

# The spreading of oil on water in the surface-tension regime

By DAVID W. CAMP AND JOHN C. BERG

Department of Chemical Engineering, University of Washington, Seattle, WA 98195, USA

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Data which describe the unidirectional spreading of several pure oils and oil-surfactant mixtures on water in the surface-tension regime are reported. Leading-edge position and profiles of velocity, thickness and film tension are given as functions of time. The data are consistent with the numerical similarity solution of Foda & Cox (1980), although the measured dependence of the film tension on the film thickness often differs from the equilibrium relationship. The configuration of the oil film near the spreading origin may be either a coherent multimolecular layer or a multitude of thinning, outward-moving lenses surrounded by monolayer. The pure oils show an acceleration zone connecting the slow-moving inner region to a fast-moving outer region, while the oil-surfactant mixtures show a much more gradual increase in film velocity.

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## 1. Introduction

A quantity of oil placed upon a water surface will spread out by surface-tension forces if the spreading coefficient,  $S$ , is positive. This is the net surface tension available to drive the spreading,

$$S = \sigma_w - \sigma_f^0 \quad (1.1)$$

where  $\sigma_f^0$  is the total tension of the oil film at the spreading origin. In the past,  $\sigma_f^0$  has always been assumed to equal  $\sigma_o + \sigma_{ow}$ , the sum of the oil-air and oil-water tensions. If the deposited volume is small enough, gravity will not be an important spreading force, and the dominant resistance to spreading will be the viscous drag exerted on the oil film by the underlying water.

Many oils, including the heavier hydrocarbons, have negative spreading coefficients and will not spread on water. They will spread, however, if they contain a sufficient concentration,  $C$ , of surfactant, which reduces  $\sigma_{ow}$  to the extent that  $S$  becomes positive. These surfactant-oil mixtures are of great practical interest since most crude or commercial oils contain at least traces of surface active materials. In many commercial processes, the spreadability of an oil in the surface-tension regime can be controlled as desired by adding or removing surfactant.

The spreading of oil on water has been a subject of interest since ancient Phoenician navigators were reported to have used the process to damp waves in the sea. Interest continues today as we seek to understand and to cope with the threat of oil spills from tankers and other craft. While the overall spreading of large oil masses is driven chiefly by gravity, the morphology of the spread near the leading edge and over the entire covered area in the terminal stages of spreading is strongly affected by surface

† Present address: Lawrence Livermore Laboratories, Livermore, CA, USA.

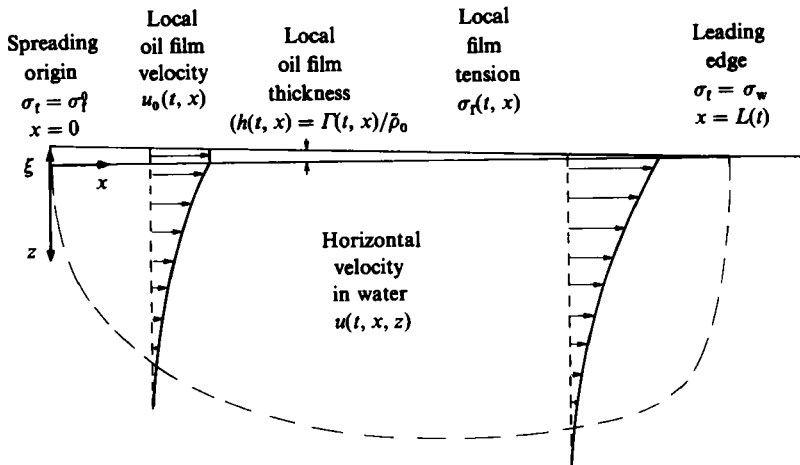


FIGURE 1. Spreading of an oil film on water due to surface tension. The  $Z$ -scale has been expanded to show detail in the water phase.

forces. Other situations, in which the spreading of smaller oil masses is important, include the casting of membranes from spread films, the deployment of antifoams, the elimination of pigment flotation (Bénard cells) from drying paint films and the fighting of liquid fuel fires by spreading oils which smother the flames.

For most of the above processes, it would be desirable to know several features of the expected spreading behaviour of a given oil, as shown in figure 1. First is the position of the leading edge as a function of time,  $L(t)$ . This in turn depends on the value of the spreading coefficient  $S$  over the entire area of the spread. Second are the velocity and thickness of the oil film as functions of time and position,  $u_0(t, x)$  and  $h(t, x)$ , respectively. These will describe the volumetric rate of oil transport. Knowledge of  $S(t, x)$  requires the film-tension profile,  $\sigma_f(t, x)$ .

Most earlier studies have focused only upon the leading-edge position,  $L(t)$ , but any analysis of the process free of *ad hoc* assumptions must be able to predict all of the internal characteristics above. Conversely, any experimental study capable of verifying such an analysis must include measurements of all the internal variables. The present work addresses itself to such an investigation.

The recent analysis of Foda & Cox (1980), extending the work of DiPietro, Huh & Cox (1978), describes the unidirectional spreading of oils in the surface-tension regime assuming only that the oil is pure, insoluble and non-volatile, the film remains coherent from the spreading origin to the leading edge, the spreading film itself moves in plug flow, and the equilibrium constitutive relationship between the film tension and the film thickness holds during the spreading process. A similarity solution was found numerically eliminating time from the governing equations and boundary conditions. It yielded  $L(t)$  and, together with an independently-measured constitutive equation, the velocity profile of the film,  $u_0(t, x)$ . The determination of the constitutive equation yielded the dependence of the film tension on relative changes in film thickness, but did not permit computation of the actual thickness profile,  $h(t, x)$ . The film tension profile was not computed. The experiment, using a 1000 cs silicone oil, showed good agreement with respect to the leading-edge location, but less convincing agreement with respect to the velocity profile. The profile was measured by tracking the motion of talc particles deposited on the surface during spreading. From the motion picture record, the locations of the tracer particles were noted every one or

two seconds (a very large spacing) and plotted as  $x$  vs.  $t$ . Smooth curves through the widely-spaced points were drawn for each particle. The scaled slope of these smooth curves at various dimensionless locations did not appear to depend on time explicitly, in agreement with the similarity solution. From the plot of the original  $x, t$  data in Foda & Cox (1977), the local velocity data were re-computed (Camp 1985) and found to suggest that for  $t < 4$  s, the scaled velocity profile does depend upon time (in contradiction to the similarity transformation), and that the velocity profiles contain a fairly sharp change at some value of scaled position (increasing with  $t$ ), something not predicted by the numerical calculations. These observations suggest the need for further experimentation.

