# Spontaneous Spreading of Emulsions on Solid Surfaces: Morphology and Dynamics

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**ABSTRACT:** The spontaneous spreading of emulsions of water dispersed in silicone oil onto glass surfaces is examined using differential interference contrast (DIC) microscopy. Spreading occurs via a precursor film from which the emulsion droplets are excluded. The radius of the interline of the bulk drop is found to vary as $(\text{time})^{1/10}$, as is commonly observed for the spontaneous spreading of pure liquids. The spreading rate constant decreases linearly with the volume percent of the dispersed phase, but drops suddenly to zero at approximately 73% dispersed phase. The width and spreading rate of the precursor film also is found to decrease with dispersed phase concentration. A fingering type of instability is evident at the leading edge of the precursor film, yet has little effect on the spreading rate of either the precursor film or the droplet interline. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 1817–1825, 2001

**Key words:** spontaneous spreading; spreading kinetics; emulsions; precursor film; Tanner's law; fingering instability

## INTRODUCTION

In most of their applications, emulsions are to be spread over a given solid surface. Examples include cosmetics and topical medicinal preparations (skin), agricultural sprays (plant surfaces), inks (paper and other print media), polishes and protectants (wood surfaces), etc.[1] In some cases, the spreading is facilitated by mechanical action of various kinds (brushes, coaters, etc.), but in others, one is dependent on spontaneous spreading alone.[2] Even when forced spreading is used, one often depends on spontaneous spreading for the formation of the final uniform coating. Although considerable attention has been given to the spontaneous spreading of pure liquids on solid substrates, little attention has been given to the spreading of emulsions. It might be anticipated that both the dynamics and the morphology of the spreading of emulsions may differ from that of single-phase liquids.

The thermodynamic driving force for the spontaneous spreading of a liquid over a solid surface is the spreading coefficient ($S$), defined as the difference between $\sigma_{sg}$, the surface free energy of the solid/gas interface and ($\sigma_{1g} + \sigma_{s1}$), the sum of the liquid surface tension and the free energy of the solid/liquid interface,[3] viz.:

$$S = \sigma_{sg} - (\sigma_{1g} + \sigma_{s1}). \tag{1}$$

The solid interface free energies are not directly measurable, but their difference is related to the equilibrium contact angle ($\theta$) by Young's equation:
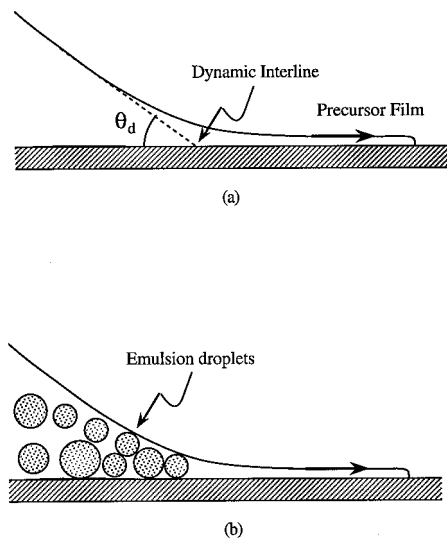
**Figure 1** Spontaneous spreading of a liquid on a solid surface: (a) Pure liquid, showing the precursor film, the location of the dynamic interline and the dynamic contact angle, $\theta_d$; (b) Emulsion, showing dispersed phase droplets trapped behind the interline.

$$\cos\theta = \frac{\sigma_{sg} - \sigma_{s1}}{\sigma_{1g}}. \tag{2}$$

Substitution of eq. (2) into eq. (1) gives

$$S = \sigma_{1g}(\cos\theta - 1), \tag{3}$$

which shows that a necessary condition for the spreading coefficient to be positive is for the contact angle to be zero.

When $S$ is positive, spontaneous spreading is known to occur through the agency of a precursor "foot" or film,[4] as pictured in Figure 1(a). It moves out in advance of the observed dynamic contact line by as much as several mm, and is generally, no more than a few nanometers in thickness. As spreading of the main body of liquid proceeds, the dynamic contact angle, $\theta_d$, decreases to zero. Both theoretical and empirical studies of this rate process have been reported.[5–10] One of the most often-used results is what is now commonly known as Tanner's Law,[11] obtained from the hydrodynamic analysis of steady-state forced spreading of Newtonian liquids. A similar result has also been reported by Voinov.[12] It takes the form:

