, since the nonturbid $M(D'E_{12}OH)M$ solutions likewise spread poorly. This suggests that the presence of a dispersed second phase is also important. These results therefore agree with the previous studies: surfactant-enhanced spreading on Parafilm appears to be specific to turbid mixtures of trisiloxane surfactants. Since $M(D'E_{12}OH)M$ and the more conventional surfactants also significantly lower the surface tension of water,[18] these results reinforce the point that increased spreading rates do not necessarily result from simply lowering the liquid−vapor interfacial tension. On the basis of these observations alone, the spreading behavior appears to be dominated by surfactant dynamics and/or surfactant−substrate interactions. In order to elucidate the spreading process, spreading rates were obtained for all of the surfactants discussed above as a function of both surface energy and surfactant concentration. Varying the composition of the organosulfur monolayers enabled examination of the influence of substrate surface energy on surfactant-enhanced spreading. We refer to substrates subtending a large sessile contact angle, $\theta > 90°$ ($\cos\theta < 0$), relative to 18 MΩ water as very hydrophobic. Surfaces exhibiting smaller contact angles, $\theta < 90°$, will be distinguished as increasingly hydrophilic (Figure 1). Finally, it is important to note that, at low surfactant concentration (<1 wt %), physical properties, such as density, viscosity, etc., of the aqueous mixtures do not differ greatly from those of pure water.

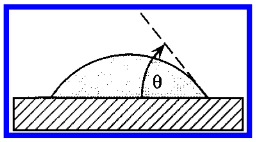

Figure 1. Schematic of a liquid droplet on a solid substrate and the resulting contact angle, θ. Substrates exhibiting large values for θ ($\theta \geq 90°$, $\cos\theta \leq 0$) are termed very hydrophobic. Surfaces exhibiting lower values of θ are increasingly hydrophilic.

Table 2. Spreading Rate Results of 0.4 wt % Aqueous Surfactant Mixtures on Parafilm at 22 °C and >95% Relative Humidity

name	turbid	rate (mm^2/s)
$M(D'E_4OH)M$	yes	5.85
$M(D'E_8OH)M$	yes	4.95
$M(D'E_8OMe)M$	yes	11.3
$M(D'E_8OAc)M$	yes	4.1
$M(D'E_{12}OH)M$	no	<0.1
SDS	no	<0.1
DTAB	no	<0.1
$C_{12}E_3$	yes	<0.1
$C_{12}E_4$	yes	<0.1
$C_{12}E_5$	no	<0.1

Spreading of $M(D'E_4OH)M/H_2O$ Mixtures. The data obtained for $M(D'E_4OH)M$ mixtures display a pronounced maximum in spreading rate on surfaces of moderate hydrophobicity ($0 < \cos\theta < 0.6$) at all concentrations investigated (Figure 2a). Such a maximum, while not necessarily expected, suggests that interactions at the substrate−liquid interface are important. Aqueous dispersions of $M(D'E_4OH)M$ were among the most turbid and the concentrations examined were all well above the break in the surface tension vs concentration curve that marks the onset of aggregation. Nevertheless, the spreading rate can be seen to increase roughly linearly with increasing surfactant concentration (Figure 3a). This suggests the importance of dynamic effects over simple energetics since the equilibrium interfacial tensions at these different concentrations should be very similar. The

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[17] NIH Image is a public domain image analysis program written by Wayne Rasband at the U.S. National Institutes of Health and available from the Internet by anonymous ftp from zippy.nimh.nih.gov or on floppy disk from NTIS, 5285 Port Royal Rd., Springfield, VA 22161, part number PB93-504868. The macro is available from the authors upon request.

[18] The surface tension of aqueous mixtures well above the respective critical aggregation/micelle concentrations of the trisiloxane compounds is ≈21 mN m^{-1}, of SDS is ≈44 mN m^{-1}, of DTAB is ≈35 mN m^{-1}, of the $C_{12}E_n$ mixtures is ≈32 mN m^{-1}.