The present work seeks specifically to perform unidirectional spreading experiments with a variety of pure oils and oil-surfactant mixtures and to compare the results with the analysis of Foda & Cox. All of the internal variables are to be measured, including the previously unmeasured film tension profile during spreading. Comparison of the measured film tension profile with that which is predicted using the equilibrium constitutive equation should validate or refute the appropriateness of using the equilibrium relationship for describing the spreading dynamics. The latter may be especially inappropriate for oil-surfactant mixtures. We seek to provide any necessary extensions or modifications to the Foda & Cox analysis to render it applicable to oil-surfactant mixtures.

## 2. Governing equations

Following Foda & Cox (1980) and with reference to figure 1, the coordinate system is fixed with respect to the undisturbed water, with the origin located where the oil is deposited. At some time  $t$ , after the oil is deposited, the leading edge of the film is located at  $x = L(t)$ , with the oil having thickness and film tension profiles,  $h(t, x)$  and  $\sigma_f(t, x)$ , respectively. The oil-layer thickness is used in a material balance and is a measure of the number of moles of oil per unit surface area or surface concentration  $\Gamma$ . It is thus defined as  $h = \Gamma/\rho_o$  where  $\rho_o$  is the bulk oil molar density, a constant. This definition allows  $h$  to be used for both multi- and monomolecular films. The induced flow in the water has  $x$  and  $z$  components  $u(t, x, z)$  and  $w(t, x, z)$ .

The velocity profile in the water is governed by the unsteady boundary-layer equations

$$\frac{\partial u}{\partial t} + u \left( \frac{\partial u}{\partial x} \right) + w \left( \frac{\partial u}{\partial z} \right) = \nu_w \left( \frac{\partial^2 u}{\partial z^2} \right), \quad (2.1)$$

and

$$\frac{\partial u}{\partial x} + \frac{\partial w}{\partial z} = 0, \quad (2.2)$$

where  $\nu_w$  is the kinematic viscosity of water. The boundary conditions for the boundary-layer equations are zero velocity at great depths

$$u(t, x, \infty) = 0; \quad (2.3)$$

no vertical flow through the surface,

$$w(t, x, 0) = 0, \quad (2.4)$$

and a tangential force balance on the oil film,

$$\tau_o = -\mu_w \left( \frac{\partial u}{\partial z} \right)_{z=0} = \frac{\partial \sigma_f}{\partial x}, \quad (2.5)$$

where  $\tau_o$  is the viscous shear stress and  $\mu_w$  is the viscosity of water.

The velocity in the oil film is assumed to be uniform over its thickness,  $\xi$ . For single-component oils, Foda & Cox assumed that the equilibrium constitutive equation,

$$\sigma_f = \sigma_f(h \text{ or } \Gamma), \quad (2.6)$$

holds. For monomolecular films, this is the ' $\Pi$ -A' curve (cf. Adamson 1982), while for continuous bulk films of oil with thickness less than 1000 Å, disjoining pressure forces can cause  $\sigma_f$  to depend upon  $h$  (Sheludko 1966).

Assuming that a constitutive relation can be specified independently, the equation set is closed by relating  $h$  to the film velocity through a material balance on the oil,

$$\frac{\partial h}{\partial t} + \frac{\partial(u_0 h)}{\partial x} = 0. \quad (2.7)$$

The case of surfactant-assisted spreading has not yet been analysed. We expect that the hydrodynamic equations and boundary equations above should hold. For mixtures, however,  $\sigma_f$  might be expected to depend on interfacial composition, i.e.

$$\sigma_f = \sigma_o + \sigma_{ow}(\Gamma_{2,1}), \quad (2.8)$$

where  $\Gamma_{2,1}$  is the relative adsorption of component 2 (surfactant) at the oil-water interface. Adsorption of ordinary aqueous surfactants at the oil-air interface is thermodynamically disfavoured and therefore assumed to be zero. The possible importance of surfactant adsorption at the oil-water interface is examined in §3.

Foda & Cox eliminated the explicit dependence on time of the governing equations and boundary conditions by defining the variables:

$$\left. \begin{aligned} \bar{x} &= x\beta^{-\frac{1}{2}}t^{-\frac{3}{4}}, \\ \bar{z} &= z\nu_w^{-\frac{1}{2}}t^{-\frac{1}{4}}, \\ \bar{u} &= u\beta^{-\frac{1}{2}}t^{\frac{1}{4}}, \\ \bar{w} &= w\nu_w^{-\frac{1}{2}}t^{\frac{1}{4}}, \end{aligned} \right\} \quad (2.9)$$

where  $\beta = S/\mu_w^{\frac{1}{2}}\rho_w^{\frac{1}{2}}$ . The dependent variables become functions of  $(x, z)$  only. In addition, it was useful to define dimensionless film tension and thickness:

$$\left. \begin{aligned} \sigma^* &= (\sigma_f - \sigma_f^0)/(\sigma_w - \sigma_f), \\ h^* &= h/H, \end{aligned} \right\} \quad (2.10)$$

where  $H$  is an arbitrary thickness scale. They obtained analytical solutions for the asymptotic limits of  $\bar{x} \rightarrow \bar{L}$  and  $\bar{x} \rightarrow 0$ , and solved the equations numerically over the full range of independent variables for a limited number and type of constitutive relations.

One of the results obtained was a scaling law for the leading-edge position, viz.

$$L = k\beta^{\frac{1}{2}}t^{\frac{3}{4}}, \quad (2.11)$$

coincident with the result obtained earlier by Fay (1969) using dimensional analyses.  $k$  is a constant characteristic of the given oil, and for the constitutive equations examined by Foda & Cox, ranged between 1.36 and 1.39.

In terms of the scaled variables,  $u_0$ ,  $\sigma^*$  and  $h^*$  depend only upon  $\bar{x}$ . The solution for the limiting case of the outer edge of the advancing film ( $\bar{x} \rightarrow \bar{L}$ ) is coincident with that for the quasi-steady motion of a flat plate, independent of the constitutive

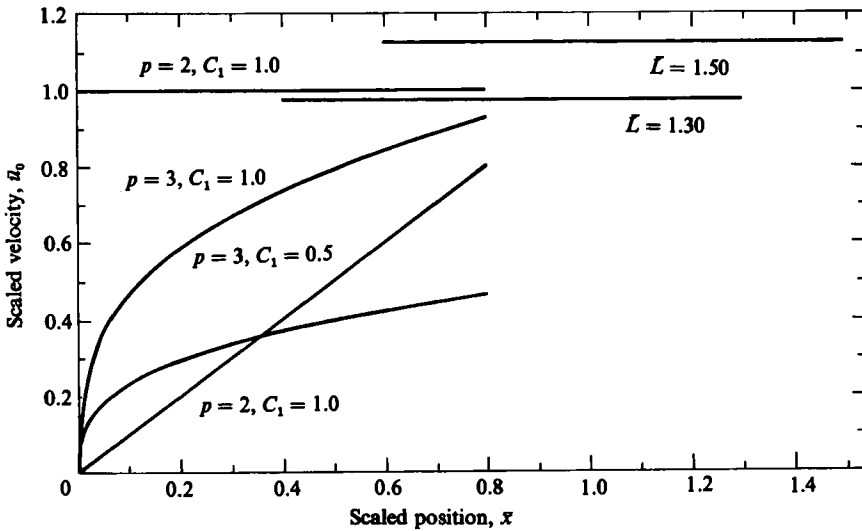


FIGURE 2. Velocity profiles given by the leading-edge and near-origin asymptotic solutions of Foda & Cox (1980) for various values of  $\bar{L}$ ,  $p$ , and  $C_1$ .

equation. The flat-plate assumption had earlier been applied to the entire film by Landt & Volmer (1926) and Huh, Inoue & Mason (1975).