$$\theta_d^3 \propto Ca = \left(\frac{\mu U}{\sigma}\right), \tag{4}$$

where $\mu$ is the liquid viscosity, $U$ is the linear interline velocity, $\sigma$ is the surface tension of the liquid, and $Ca$ is the (dimensionless) Capillary Number, representing the ratio of viscous to surface tension forces. Equation (4) is in good agreement with the well-known earlier data of Hoffman[13] for the steady forced movement of silicone oils in glass capillaries, for the case of $Ca \leq 0.1$, and may more properly be named the Hoffman-Voinov-Tanner (HVT) Law.[9] If the spreading liquid is in the form of a spherical cap, and $\theta_d$ is small ($\ll \pi/2$), it can readily be shown that the radius ($r$) of the spreading drop varies in accord with a 1/10th power law:[14]

$$r(t) \propto t^{1/10}, \tag{5}$$

where the coefficient is dependent upon the original drop size, but is independent of the magnitude of the spreading coefficient, provided it is positive. The latter puzzling observation has been rationalized by de Gennes,[14] who showed that the thermodynamic driving force represented by the spreading coefficient is consumed entirely by viscous dissipation in the precursor film. Experimental accord with eq. (5) has ample documentation in the literature for cases in which the interline region is free of temperature or composition gradients (which lead to complicating Marangoni effects).

If the spreading liquid of interest is an emulsion containing dispersed-phase droplets larger than the thickness of the precursor film, it may be speculated that the nature of the spreading process should differ markedly from that described by the HVT or 1/10th power laws. As pictured in Figure 1(b), the droplets of the emulsion in such a case would be sieved out of the advancing precursor film and concentrated inside the droplet in the region just behind the advancing interline. It might be expected that the rate of interline advance could be significantly reduced from that to be observed by the continuous phase liquid alone, and should be dependent upon the droplet concentration in the emulsion. Under these circumstances, it is not evident that the HVT spreading law should necessarily be observed.

The objective of the present study was to perform a preliminary experimental investigation of the spreading of a given model emulsion onto a smooth, horizontal glass surface. It was in particular desired to determine the influence of droplet volume fraction on the spreading dynamics and

morphology. For this purpose, W/O emulsions of varying water volume fractions were prepared with pure water dispersed in a silicone oil and stabilized using a silicone-based emulsifier. These liquids were allowed to spread as spherical caps on smooth, horizontal glass surfaces as they were observed and recorded using optical video microscopy.

## MATERIALS AND METHODS

### Sample Preparation

The chemicals used to prepare the W/O emulsions were Dow Corning 245 fluid (DC-245), Dow Corning 5225C formulation aid (DC-5225C), and triply-distilled water. DC-245 is a pure silicone oil, while DC-5225C is silicone oil with 10% emulsifying surfactant. All emulsion samples were prepared such that the total liquid volume added was 150 mL, and the final surfactant content was 2% v/v. Consequently, to each sample, 30 mL of DC-5225C was added to all samples, while the volumes of the DC-245 and water were varied to obtain variable dispersed phase concentrations. The water contents prepared were 0, 10, 20, 30, 40, 50, 60, 70, 72, 73, 74, 75, and 80%.

The oil phase for each case studied was first prepared by mixing the appropriate volumes of DC-245 and DC-5225C. The desired amount of water was then added to the oil, contained in a 400-mL beaker and continually mixed using a ViTris 23 mixer at 1200 RPM, in 0.5 mL increments. After each increment of water was added, the beaker was manually moved around the mixing blades at least five times, with the inner wall of the beaker in constant contact with the mixing blades to ensure that all the water was dispersed into silicone oil without the formation of pockets at the edges of the beaker wall. Once all the water was added, the emulsion was further mixed for as long as it had taken to add the water increments to the silicone oil; typically, this resulted in mixing the sample for an additional 30 to 45 min. Once the emulsion samples were completely mixed, they were transferred and stored in 4-oz. glass sample bottles. It was found that the emulsions prepared as above would slowly break down, but just a small amount of mixing would restabilize them. Consequently, before any sample was used in a spreading experiment, its contents were remixed for 2 min with the ViTris 23 mixer at a speed of 1200 rpm.

### Spreading Observations

A Nikon TE200 inverted microscope, equipped with a Nikon ELWD 40X/0.60 Ph2 DM lens and a Nikon 10X/22 eyepiece was used to observe the spreading of the samples. For all observations, the microscope was set to the Differential Interference Contrast (DIM) mode[15] by using a Nikon LWD condenser set to "M." The DIC phase was employed because it alone could effectively show the contrast between the silicone oil and the dispersed aqueous droplets. The spreading of all emulsions were observed on clean 25 mm$^2$ Corning No. 1 cover glass slides, onto which a single emulsion droplet would be deposited using a 50-$\mu$L Hamilton syringe. To ensure that the height and angle from which the droplets were deposited always remained the same, a ring stand and ring clamp system was used to hold the syringe. The height of the syringe tip above the slide was measured for each run to ensure that it remained constant.