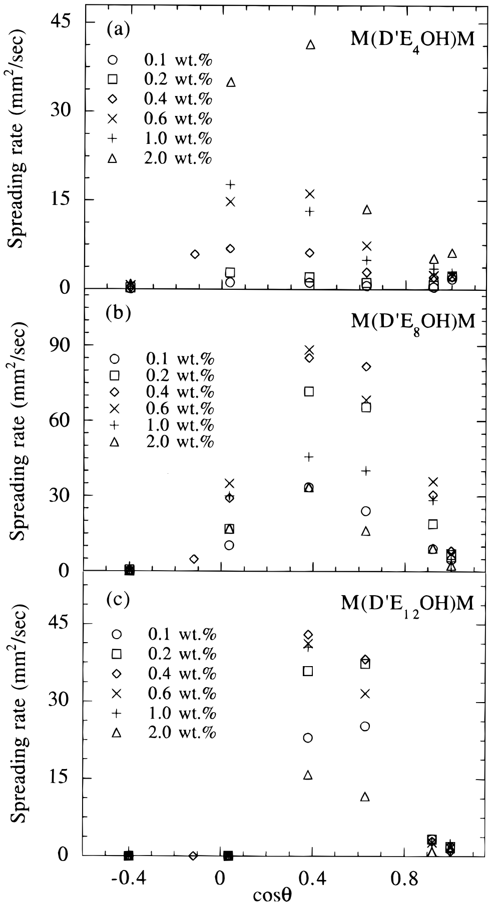

Figure 2. Spreading rate dependence on substrate surface energy (at 22 °C and >95% relative humidity) for aqueous mixtures of (a) $\mathrm{M(D'E_4OH)M}$, (b) $\mathrm{M(D'E_8OH)M}$, and (c) $\mathrm{M(D'E_{12}OH)M}$. Substrate surface energy was modified by the deposition of mixed organosulfur monolayers on rough gold-coated quartz crystals and characterized in terms of the cosine of the observed contact angle of 18 MΩ deionized water. On the basis of this characterization, the corresponding 0.4 wt % mixture spreading rate results on Parafilm have been included as the open diamonds (◇) at cos $\theta = -0.12$. The spreading rate reproducibility is approximately ±10%.

order of the spreading rates of the different concentrations does not appear to depend strongly on substrate surface energy. The final covered area of the spreading droplet is also of interest and such values have been reported previously. However, because the 2.0 μL test droplets generally wet the entire gold surface, meaningful values for these areas could not be obtained.

The spreading rates apparent in Figures 2 and 3 are quite high, certainly too large to be explained in terms of surface diffusion of the surfactant over a dry substrate. Recent ellipsometric measurements have determined the surface diffusion coefficient to be $<10^{-4}$ mm^2/s for pure nonionic surfactants on both hydrophobic and hydrophilic surfaces.[19] Days instead of seconds therefore would be necessary if droplet spreading was governed by surface diffusion on the 12 mm diameter gold surface. Another possible mechanism involves the liquid−vapor Marangoni effect, which describes flow in the direction of increasing surface tension induced by a surface tension gradient at the air−liquid interface.[20] The gradient could be produced by contact between the surfactant-containing droplet and a preexisting water film and by continued rapid adsorption of surfactant onto the substrate at the spreading front. Marangoni flow would be expected to be much more rapid than spreading by surface diffusion over a dry substrate and could lead to the high spreading rates observed. While this argument is appealing, it is not entirely satisfactory. It is not supported by the observed spreading rate dependence on concentration, nor does it explain the apparent specificity to turbid trisiloxane surfactants on Parafilm. Conventional ionic surfactant solutions, ethoxylated dodecyl surfactant mixtures, and the nonturbid solutions of $\mathrm{M(D'E_{12}OH)M}$ are expected to experience similar gradients and spread rapidly if the liquid−vapor Marangoni effect between the leading edge of the drop and a preexisting water film dominates. Moreover, in strong contrast to the Parafilm results, our investigation of the spreading rate on both rough and smooth thiol monolayer modified gold substrates failed to reveal any significant rate dependence on relative humidity.[21] Assuming the spreading is driven by the surface tension gradient produced between the drop and a preexisting

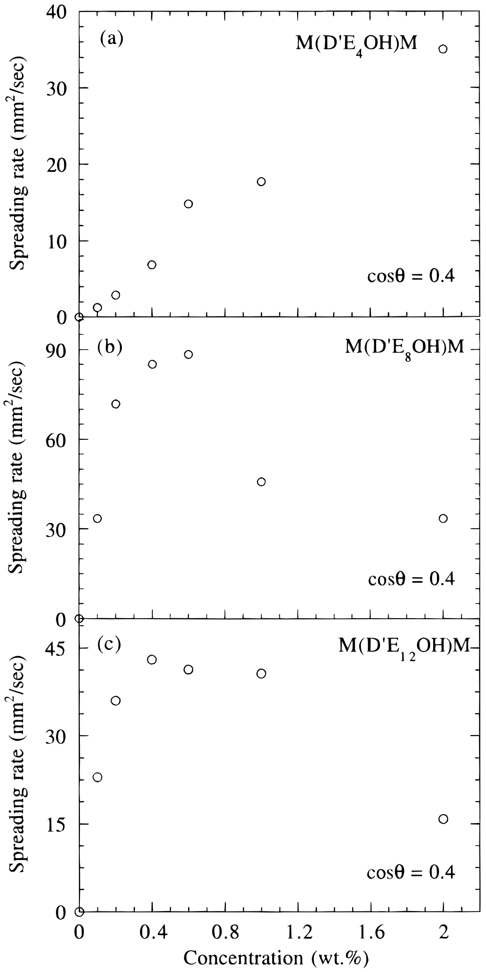

Figure 3. Spreading rate dependence on the concentration of aqueous mixtures of (a) $\mathrm{M(D'E_4OH)M}$, (b) $\mathrm{M(D'E_8OH)M}$, and (c) $\mathrm{M(D'E_{12}OH)M}$. For clarity, only the results on the cos $\theta = 0.4$ substrates are presented.