The limiting solution near the spreading origin,  $\bar{x} \rightarrow 0$ , depended upon the constitutive equation which was often written in the form

$$\sigma^*(h^*) \propto (h^*)^{-p}, \tag{2.12}$$

where  $p$  is a constant. Self-consistency of the asymptotic solution required that  $p > 2$ , although there are no thermodynamic grounds for excluding smaller values of  $p$ . Closed-form solutions were provided for  $\bar{u}_0(\bar{x})$  and  $\sigma^*(\bar{x})$  to within a multiplicative constant  $C_1$ , whose value depended on the spreading behaviour over the entire film.

The two limiting solutions for  $\bar{u}_0$  and  $\sigma^*$  for various values of  $L$ ,  $p$  and  $C_1$  are shown in figures 2 and 3. Foda & Cox solved the full similarity equations numerically for  $\bar{u}_0$  for the intermediate region, between  $\bar{x} = 0.25$  and  $\bar{L} - \bar{x} = 0.1$ .

Several experimental studies of leading-edge motion for unidirectionally spreading film are reported in the literature (e.g. Landt & Volmer 1926; Garrett & Barger 1970; Huh *et al.* 1975) with  $\bar{L}$  ranging between 1.38 and 1.70. No studies of  $\bar{u}_0(x)$  have been reported except the single system examined by Foda & Cox, and thickness profiles for several radially spreading silicone oils are reported by Mar & Mason (1968). Measurement of the change in film tension during oil spreading has not been reported.

### 3. The constitutive relation for oil-surfactant mixtures

For bulk films of oil-surfactant mixtures, the film tension depends on the relative adsorption of surfactant at the oil-water interface,  $\Gamma_{2,1}$ , in accord with (2.8). We will now show that this equation reduces to the same effective constitutive relation as that for pure oils if the spreading films are sufficiently thin that diffusion maintains a vertically uniform concentration of surfactant within it. This will be the case when  $Dt/h^2 \gg 1$ , a condition easily satisfied in the present study for spreading times in excess of 0.01 s.

The adsorption isotherm required in the formation of the constitutive relation in

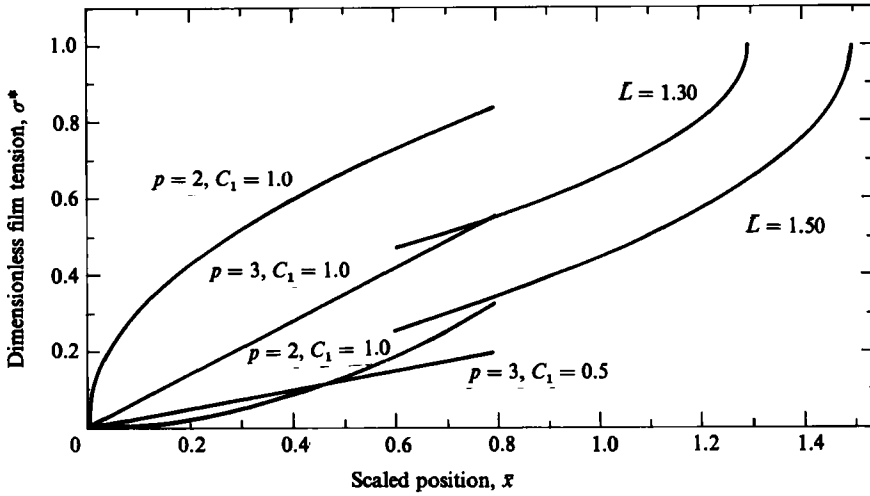


FIGURE 3. Profiles of film tension given by the leading-edge and near-origin asymptotic solutions of Foda & Cox (1980) for various values of  $L$ ,  $p$ , and  $C_1$ .

accord with (2.8) can be determined by measuring the oil (with surfactant)–water interfacial tension as a function of the concentration of surfactant in the oil, and applying the Gibbs adsorption equation:

$$\Gamma_{2,1} = \frac{-\left(\frac{d\sigma_{ow}}{d \ln C}\right)}{\left(1 + \frac{d \ln \gamma}{d \ln C}\right) RT}, \quad (3.1)$$

where  $\gamma$  is the activity coefficient of the surfactant in the oil.

Since the vertical profile of velocity in the oil film is also uniform ( $\nu_0 t/h^2 \gg 1$ ), there is no differential lateral transport of surfactant. Thus the total local concentration of surfactant, including both bulk and interface, remains unchanged from its initial value,  $C_1$ , even though the distribution of surfactant between bulk and interface may vary:

$$C_1 = C + \Gamma_{2,1}/h. \quad (3.2)$$

Combination of the interfacial tension relationship,  $\sigma_{ow} = \sigma_{ow}(C)$  with (2.8), (3.1) and (3.2) results in a constitutive equation relating the spreading tension to the effective film thickness. The existence of such a constitutive relation for oil–surfactant mixtures means that the treatment of Foda & Cox may be extended to such systems. It should be applied with caution at very small  $\sigma^*$  values (close to the origin), where the assumptions of uniform concentration and velocity profiles may break down and where (for the relatively thicker films that may exist there) the exponent  $p$  in (2.12) is generally less than 2 (Camp 1985).

#### 4. Experimental

Unidirectional spreading experiments were carried out in the apparatus shown schematically in figure 4. The Teflon trough measured  $42 \times 37 \times 5$  cm and had a black bottom for photographic purposes (Camp 1985). Up to four parallel  $42 \times 7$  cm channels (channel widths less than 3 or 4 cm exhibited excess sidewall drag) could be created by overfilling the trough to form a proud meniscus and placing Teflon bars

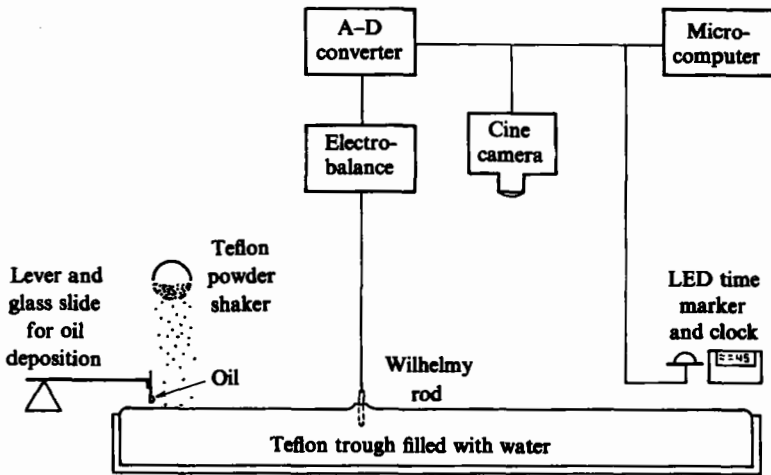


FIGURE 4. Schematic of apparatus for investigating oil spreading.