The spreading process was recorded using a Sony SVHS Hi-Fi VCR, which received the imaging signal from a C2400 Hamamatsu CCD camera connected between the objective lens and the eyepiece. From the VCR, the imaging signal was sent to an 11″ Sony monitor, allowing immediate viewing of what was being recorded. To initiate a run, the VCR was set to RECORD, and the syringe was gently pressed until a single drop was administered to the slide. The platform of the microscope was then adjusted until the leading edge of the emulsion droplets (compacted against the advancing interline) was moving left with no apparent vertical shift. The droplet front was then observed as it moved across the screen. Once the leading edge of the emulsion droplets reached the left edge of the monitor screen, the platform was quickly adjusted so that the leading edge of the droplets was back at the far right edge of the monitor. This process was repeated until the movement of the leading edge became negligible, and the VCR was stopped. The drop on the slide was visually inspected to determine if it had spread in a circular manner. The slide was then discarded and a new slide placed above the objective lens for the start of a new run.

The observed direction that the emulsions spread (left) was chosen arbitrarily. It was assumed that if the drops appeared to spread in a circular manner, the displacement in all directions would be the same. To verify this assumption, initial test runs were made in other direc-
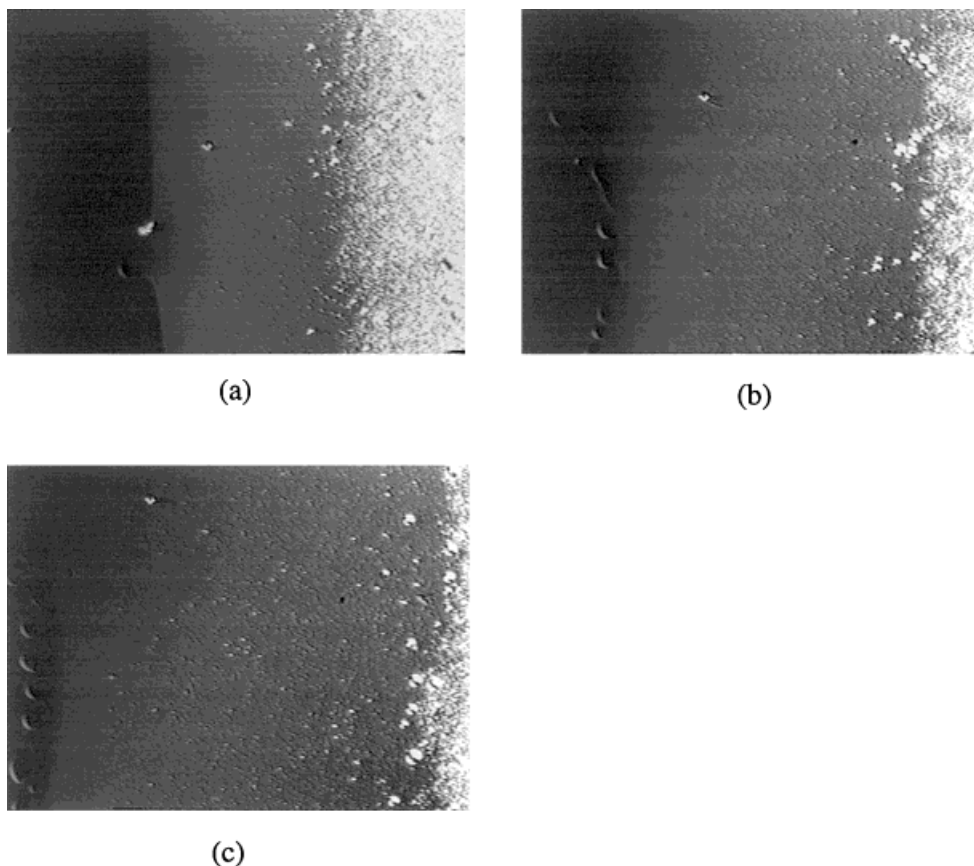
**Figure 2**    Photographs of spreading silicone emulsions containing 20% v/v dispersed phase (water) droplets (view shown: $370 \times 500 \; \mu$m) after (a) 30 s, (b) 1 min, (c) 2 min.

tions. The results of these runs showed that as long as the drops appeared circular, there was no distinguishable difference in the measured displacement of the drop in different directions. Consequently, the spreading direction of all the samples run was to the left.