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[21] Mixtures at 0.2 wt % of $\mathrm{M(D'E_4OH)M}$, $\mathrm{M(D'E_8OH)M}$, and $\mathrm{M(D'E_{12}OH)M}$ were studied extensively as a function of substrate surface energy. No systematic spreading rate dependence on relative humidity (within 10% error) was observed between 5% and 95% relative humidity, the calibration limits of our hygrometer, on the mixed monolayer modified surfaces. It is therefore interesting to note that the spreading rate of 0.2 wt % dispersions of $\mathrm{M(D'E_8OH)M}$ on Parafilm were found to be strongly dependent on relative humidity. In fact, these solutions would not spread at all below 25% relative humidity and exhibited the highest rates (≈5 mm^2/s) under saturated (>95% relative humidity) conditions.

water film, the rate would be expected to increase (at least initially) with humidity and the corresponding thickness of the aqueous surface film.[22]

Spreading of M(D′E$_8$OH)M/H$_2$O Mixtures. Due to the longer hydrophilic poly(oxyethylene) tail this compound is more soluble than M(D′E$_4$OH)M and, while the aqueous mixtures were still visibly turbid, they were less so than the M(D′E$_4$OH)M/H$_2$O mixtures. The spreading rate vs surface energy and concentration data for M(D′E$_8$OH)M again indicate that spreading occurred on all the substrates examined (Figure 2b). As with the M(D′E$_4$OH)M mixtures, the data display a pronounced maxima for substrates having moderate hydrophobicity. These maxima appear somewhat sharper and shifted to slightly more hydrophilic substrates than those exhibited by M(D′E$_4$OH)M. Again, the positions of the maxima do not depend strongly on surfactant concentration. The spreading rate initially increases with concentration, but, unlike the M(D′E$_4$OH)M mixtures, the rates progressively decrease at concentrations exceeding $\approx$0.7 wt % (Figure 3b). This peak in rate vs concentration is not yet understood.[23] The order in spreading rate for the different concentrations on different surfaces is again independent of substrate surface energy to within the error of our measurements.

Studies using M(D′E$_8$OH)M were also performed to determine the effect of substrate roughness on the spreading rate. Wetting of rough substrates was found to occur significantly faster (by as much as 50%) at all concentrations, surface energies, and humidities. This increase in spreading rate was systematic so that the major features (the maxima in rate vs concentration and surface energy) were similar for smooth and rough substrates. The enhanced spreading rate may simply be attributed to the increased capillarity associated with the rough surface.[6] Substrate roughness did not affect the independence of spreading rate on humidity for the mixed monolayer modified surfaces.

Because the maximal spreading rates exhibited by M(D′E$_8$OH)M are larger than those of M(D′E$_4$OH)M, and since both spread on even the most hydrophobic surfaces, M(D′E$_8$OH)M would appear to be the more effective wetting agent and of more practical interest. The maximal spreading rates are also an order of magnitude larger than the rates observed on Parafilm (Table 2). However, Parafilm is quite hydrophobic, exhibiting a contact angle for water of approximately 97° (cos $\theta \approx -0.12$). The spreading rate data on Parafilm (indicated in Figure 2 by the ◇ symbol) are highly consistent with the trends observed on the mixed monolayer modified surfaces. Therefore, while the results presented in the preceding two sections provide new insight into the role of substrate surface energy, they generally support the conclusions based on previous studies using Parafilm and other strongly hydrophobic surfaces.

Spreading of M(D′E$_{12}$OH)M/H$_2$O Mixtures. Whereas M(D′E$_4$OH)M and M(D′E$_8$OH)M were shown to enhance spreading on Parafilm, solutions of M(D′E$_{12}$OH)M spread poorly on Parafilm. This compound was therefore thought to lack the qualities necessary to facilitate significant surfactant-enhanced spreading. It was suggested that this distinction was related to the fact that M(D′E$_{12}$OH)M/H$_2$O mixtures are one-phase solutions, owing to the further increased solubility associated with the longer hydrophilic oxyethylene tail. As expected from previous studies, the spreading rates measured on the mixed monolayer modified surfaces indicate that aqueous solutions of M(D′E$_{12}$OH)M do not spread well on substrates with surface energies similar to that of Parafilm (Figure 2c). However, these solutions were found to spread rapidly on more hydrophilic surfaces. In fact, while the maximal spreading rates are lower than those observed for M(D′E$_8$OH)M, they are very similar to those exhibited by M(D′E$_4$OH)M. This indicates that mixtures need not be turbid, i.e., biphasic, to promote rapid spreading on relatively hydrophobic surfaces and demonstrates that conclusions based on the limited data obtained on Parafilm are not general. On the basis of the similarities between these data sets, it is reasonable to assert that the mechanism driving the enhanced spreading is similar for the three compounds.