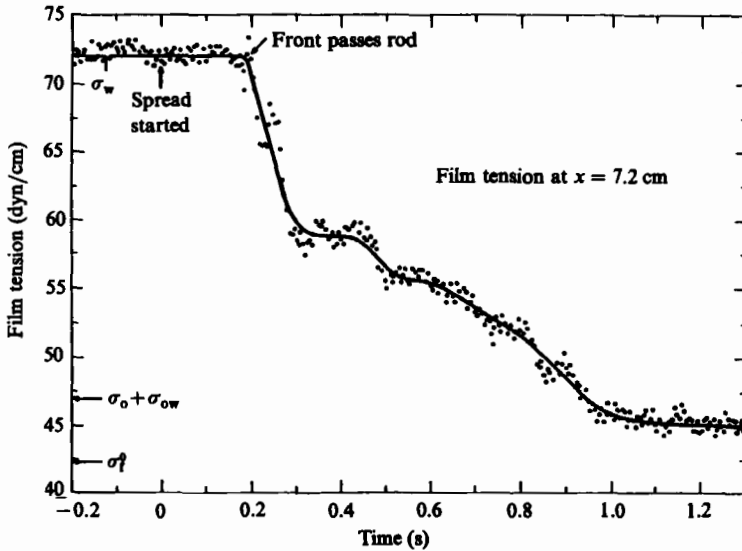


FIGURE 5. Film-tension record from one oleic acid run with the Wilhelmy rod located 7.2 cm from the origin.

across the top, 7 cm apart. The bars were also used for sweeping each channel water surface free of trace contaminants immediately before each run. The oil was distributed along the lower 2 mm of the front side of a 6.0 cm wide microscope cover glass. The spread was then started by touching the coverglass to the water and holding it there until the leading edge reached the far wall.

The progress of the spreading was followed by cine-photography at 60 frames/s. Fine Teflon particles were continuously deposited onto the surface near the origin of the spreading film. These non-wetted particles were carried along the surface, revealing its motion. Some particles were sprinkled along the entire length of the water surface before the spread was started. These were swept into a bank by the oil film, showing the leading-edge location. By reflecting light from the surface into the camera, coloured interference fringes, from which the film-thickness profile could

Oil	Source	$\sigma_o$ (dyn/cm)	$\sigma_{ow}$ (dyn/cm)	ESP† (dyn/cm)	V' (cm <sup>3</sup> )
Oleic acid (USP)	Baker (USP)	32.4	13.3	31.3 ± 0.5	0.007
Oleic acid (pure)	Sigma (99+ %)	32.4 (USP)	15.0 (lit.)	30.5	0.007
Non-anoic acid	MCB (practical)	29.1	9.3	36 ± 2	0.02
Undecanol	Aldrich (99%)	29.0	8.9	41.4 ± 2	0.002
Silicone, DC-200 (5 cs)	Dow Corning (filtered with Florisil)	19.2	41.9	11.3	0.02
Silicone, DC-200 (1000 cs)	Dow Corning (filtered with Florisil)	21.0	38.6 ± 2	12.8	0.02
Tetradecane	Kodak (reagent)	26.5	51.0	0	—
Oleic acid in tetradecane	(0.2 M)	26.6	28.7	—	0.045
Oleic acid in tetradecane	(0.02 M)	26.5	38.2	—	0.045
Oleic acid in	(0.002 M)	26.5	44.7	—	0.09

† Equilibrium spreading pressure.

TABLE 1. Properties and volumes of oils used

be obtained (cf. Reinold & Rucker 1887), were photographed, when present. The photographic records were analysed using an NAC Model 76 film motion analyser to obtain leading-edge, velocity, and sometimes colour-thickness profiles.

While the spreading film was being photographed, simultaneous measurement of the changing film tension at a given position was made using a modification of the Wilhelmy technique (Adamson 1982). Instead of the usual slide however, a very small diameter 0.065 or 0.016 cm rod was used to achieve a quick response with minimal disturbance of the spreading films. Accurate tension measurements on monomolecular films require the rod to be perfectly wet out by the monolayer-covered water (zero contact angle). For bulk oil films, both interfaces must meet the rod at a zero contact angle; i.e. the rod must be wetted by oil in preference to air and by water in preference to oil. These wetting conditions were achieved by using rods of platinum-blackened platinum wires, for monomolecular films, and quartz fibres etched in hydrofluoric acid solution and soaked in hot Nochromix, for oils which spread as thin bulk films as well as monolayers. Whichever rod was used, it was suspended from the arm of a Cahn RG electrobalance so as to pass through the water-air interface. The electrobalance circuits were powered by high-voltage, rechargeable batteries to eliminate electrical noise in the balance (filtering would have greatly slowed the naturally quick response of the balance). As the oil film spread past the rod, the electrobalance transmitted a voltage signal proportional to the film tension. This voltage was sampled at a rate of two hundred times per second by an analog-to-digital converter which sent the data to a microcomputer system for storage and processing. Film-tension data from one run are shown in figure 5. From several such runs, made with the rod at various distances from the film origin, the complete time and spatial dependence of the film tension was obtained. The film-tension records were synchronized with the photographic records using a clock and computer-switched LED in the field of view.