### Data Acquisition and Analysis

The recorded VCR tapes were analyzed off-line using a 25-inch Sharp television and VCR, from whose screen length measurements were taken directly. For each run recorded, a Sportline Alpha 470 100 Mem Stopwatch was used to obtain the relevant time data. First, the VCR was set to PLAY at the specified start time for the given run, and the stopwatch was started. The moment that the liquid drop was observed contacting the slide, the lap timer button was pressed. Once the microscope platform was fully adjusted so that the leading edge was appropriately set on the screen, the lap timer was again pressed as the leading edge passed the next tick mark on a precalibrated scale on the screen. Each time the leading edge of the emulsion droplets passed subsequent tick marks, the lap timer was pressed. Typically, the emulsions would move rapidly at first so that 4″ tick marks were used between subsequent times. However, as the liquid slowed down, the lap timer was pressed each time the liquid traveled 2″, and still later, it was pressed after the liquid was displaced by only 1″ on the screen.

Once a run had been completed, the VCR was stopped. The times were then recalled from the lap timer memory and entered into a spreadsheet. The first lap time in the stopwatch actually corresponded to the time that the emulsion drop hit the slide. From the perspective of spreading times, the time that the drop contacted the slide should be time zero. Consequently, the first lap time was subtracted from all the other times recorded. The second lap time was the time at which the leading edge displacement measurements were started. It is important to note that the initial distance traveled by the leading edge be-
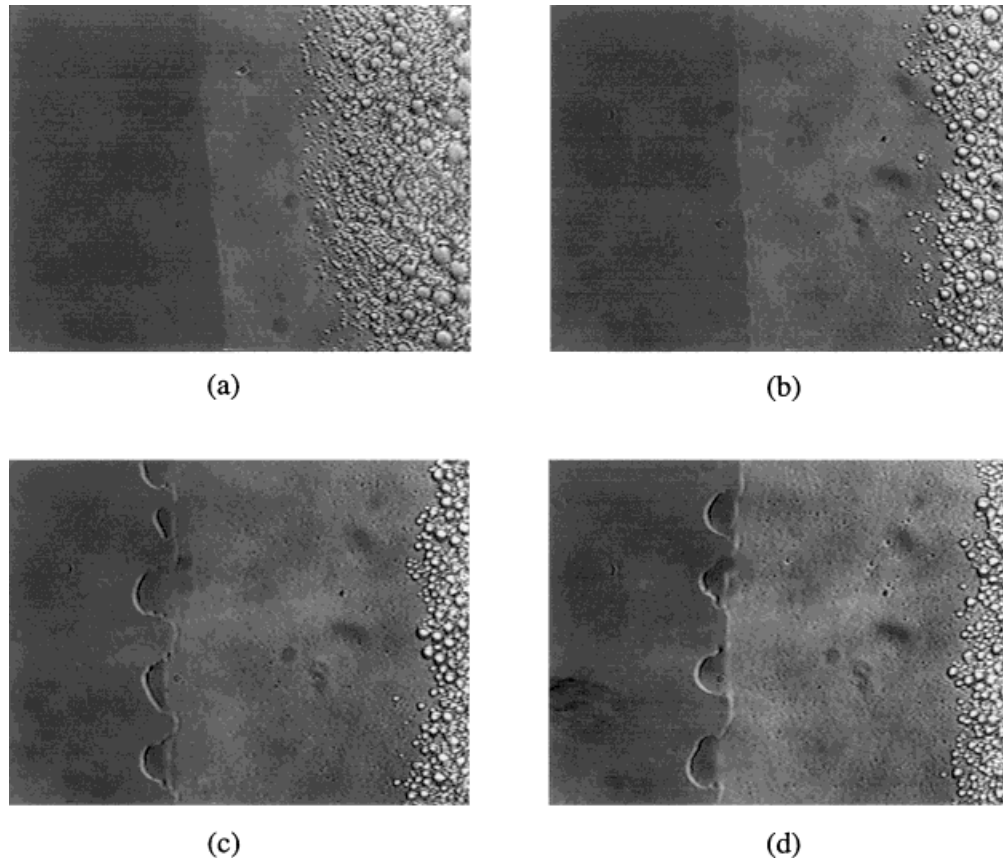
**Figure 3**  Photographs of spreading silicone emulsions containing 40% v/v dispersed phase (water) droplets (view shown: $370 \times 500$ $\mu$m) after (a) 30 s, (b) 1 min, (c) 2 min, (d) 3 min.