As in the case of the M(D′E$_8$OH)M data, the spreading rate data on M(D′E$_{12}$OH)M exhibit peaks as a function of both concentration and surface energy. However the transition between poor spreading to very rapid spreading as a function of increasing substrate hydrophilicity occurs much more abruptly for M(D′E$_{12}$OH)M than for either M(D′E$_4$OH)M or M(D′E$_8$OH)M. This difference in surface energy dependence is somewhat surprising in light of the obvious structural similarity and the similarity of the equilibrium surface tensions of M(D′E$_{12}$OH)M, M(D′E$_8$OH)M, and M(D′E$_4$OH)M aqueous mixtures (21.3, 21.0, and 21.0 mN m^{-1}, respectively). The narrower peak suggests increased spreading specificity to substrate surface energy. Furthermore, the maxima in the rate vs surface energy data continue the shift noted in the previous section toward more hydrophilic surfaces as the poly(oxyethylene) chain length (and solubility) is increased. Despite this shift, M(D′E$_{12}$OH)M solutions spread more poorly than either M(D′E$_8$OH)M or M(D′E$_4$OH)M dispersions on the most hydrophilic surfaces. The maximum in spreading rate vs concentration is again observed but appears to be broader than that exhibited by the M(D′E$_8$OH)M dispersions (Figure 3c).

Spreading of M(D′E$_4$OH)M/M(D′E$_{12}$OH)M/H$_2$O Mixtures. The previous sections demonstrate intriguing behavior based on the length of the hydrophilic poly(oxyethylene) group. This length is expected to affect not only the turbidity but also the nature and microstructure of the dispersed aggregates in the test mixtures.[24] The surfactants studied in the previous sections were somewhat polydisperse due to the nature of their synthesis. In order to more thoroughly investigate the effect of turbidity and the average length of the hydrophilic group, studies were also performed as a function of average tail length, which was varied by preparing 0.2 wt % aqueous mixtures containing different proportions of M(D′E$_4$OH)M and M(D′E$_{12}$OH)M. These mixtures were classified in terms of their average ethoxylation (AE) length, so that a mixture containing equal proportions of M(D′E$_4$OH)M and M(D′E$_{12}$OH)M would be termed AE = 8. Every sample, other than the M(D′E$_{12}$OH)M solution, was visibly turbid. However, a clear progression was apparent. The AE = 10.6 mixture was only slightly turbid while AE = 5.3 and M(D′E$_4$OH)M mixtures were very turbid. The spreading rate vs surface energy data of these mixtures are summarized in Figure 4. As expected from the results described in previous sections, the most rapid spreading

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[22] (a) Troian, S. J.; Wu, X. L.; Safran, S. A. *Phys. Rev. Lett.* **1989**, *62*, 1496. (b) Troian, S. J.; Herbolzheimer, E.; Safran, S. A. *Phys. Rev. Lett.* **1990**, *65*, 333.

[23] Similar rate dependences on substrate surface energy and surfactant concentration have been reported previously for M(D′EO$_8$H)M/H$_2$O mixtures using a quartz crystal microbalance (QCM) to measure the spreading rate.[15] We have since determined that the use of overly small electrodes ($\approx$6 mm diameter) systematically influenced the measurement to yield artificially low spreading rates. New data obtained using larger electrodes ($\approx$12 mm diameter) and faster data acquisition are consistent with the results obtained using the video-based technique presented in this paper. A companion paper describes the modification to the QCM method.

[24] Doumaux, H. A. Ph.D. Thesis, University of Minnesota, 1995.

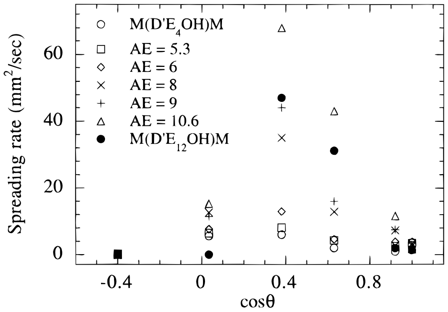

Figure 4. Spreading rate data for 0.2 wt % aqueous mixtures (at 22 °C and >95% relative humidity) of surfactant mixtures resulting in differing average ethoxylated (AE) tail lengths as a function of substrate surface energy. The mixtures are comprised of varying proportions of M(D′E_4OH)M and M(D′E_{12}OH)M. Note that the AE = 8 mixture spreads significantly slower than the corresponding M(D′E_8OH)M dispersion presented in Figure 1b. The spreading rate reproducibility is approximately ±10%.