The trough was cleaned by aspirating the surface after a set of experiments, swabbing with reagent grade cyclohexane or isopropanol, rinsing with water, soaking



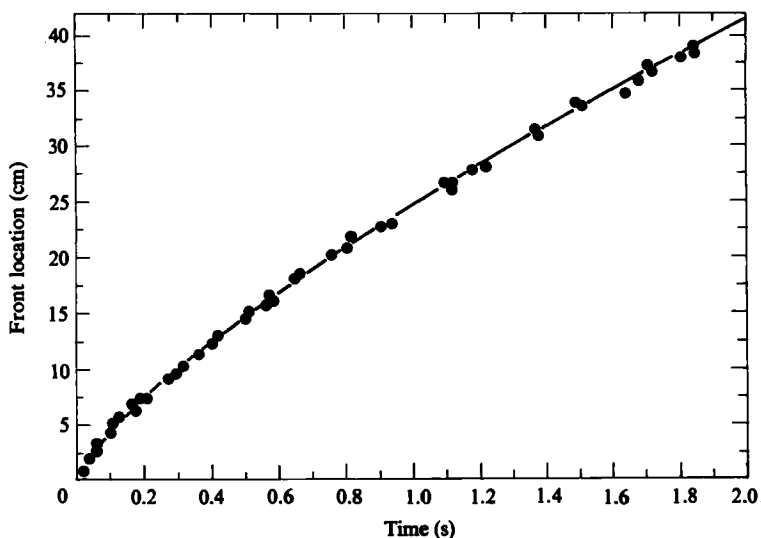


FIGURE 6. Leading-edge position as a function of time for several runs with oleic acid, —, fit by the power law curve  $L = 24.8 \text{ cm } S^{-0.75} t^{0.75}$ .

Oil (configuration)	$K$	$B$	$\beta^{\dagger}$	$\bar{L}$
Oleic acid, USP (m)	24.70	0.75	17.9	1.38
Oleic acid, pure (m)	24.25	0.76	17.7	1.37
Non-anoic acid (m)	28.22	0.75	20.6	1.37
DC-200 silicone 5 cs (b)	15.44	0.76	10.8	1.43
DC-200 silicone 1000 cs (b)	16.19	0.77	11.4	1.42
Oleic acid (0.2 M) in tetradecane (b)	18.89	0.74	13.3	1.42
Oleic acid (0.02 M) in tetradecane (b)	12.37	0.75	8.9	1.39
Oleic acid (0.002 M) in tetradecane (b)	4.93	0.73	3.4	1.45

TABLE 2. Power law fits to leading-edge data,  $L = Kt^B$ . The observed configuration at the origin is noted as m or b (monolayer-lens or bulk). The appropriate value of the spreading coefficient (ESP or  $\sigma_w - \sigma_o - \sigma_{ow}$ ) is used to compute  $\beta^{\dagger}$ . Since  $B$  is effectively 0.75 for all cases,  $\bar{L}$  is calculated as  $K/\beta^{\dagger}$ .

in Nochromix, and rinsing copiously with water. It was filled with triply distilled water for each set of runs. When studying fatty acids, the water was acidified to pH 2 with HCl to prevent film loss by dissolution. Table 1 shows the source and purity of the oils used, their interfacial properties (as measured), and the volume used in the experiments.

## 5. Results

The leading-edge position as a function of time for several runs made with oleic acid is shown in figure 6, along with a power law curve fit through the data. The result is typical of those obtained for all oils studied.

An important observation was made upon viewing the surface near the origin of the spreading oleic acid film at a shallow angle. The film consisted of a multitude of tiny lenses moving outward from the origin and disappearing. The film tension in the lens region was the equilibrium spreading pressure (ESP) of oleic acid, indicating that

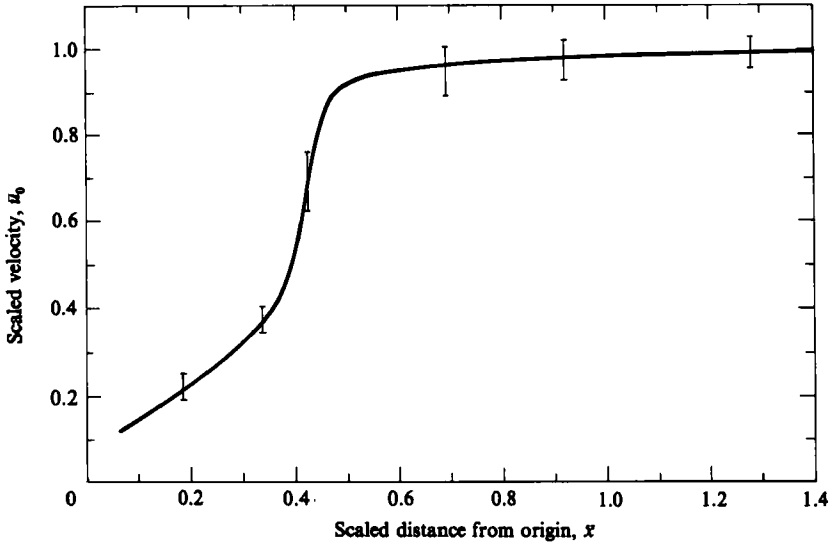


FIGURE 7. Scaled velocity profile for oleic acid. The curve is a composite of data taken at times of 0.40, 0.80, 1.35 and 1.95 s. Errors bars show the 95% confidence limits.

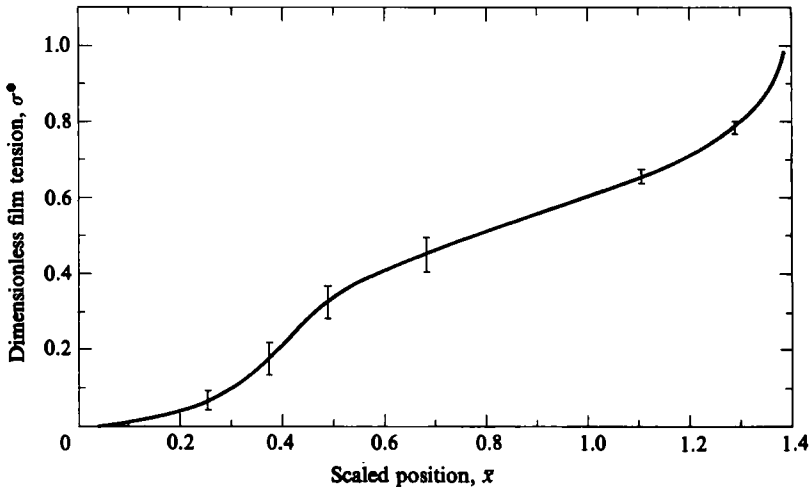


FIGURE 8. Oleic acid film-tension data taken at various distances from the origin (0.8, 2.8, 5.3, 10.6, 18.5 and 27.5 cm).

the lenses were surrounded by monolayer. The appropriate values for  $S$  and  $\beta^{\frac{1}{2}}$  were thus 31.3 dyn/cm and 17.9 cm/s<sup>2</sup>, respectively so that  $\bar{L}$  becomes 1.38. Not all oils studied exhibited the lens-monolayer configuration of oleic acid near the spreading origin, but instead showed a coherent thinning bulk film. In these cases, the spreading coefficient  $S$  was found to be, as expected,  $\sigma_w - \sigma_o - \sigma_{ow}$ . In the single experiment reported by Foda & Cox, using 1000 cs silicone oil, spreading was of the coherent bulk film type. Table 2 summarizes the leading-edge results for all the oils listed in table 1. It is to be noted that the fatty acids and alcohols produced the lens-monolayer configurations near the spreading origin while the silicone oils and the oil-surfactant mixtures produced coherent bulk films.