tween the drop contacting the slide and the second lap time was unknown. This distance was extrapolated by assuming that the initial displacement of the liquid was linear. In so doing, the first three to five data points, depending on the consistency in the data, were used to calculate the initial least squares linear trend line. In so doing, the initial displacement was determined from the extrapolation of the trend line back to time zero. In essence, the absolute value of the calculated intercept represented the initial distance displaced by the leading edge of the emulsion. The distance traveled between time measurements was also entered into the spreadsheet. For most samples, the initial displacement was approximately 4″. The screen monitor lengths were converted to actual distances using the preset calibration. The determined displacements were then consecutively added on to the initial extrapolated displacement to obtain the total distance traveled up to any specified time.

In addition to observing the spreading behavior of the leading edge of the bulk emulsion, it was also of interest to observe the spreading behavior of the precursor foot. The same video footage was used to analyze the precursor foot as was used to determine the spreading characteristics of the bulk emulsion. In analyzing the precursor foot, the video was played, and the VCR timing was reset to zero the instant that the droplet contacted the slide. Then, at various time intervals, the tape was paused, and the width of the precursor foot was measured.

For each water content, three to six individual runs were made in which all of the above-mentioned data were recorded.

## RESULTS

The photographic results in all cases, as illustrated in Figures 2–5, for the spreading of emulsions containing 20, 40, 60, and 70% v/v dispersed phase, respectively, show the spreading of a precursor film ahead of the main droplet interline, which is clearly demarcated by the trapped drop-
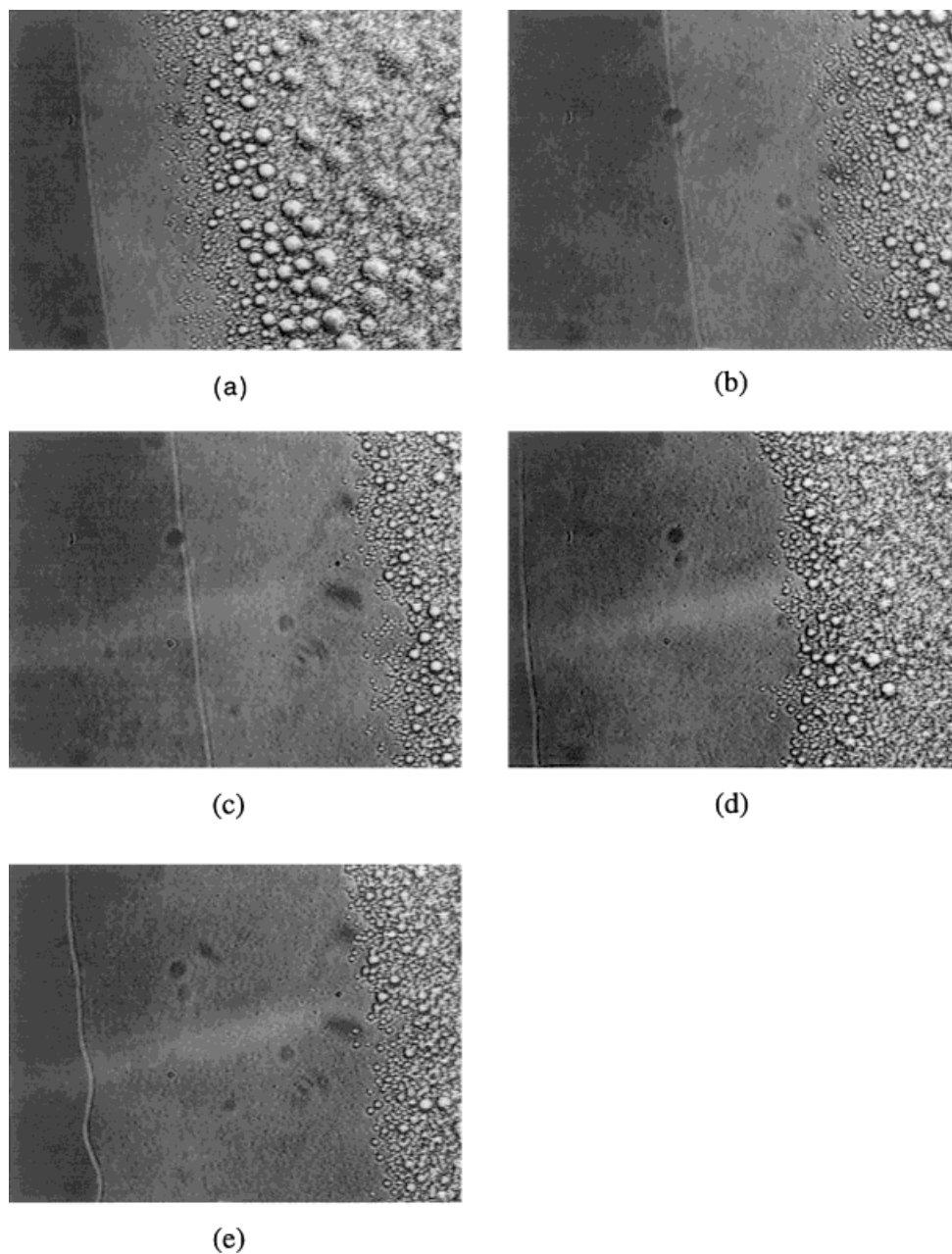
**Figure 4** Photographs of spreading silicone emulsions containing 60% v/v dispersed phase (water) droplets (view shown: $370 \times 500$ $\mu$m) after (a) 30 s, (b) 1 min, (c) 2 min, (d) 3 min, (e) 4 min.