occurs on surfaces of moderate hydrophilicity ($0 < \cos\theta < 0.6$) for each data set. The peaks in spreading rate become broader and less pronounced, shifting to slightly more hydrophobic surfaces as AE is reduced. The shift may be observed by examining the rates on the $\cos\theta \approx 0.0$ and 0.6 surfaces. It is interesting to note that, while M(D′E_{12}OH)M solutions spread very poorly on the more hydrophobic surfaces, the only slightly turbid AE = 10.6 mixture spreads quite well on such substrates. In fact, the AE = 10.6 mixture wets all but one of the surfaces more readily than the other mixtures. These data therefore suggest a maximum in the spreading rate associated with the onset of turbidity, perhaps due to the size and/or nature of the dispersed aggregates. It is important to observe, however, that the AE = 8 mixture spreads considerably more slowly than the aqueous dispersions of M(D′E_8OH)M (Figure 2b); hence these bimodal mixtures do not precisely mimic solutions or dispersions prepared from less polydisperse or monomodal compounds. The data presented in Figure 4 clearly indicate a strong dependence of the spreading rate on average hydrophile length and surface energy, supporting the results presented in Figure 2. Furthermore, while turbidity is significant and the precise nature of the dispersed aggregates undoubtedly plays a role, these data again indicate that the spreading rate does not depend on turbidity in a direct manner.

Spreading of M(D′E_8OMe)M/H_2O and M(D′E_8OAc)M/H_2O Mixtures. These two trisiloxane surfactants, which are of commercial interest, were investigated for comparison with the aforementioned examples. Extensive studies have been performed to map out the aqueous phase diagrams of these two compounds as well as M(D′E_8OH)M.[12,13] Upon increasing temperature, low concentration surfactant/water mixtures are expected to pass through a cloudy birefringent A ($W + L_\alpha$) region to cloudy birefringent B ($L_3 + L_\alpha$) to clear isotropic flow birefringent (L_3) to cloudy isotropic flow birefringent X ($W + L_3$) regions. Here L_α represents a lamellar phase, L_3 a sponge phase, and W a dilute isotropic aqueous solution. The distinction between the mixtures A and B was found not to be sharp. This work also demonstrated that the phase diagrams, particularly transitions involving the L_3 phase, strongly depend on the nature of the endcap group. The L_3 regions of M(D′E_8OMe)M and M(D′E_8OAc)M are shifted downward by approximately 15 and 30 °C, respectively, relative to M(D′E_8OH)M. However, at the concentrations examined here, at room temperature, both compounds form turbid dispersions well below their L_3 regions. The dependence of spreading rate on surface energy and concentration for these M(D′E_8OMe)M and M(D′E_8OAc)M dispersions is qualitatively similar to the data presented on M(D′E_8OH)M (Figure 5a,b). Peaks in the spreading rate as a function of both concentration and surface energy are clearly apparent. In the case of M(D′E_8OMe)M, the maximal rate shifts to lower energy surfaces as the concentration is increased. It should be noted that both M(D′E_8OMe)M and M(D′E_8OAc)M dispersions spread more rapidly on more hydrophobic surfaces over wider concentration ranges than their M(D′E_8OH)M counterparts. Even though the maximal spreading rates are not quite as great as those exhibited by M(D′E_8OH)M, the apparent enhanced ability of these dispersions to wet very hydrophobic surfaces may be of practical interest.

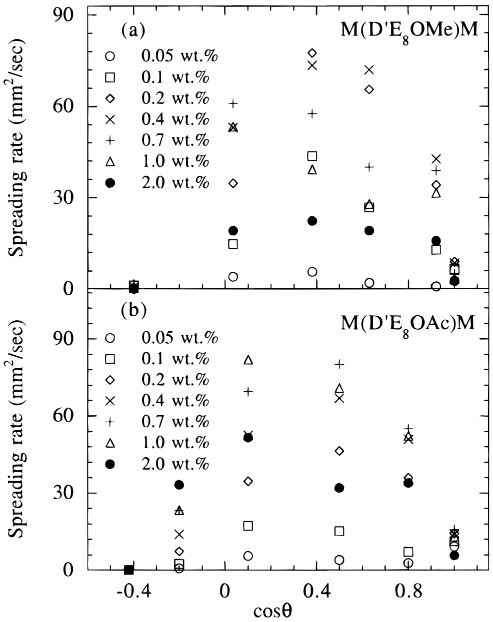

Figure 5. Spreading rate dependence on substrate surface energy (at 22 °C and >95% relative humidity) for aqueous mixtures of (a) M(D′E_8OMe)M and (b) M(D′E_8OAc)M. The spreading rate reproducibility is approximately ±10%.