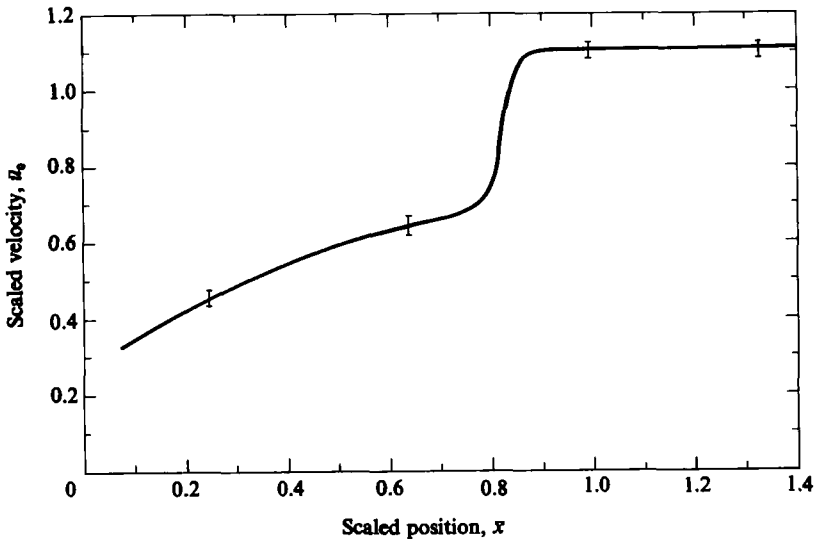


FIGURE 9. Velocity data for 1000 cs silicone oil taken at various times (0.5, 1.0, 2.05 and 3.2 s).

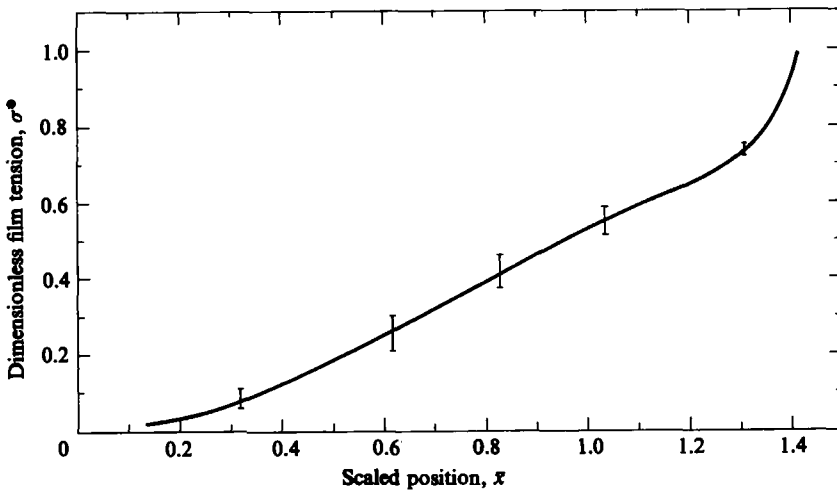


FIGURE 10. 1000 cs silicone oil film-tension data taken at various distances from the origin (4.1, 8.5, 12.9 and 20.3 cm)

Data for the internal velocity profiles and the film-tension profiles showed excellent concurrence with the similarity treatment of Foda & Cox, and results for oleic acid are presented in figures 7 and 8 and for 1000 cs silicone oil in figures 9 and 10. Results for the other oils are given in Camp (1985). The velocity profiles corresponding to different time values fall within the reproducibility limits for data at any specific time. On the other hand, the film-tension values corresponding to different positions in the surface are within the reproducibility bounds of the data for any specific position. Film thickness profiles were obtained directly by optical interference for those oils which spread as coherent bulk films but could not be obtained in this manner for those which exhibited the lens-monolayer configuration. For the latter, the monolayer concentration could be computed as a function of position using the independently measured surface equation of state for the monolayer. On the other hand, the

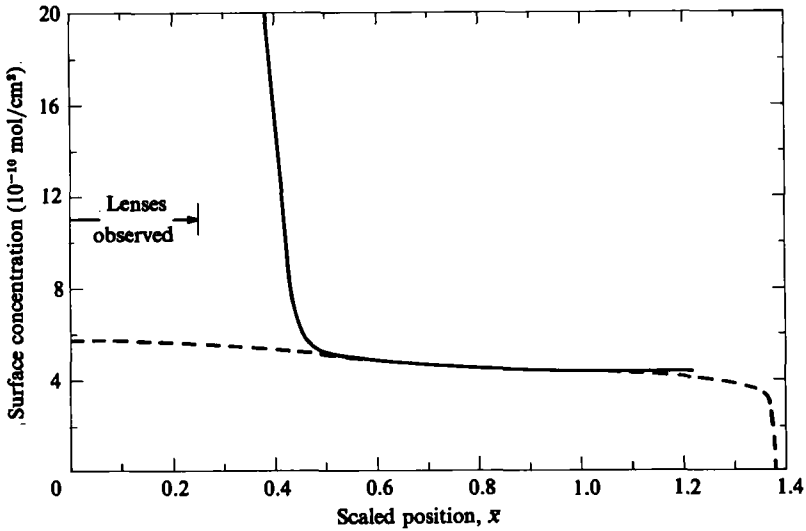


FIGURE 11. Surface concentration profiles for oleic acid. ----, calculated from the equilibrium surface equation of state. —, calculated from the measured velocity profile and (5.1).

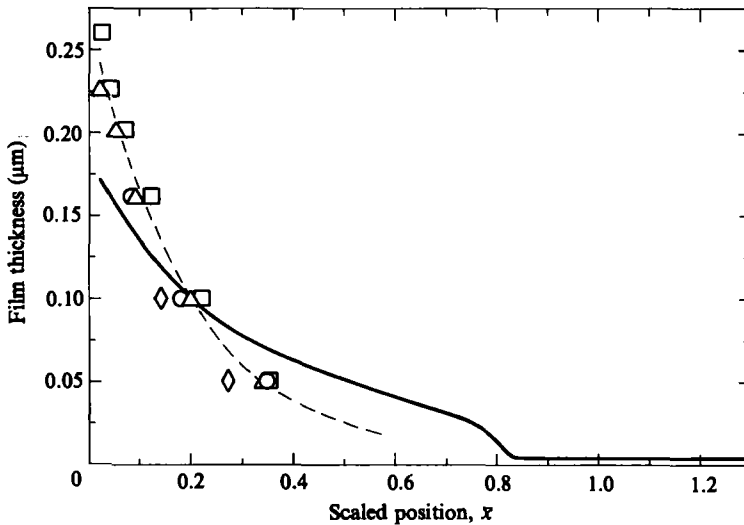


FIGURE 12. Thickness profile for 1000 cs silicone oil. Symbols represent composite data from runs at □, 0.5 s, △, 1.0 s, ○, 2.05 s, and ◇, 3.2 s. The solid curve is  $h[u_0(x)]$ , calculated assuming similarity.