lets. Smaller droplets are at the leading edge of this demarcation, because they are able to fit into the narrow wedge of liquid there. The width of the precursor film increased with time, but more slowly as the drop concentration increased. In most of the cases observed, a fingering type of instability was evident at the leading edge of the precursor film. Figure 4 illustrates one of the rare instances when fingering was not observed.

Whether present or absent, the fingering appeared to have little effect on the spreading rate, either of the precursor film or the droplet interline.

An example data set showing the relative interline position as a function of time for emulsions of various volume fractions of dispersed phase is presented in Figure 6. It shows that as the water droplet content of the emulsions increased, the
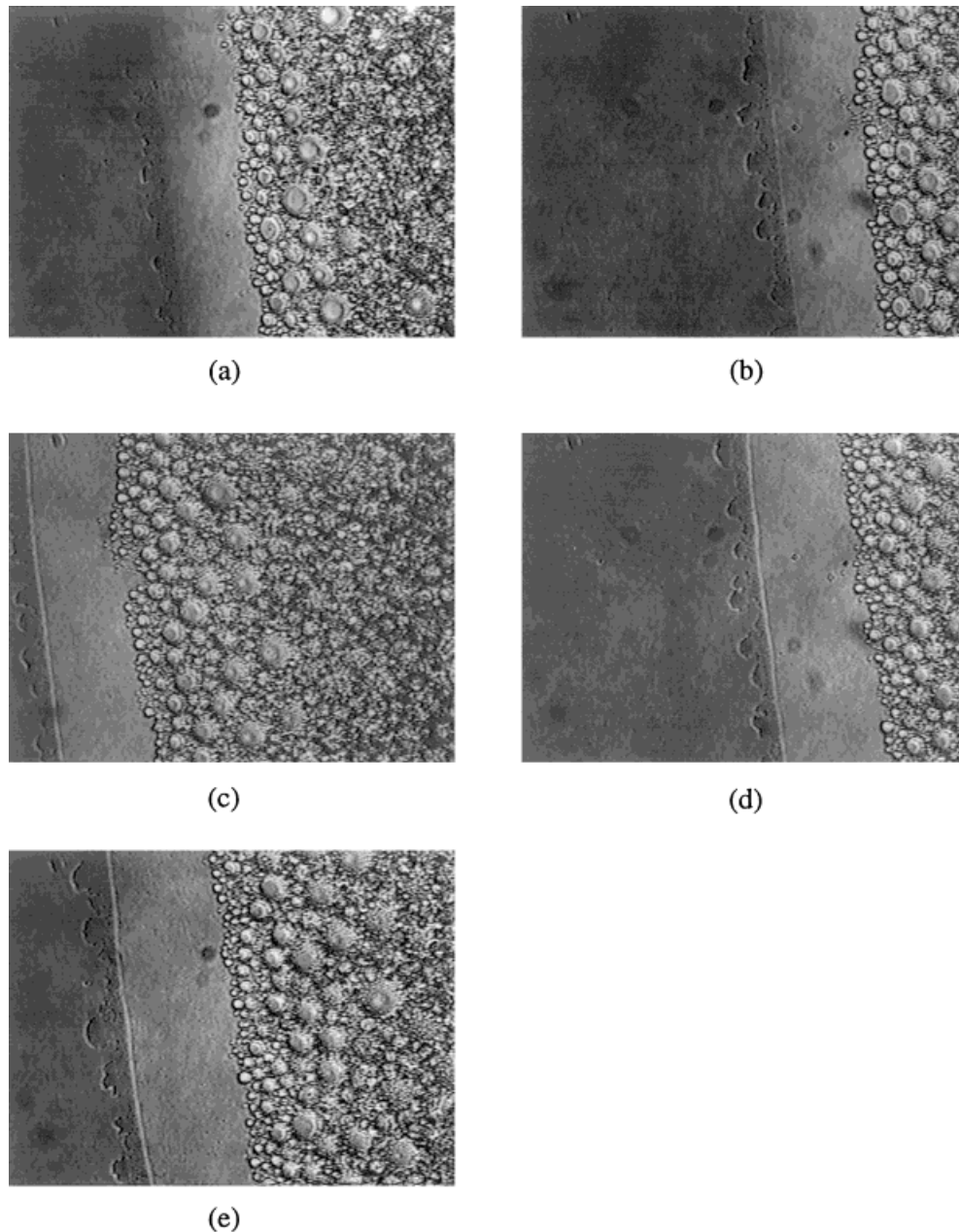
**Figure 5** Photographs of spreading silicone emulsions containing 70% v/v dispersed phase (water) droplets (view shown: $370 \times 500$ $\mu$m) after (a) 30 s, (b) 1 min, (c) 2 min, (d) 3 min, (e) 4 min.