In order to elucidate the effects of aggregate microstructure, the spreading behavior of these surfactant mixtures was examined as a function of temperature. These studies were facilitated by the fact that the upper boundaries of the L_3 regions for low concentration aqueous mixtures of these two compounds are readily accessible, ≈40 °C for M(D′E_8OMe)M and 30 °C for M(D′E_8OAc)M.[13] The results on M(D′E_8OMe)M are presented in Figure 6. The data on subsequent heating and cooling runs were reproducible and demonstrate a decrease in the maximal spreading rate above the L_3 region, which is expected to occur between approximately 38 and 42 °C. However, the elevated temperature data display the same general features as the room temperature data and the mixtures clearly spread very rapidly up to and through the L_3 region. The results on M(D′E_8OAc)M are qualitatively similar. Because the microstructure is expected to be substantially altered through this temperature region, these results also suggest that a specific microstructure (such as the lamellar phase) is not necessary for significant surfactant enhancement of spreading rates, providing independent support of the conclusions presented above based on the M(D′E_{12}OH)M and average ethoxylated chain length data.

Spreading of $C_{12}E_n/H_2O$ Mixtures. Even though the aggregate microstructure and turbidity were found not to be critical to the observation of trisiloxane surfactant enhanced spreading, the results above provide little insight into which, if any, other (nonsiloxane) surfactants would also promote greatly increased spreading rates. The

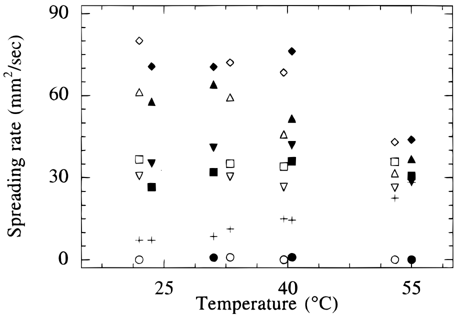

Figure 6. Temperature dependence of the spreading rate of 0.2 wt % aqueous $\mathrm{M(D'E_8OMe)M}$ mixtures. The symbols correspond to substrates with different surface energies: ○; $\cos\theta = -0.4$; □, $\cos\theta = 0.03$; ◇, $\cos\theta = 0.4$; △, $\cos\theta = 0.6$; ▽, $\cos\theta = 0.9$; +, $\cos\theta \approx 1$. The data represented by open symbols were taken on heating while the data represented by closed symbols were taken on subsequent cooling. The microstructure of the dispersed phase is expected to change near 40 °C (see text). Since these mixtures spread rapidly at temperatures as high as 55 °C, the presence of a particular microstructure does not appear to be necessary for the greatly enhanced spreading characteristics of these mixtures. The spreading rate reproducibility is approximately ±10%.

trisiloxane compounds represent fairly atypical amphiphilic molecules. The hydrophobe is short, wide, and unusually efficient, while the hydrophile is longer and not nearly as wide. It is conceivable that this unconventional structure allows the trisiloxane compounds to exhibit truly unique wetting behavior. The observation of surfactant-enhanced spreading exhibited by a more conventional surfactant mixture would therefore constitute an important result.

The trisiloxane group has been shown to exhibit hydrophobicity similar to that of a linear dodecyl hydrophobe.[9] The aqueous phase behavior of the nonionic alkyl ethoxylate surfactants C_mE_n has also been extensively investigated.[25] These studies have demonstrated significant similarities between the trisiloxane and dodecyl ethoxylate phase diagrams. Since the dodecyl head group presents a considerably smaller cross section, shorter poly(oxyethylene) tails, relative to the trisiloxanes, are required to form phases of similar curvature. Therefore, the dodecyl ethoxylate compounds $C_{12}E_n$, with $n = 3$, 4, or 5, might be expected to mimic the behavior of trisiloxane-based surfactants.

Aqueous mixtures of $C_{12}E_3$ were visibly turbid at all concentrations tested, the dispersed phase being lamellar liquid crystal.[25] These dispersions did not spread well over Parafilm or the low-energy mixed monolayer surfaces ($\cos\theta < 0.25$) (Figure 7a). However, very rapid wetting is apparent on sufficiently hydrophilic surfaces. In fact, the maximal rates are comparable to those exhibited by $\mathrm{M(D'E_8OH)M}$. As in the case of $\mathrm{M(D'E_{12}OH)M}$, there appears to be a surface energy below which $C_{12}E_3$ dispersions abruptly cease to spread rapidly. The maxima in spreading rate as a function of substrate surface energy are shifted toward considerably more hydrophilic surfaces compared with the peaks exhibited by the trisiloxane-based compounds. A maximum in rate vs concentration is also observed and is comparable to the peak exhibited by $\mathrm{M(D'E_8OH)M}$ (Figure 8). The observation of rates and wetting characteristics which are similar to those exhibited by the trisiloxane compounds (including highly linear area vs time curves), suggest a similar spreading mechanism. *This clearly indicates that surfactant-enhanced spreading is not unique to siloxane compounds and suggests that this phenomenon may be fairly general.*