'thickness' profile may be calculated from the measured velocity profiles using the oil continuity equation, (2.7). One value of  $h$  is required in this calculation, and it may be obtained from either a direct measurement or from the surface equation of state. The 'thickness profiles' obtained by both means are shown for oleic acid in figure 11. The curves coincide only in the region where lenses do not exist. The directly measured thickness profile for 1000 cs silicone oil is shown in figure 12 together with the curve computed from the velocity profile and (5.1). The disagreement between these was unique to this oil, the results for all other coherently spreading films showing agreement to within experimental reproducibility (Camp 1985).

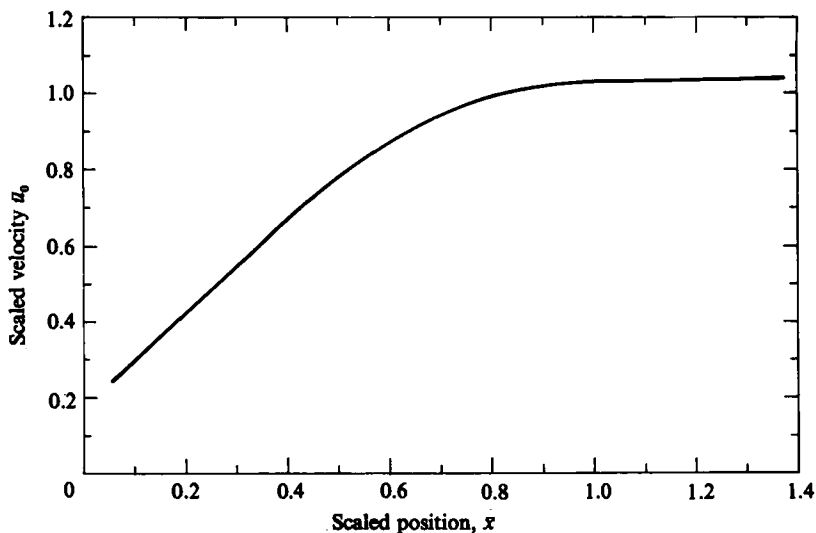


FIGURE 13. Velocity data for 0.02 M oleic acid in tetradecane.

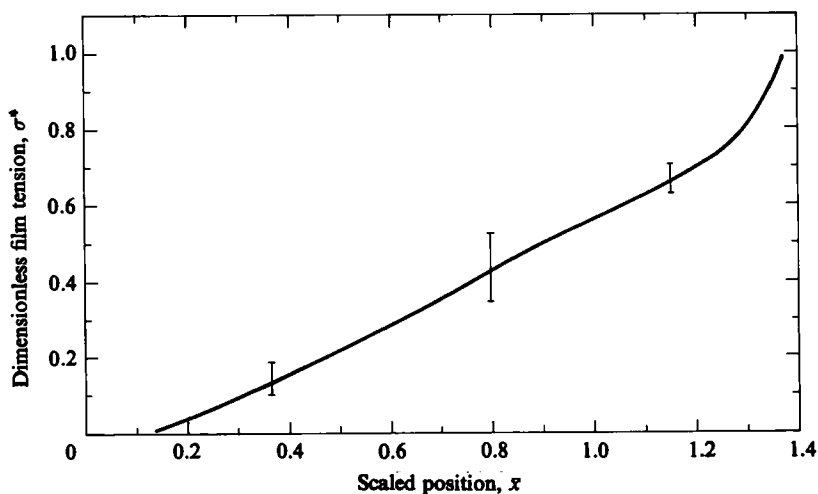


FIGURE 14. Film-tension data taken at various distances from the origin for 0.02 M oleic acid in tetradecane (4.4, 6.8, 13.1 and 19.8 cm).

Results for the oil-surfactant mixtures were similar to those for the coherently spreading pure oils with respect to the film-tension and thickness profiles but different with respect to the velocity profile. Data for  $2 \times 10^{-3}$  M solutions of oleic acid in tetradecane are shown in figures 13–15 as representative examples.

## 6. Discussion

The existence of two distinct spreading modes (lens-monolayer or coherent bulk film) near the origin may be explained as follows. For single component oils, if the equilibrium spreading pressure (ESP) is significantly greater than  $(\sigma_w - \sigma_o - \sigma_{ow})$ , as is the case for the fatty acids and alcohols studied, a monolayer-lens configuration can be expected near the origin and the spreading coefficient  $S$  should be set equal

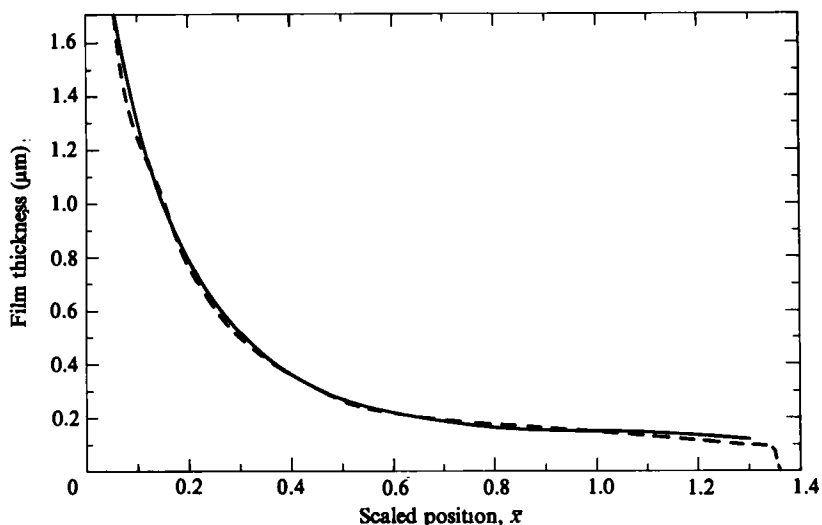


FIGURE 15. ----, film thickness data, and —, thickness profile calculated from the velocity data,  $h[u_0(x)]$ , for 0.02 M oleic acid in tetradecane. The oil film had a leading-region thickness of 0.5 to 1.5  $\mu\text{m}$ . The tightly spaced fringes near the leading edge could not be counted exactly.

to the ESP. In this case, the lower surface free energy of a monolayer, compared to that of a bulk film causes such a film to retreat into lenses surrounded by monolayer. When the ESP is nearly equal to  $(\sigma_w - \sigma_o - \sigma_{ow})$ , as is the case for the silicone oils, a configuration of bulk film is sufficiently stable to exist near the origin, at least over a time period long compared to that required for spreading, and  $(\sigma_w - \sigma_o - \sigma_{ow})$  may be used for  $S$ . For mixtures of surfactant in a non-spreading oil, a coherent bulk film is observed near the origin, and  $S$  should also be set equal to  $(\sigma_w - \sigma_o - \sigma_{ow})$ . The process of breakup into the equilibrium configuration of lenses plus monolayer must be sufficiently slow to prevent its observation during spreading. Indeed the slowness of the breakup process made possible the use of such films as 'piston oils' by Langmuir & Schaeffer (1937) for long periods of time. The longevity of these thick films can be traced to the time required for adsorption equilibrium at the oil-water interface.