spreading rate of the emulsion decreased more rapidly. It is also seen that greater water loads produced emulsions that asymptoted to somewhat shorter total displacements. Plotting the data against the 1/10th power of time, as shown in Figure 7, resulted in good straight lines in all cases, in agreement with the HVT Law.

As the water droplet content of the emulsions was increased, the slopes of the curves in Figure 7

decrease, indicating a decrease in the spreading rate constant. A crossplot of the spreading rate constants (slopes) as a function of the water content is shown in Figure 8. The spreading rate constant for each water concentration was determined by taking the mean of the calculated spreading rate constants from the individual runs, and the standard deviation in each case yielded the error bars. It appears that the pres-
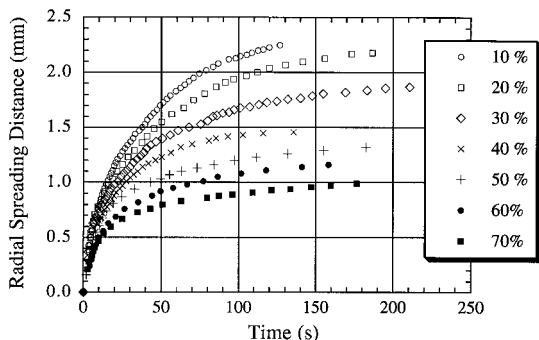
**Figure 6**   Radial spreading distance of the emulsion interline as a function of time for different concentrations of the dispersed (water) phase.



**Figure 8**   Spreading rate constant as a function of the dispersed phase (water) droplets.

ence of the water droplets trapped behind the spreading interline had a retarding effect on the flow of the continuous phase (silicone oil) out into the precursor film, and resulted, therefore, in a decrease in the rate of advance of the interline. Up to a water content of 73%, the spreading rate constant decreased in a nearly linear fashion with the water droplet concentration. However, when it reached approximately 73%, spontaneous spreading of the emulsion was completely halted, giving a spreading rate constant of zero beyond this concentration. It may be noted that this volume fraction is close to that corresponding to the maximum packing density (74%) of uniform spheres. In such a case, further outflow of continuous-phase liquid would then meet with the additional resistance of deforming the spherical shape of the dispersed-phase droplets to allow for denser packing. This may have been sufficient to prevent further spreading.
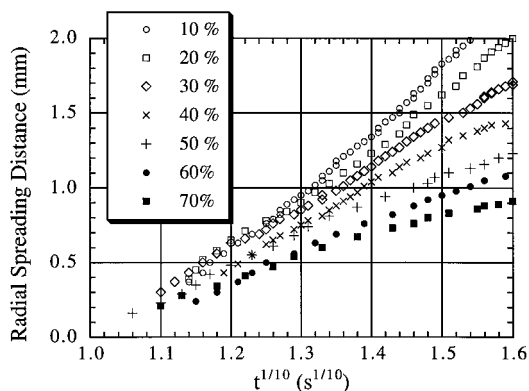
Figure 9 shows results for the precursor foot width as a function of time for various water concentrations. The change in the precursor film width appeared to be linear for all water contents, meaning that the rate of change in the width remained constant for all water concentrations. This result suggests that the spreading rate law that applies to the leading edge of the precursor foot is the same as the spreading rate law for the bulk emulsion, i.e., the leading edge of the precursor film obeys a 1/10th power law as well. Even though the spreading rate laws are the same, however, the constant of proportionality for the edge of the precursor film is greater than that of the droplet interline, because its width increases with time. A crossplot of the rate of change in the precursor foot width as a function of the water content is presented in Figure 10. Again, the rate of change in the precursor film width was calculated for each water content from the mean of the results of the multiple runs, and the error bars