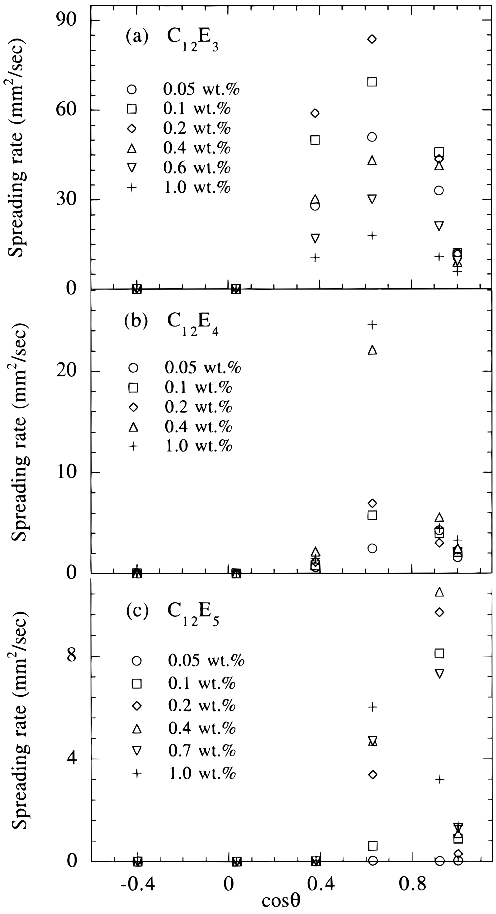

Figure 7. Spreading rate dependence on substrate surface energy (at 22 °C and >95% relative humidity) for aqueous mixtures of (a) $C_{12}E_3$, (b) $C_{12}E_4$, and (c) $C_{12}E_5$. These plots are qualitatively very similar to those presented as Figure 1. The spreading rate reproducibility is approximately ±10%.

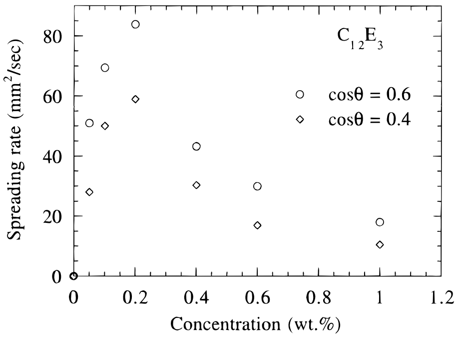

Figure 8. Spreading rate dependence on the concentration of aqueous dispersions of $C_{12}E_3$. For clarity, only the results on the $\cos\theta = 0.4$ and $\cos\theta = 0.6$ substrates are presented. The peaks in rate vs concentration are qualitatively similar to the peak exhibited by $\mathrm{M(D'E_8OH)M}$ (Figure 2b). The spreading rate reproducibility is approximately ±10%.

The longer hydrophilic chain of $C_{12}E_4$ increases the solubility compared to $C_{12}E_3$, leading to less turbid dispersions. While $C_{12}E_4$ also clearly enhances the spreading, the maximal spreading rates are substantially lower than those achieved with $C_{12}E_3$ (Figure 7b). Again, the maximal rates are observed on substrates significantly more hydrophilic than Parafilm. The maximum in rate vs surface energy is much sharper than the peak exhibited

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(25) (a) Mitchell, J. D.; Tiddy, G. J. T.; Waring, L.; Bostock, T.; McDonald, M. P. *J. Chem. Soc., Faraday Trans. 1* **1983**, *79*, 975. (b) Bleasdale, T. A.; Tiddy, G. J. T. *NATO ASI Ser., Ser. C* **1990**, *324*, 397. (c) Strey, R.; Schomaker, R.; Roux, D.; Nallet, F.; Olsson, U. *J. Chem. Soc., Faraday Trans.* **1990**, *86*, 2253. (d) Lang, J. C.; Morgan, R. D. *J. Chem. Phys.* **1980**, *73*, 5849.

by $C_{12}E_3$ and occurs on slightly more hydrophilic substrates. As in the trisiloxane case, increasing the hydrophilic tail length results in an increased sensitivity to surface energy, particularly on the hydrophobic side. The peak in spreading rate is not simply shifted to more hydrophilic substrates. Furthermore, no maxima in rate vs concentration could be resolved. The highest concentrations yield the highest rates. However, the high concentration experiments were hindered by the observation of macroscopic phase separation in the micropipet tip and may not be entirely accurate. Such rapid phase separation was not observed in any of the other mixtures examined.