**Figure 7**   Radial spreading distance plotted against the 1/10th power of time for different concentrations of the dispersed phase (water) droplets.
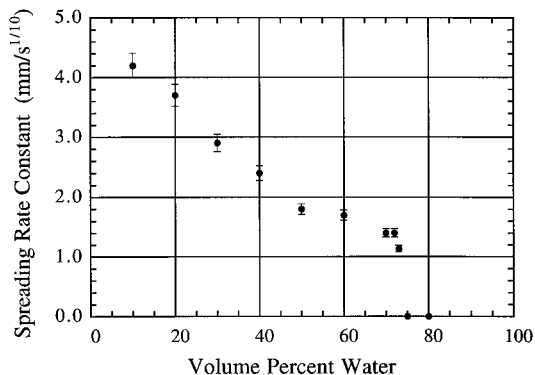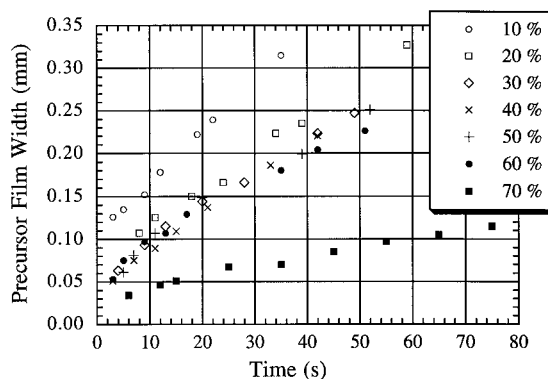


**Figure 9**   Precursor film width as a function of time for different concentrations of the dispersed phase (water) droplets.
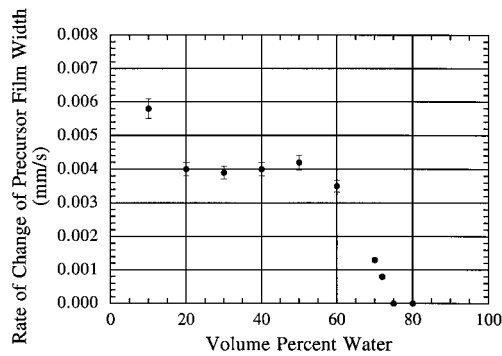
**Figure 10**   Rate of change of the precursor film width as a function of the dispersed phase (water) droplets.

from their standard deviations. For very low water concentrations, the rate of change in the precursor film width was relatively high; for water concentrations between 20 and nearly 60%, the rate of change remained essentially constant, but for greater water contents, the rate of change in film width rapidly decreased.

## CONCLUSIONS

The spontaneous spreading of emulsions on solid surfaces was examined optically using differential interference contrast (DIC) microscopy. For the water-in-silicone-oil emulsions investigated, spontaneous spreading of circular droplets onto smooth glass surfaces followed the format of the 1/10th power law (consistent for this geometry with the Hoffman-Voinov-Tanner law for the dependence of dynamic contact angle on the Capillary number) observed by many earlier investigators of the spontaneous and steady, forced spreading of pure liquids on solid substrates. The spreading displayed the presence of a precursor film, whose extent was clearly demarcated by trapped water droplets behind the advancing interline. Nearly all of the dispersed phase (water) droplets in the emulsion were excluded from the precursor film, suggesting that their diameters were larger than the thickness of this film. The spreading rate constant decreased linearly with the volume fraction of the water droplets in the emulsion, and dropped suddenly to zero at a volume fraction of approximately 73%. The position

of the leading edge of the precursor film was also found to obey the format of the 1/10th power law, but with spreading rate constants larger than the corresponding values for the droplet interline, the divergence in values being largest for the lowest dispersed phase volume fractions. For high concentrations of dispersed phase, a small precursor film was formed instantly and retained a nearly constant width throughout the spreading. In most (but not all) cases, a fingering type of instability was observed at the leading edge of the precursor film, but its presence had little effect on the spreading dynamics.

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