The aqueous mixtures of $C_{12}E_5$ at the concentrations studied are nonturbid, due to the enhanced solubility associated with the longer hydrophile. Even though the maximal rates are lower than those exhibited by $C_{12}E_3/H_2O$ or $C_{12}E_4/H_2O$ mixtures, these dodecyl ethoxylate solutions do exhibit surfactant-enhanced spreading (Figure 7c). In fact the maximum spreading rate observed for $C_{12}E_5$ (≈ 9 mm^2/s at $\cos\theta \approx 0.85$) is roughly twice that observed for $M(D'E_8OH)M$ on Parafilm. Once again, a maximum in rate as a function of concentration is observed. The spreading of these solutions on lower energy surfaces appears to be strongly disfavored relative to the $C_{12}E_3$ or $C_{12}E_4$ data, however, and the maxima in rate vs surface energy is further shifted toward hydrophilic substrates. These trends are qualitatively very similar to the behavior exhibited by the $M(D'E_nOH)M$, $n = 4, 8, 12$, mixtures. For a given hydrophobic group, increasing the length of the poly(oxyethylene) hydrophile inhibits spreading on low energy surfaces. The maxima in rate vs surface energy become correspondingly sharper as the spreading becomes more surface selective with increasing n. These results also demonstrate that, as in the case of the trisiloxane mixtures, turbidity is not critical to the observation of surfactant-enhanced spreading of aqueous mixtures of ethoxylated dodecyl surfactants.

Spreading of SDS/H_2O and DTAB/H_2O Mixtures. The spreading of conventional ionic surfactants was also studied on the mixed monolayer modified surfaces and on Parafilm. Concentrations well above, near, and well below the respective critical micelle concentrations were investigated ($\text{cmc}_{\text{SDS}} = 8.4 \times 10^{-3}$ mol/L, $\text{cmc}_{\text{DTAB}} = 0.065$ mol/L). These mixtures were not visibly turbid. Neither cationic DTAB nor anionic SDS solutions spread on Parafilm. In fact, limited spreading of these solutions (<2 mm^2/s) was observed to occur only on the most hydrophilic surfaces ($\cos\theta \geq 0.85$). No maxima in rate vs surface energy could be resolved, the most rapid spreading occurred on the most hydrophilic test substrate. Both compounds appeared to display weak maxima in rate vs concentration at concentrations near their respective cms's. The rates were somewhat difficult to determine, however, since the area vs time curves increased less than linearly and exhibited significant negative curvature as these solutions often did not wet the entire surface. Therefore, since they were determined from the portion of the event when spreading was apparent, the rates obtained probably represent considerable overestimations. The poor spreading rates, lack of a maximum in rate vs surface energy, and nonlinear area vs time curves suggest that these compounds do not promote significant surfactant-enhanced spreading of the type exhibited by the trisiloxane and ethoxylated dodecyl mixtures. Because the $C_{12}E_n$ ($n = 3, 4, 5$) data eliminate the uniqueness of the trisiloxane hydrophobe, this distinction is likely to be related to the physical and chemical nature of the hydrophilic portion of the surfactant.

Summary

We have developed a simple video-based technique to study the dynamics of wetting. The spreading rate of aqueous mixtures of a number of surfactants has been investigated, primarily as a function of surfactant concentration and substrate surface energy but also of temperature, humidity, and substrate roughness. These new data greatly extend the previously obtained results and do not support some of the prior conclusions. It is now apparent that the observed "superspreading" of trisiloxane surfactant mixtures is a particular example of a much larger set of phenomena which we have termed surfactant-enhanced spreading. Characteristics of surfactant-enhanced spreading include very rapid wetting of fairly hydrophobic substrates, highly linear wetted area vs time curves, a maximum in spreading rate on surfaces of intermediate hydrophobicity, and often a maximum in spreading rate as a function of surfactant concentration. The enhanced wetting ability of trisiloxane mixtures was previously related to their turbidity (biphasic character). However, in the present study, clear solutions of $M(D'E_{12}OH)M$ were observed to effectively wet substrates with slightly higher surface energies than those previously investigated. The existence of a dispersed surfactant-rich phase is therefore not critical to the observation of surfactant-enhanced spreading. Additional experiments as a function of temperature and surfactant structure have also demonstrated that the enhanced spreading of the trisiloxane compounds depends only weakly on specific supramolecular microstructure (i.e., micells vs L_3 phase vs L_α phase). Moreover, the nonionic ethoxylated dodecyl surfactants ($C_{12}E_n$, $n = 3, 4, 5$) were also observed to greatly enhance the spreading rates of aqueous mixtures, albeit on more hydrophilic surfaces than the trisiloxanes. Surfactant-enhanced spreading is therefore not unique to the siloxane compounds. There is a marked similarity in the spreading rate dependence on hydrophile length for these two types of surfactants. Increased hydrophile length results in poorer spreading on hydrophobic surfaces, shifting the peak in spreading rate vs substrate surface energy to correspondingly higher surface energies. Not all surfactants promote significantly enhanced spreading, however, as neither anionic SDS nor cationic DTAB wet the test substrates effectively. This result further demonstrates the importance of the hydrophilic portion of the surfactant to the observation of enhanced spreading. Uniformly higher spreading rates were obtained on rough substrates. The rate dependence on humidity was, however, found to be negligible on the mixed monolayer modified substrates tested. While these results demonstrate "superspreading" to be a particular example of the more general class of surfactant-enhanced spreading, the trisiloxane surfactant dispersions remain remarkable for their ability to rapidly wet even very hydrophobic substrates.

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