With one exception, the observed velocity, film-tension, and thickness profiles at various times or positions for each oil superimpose when plotted in terms of similarity variables, confirming the similarity transformation of Foda & Cox as well as the use of the effective constitutive relation for oil-surfactant mixtures presented earlier. The thickness profiles of the 1000 cs silicone oil are significantly non-similar, however, with the thickness increasing with time at constant scaled position. Interestingly, both the velocity and tension profiles for this oil do appear to be similar. One possible explanation for the non-similar thickness behaviour of this oil is that the tensions and the disjoining pressure may depend on the conformation of the molecules as well as the film thickness. Because of the high molecular weight ( $> 30000$ ), achievement of equilibrium conformation may occur on timescales comparable to those for the spreading process itself.

All of the single-component oils exhibited velocity profiles which are quite different from those predicted or observed by any previous workers, including Foda & Cox. Specifically, a sharp 'acceleration zone' is seen to divide inner and outer regions of spreading. The outer region moves at a uniform velocity equal to that of the leading

edge, and as argued below, is likely to consist of a monomolecular film. The inner region has a much smaller film velocity which increases with  $x$ , and corresponds to a configuration of either continuous bulk film or monolayer with lenses.

The extrapolated film thicknesses of the silicone oils are consistent with the leading region ahead of the acceleration zone being a monomolecular film. This must certainly also be the case for oleic acid and the other fatty acids and alcohols, as evidenced by the agreement between the oleic acid surface concentration curves between  $0.5 < \bar{x} < 1.2$  as computed in figure 11. As further evidence, the measured oleic acid film tension at the acceleration zone is approximately equal to  $(\sigma_o + \sigma_{ow})$ , which is the highest tension at which lenses of bulk oleic acid can exist in contact with a monolayer. This is a consequence of requiring a balance of boundary-tension forces at the lens-monolayer interline. Above a tension of  $(\sigma_o + \sigma_{ow})$  only a monomolecular film may exist. Below this tension, in the inner region, lenses may exist with their thickness (actually their interline angles) increasing with decreasing tension in accord with the balance of forces at the interline. For the oleic acid system, the possibility of lenses for  $\bar{x} < 0.42$  (and the actual observance of lenses for  $\bar{x} < 0.25$ ) explains the discrepancy between the two surface concentration curves of figure 11 for  $\bar{x} < 0.42$ . The dashed curve is the surface concentration of that fraction of the film which is monomolecular, while the solid curve represents the material-balance-average surface concentration of oleic acid including both monolayer and lenses. For the silicone oils, it appears that a coherent bulk film exists in the inner region from the origin out until the tension increases to a value above which the bulk configuration is unable to exist, i.e. very unstable.

The spreading behaviour of the oil-surfactant mixtures is qualitatively similar to that predicted by the Foda & Cox analysis for single-component oils. From the origin to the leading edge, there is a smooth increase in velocity without the acceleration zone characteristic of pure oils, a smooth decrease in film thickness, and a smooth increase in film tension.

An important objective of this work was to test the validity of the asymptotic solutions of Foda & Cox. The leading-edge asymptote is in excellent agreement with the data. The scaled velocity of all the oils is very nearly constant at  $\frac{3}{4}\bar{L}$  near the leading edge, extending back to the acceleration zone for single-component oils, and for a considerable extent for the mixtures. A more critical test of the leading-edge asymptotic solution is a comparison between measured and predicted tension profiles. Figures 8, 10, and 14 show the computed leading-edge asymptote to agree well with the data. At, and ahead of, the acceleration zones, the measured tensions of the single-component oils exhibit a different shape from the leading-edge asymptote.

Foda & Cox's inner asymptotic solution requires knowledge of the coefficient  $p$  in the constitutive relation for the oil at low tensions, and  $C_1$ , whose value requires the numerical solution to the entire spreading problem. *A priori* specification of  $p$  for single component systems with lens-monolayer configurations is impossible since any number and size of lenses can exist at a given tension as long as the lens angles permit a balance of forces at the interline. This makes  $h(\sigma)$  multi-valued. Reliable data for the constitutive equations for the coherently spreading films under spreading conditions are also unavailable so that it is not possible to compare the spreading data to *a priori* predictions of Foda & Cox's inner asymptotic solution. Nonetheless, a good test of the validity of this solution can be made by comparing the measured and predicted relationship between film velocity and film tension. To do this, we fit  $C_1$  and  $p$  to the measured velocity profile and then compare the corresponding tension

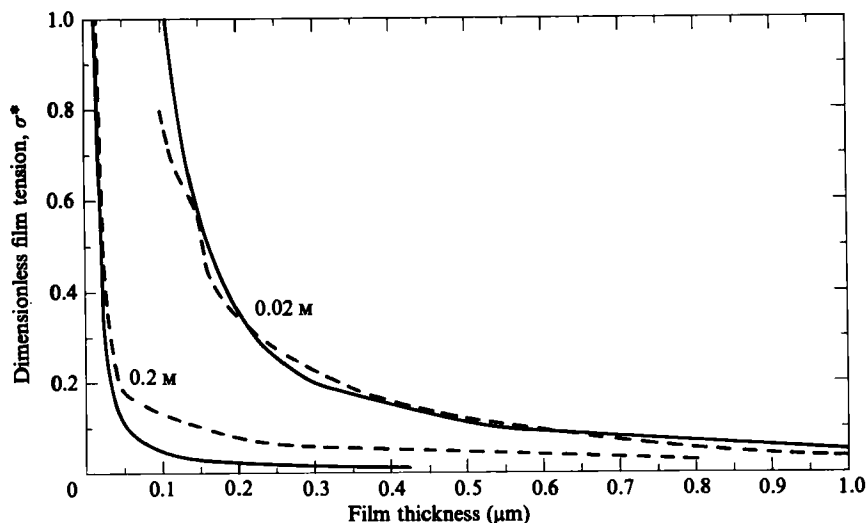


FIGURE 16. ----, measured and —, predicted constitutive relations for solutions of oleic acid surfactant in tetradecane.

profile predicted by the asymptotic solution to the tension data. Plots of these comparisons are given in Camp (1985), but in all cases, the film-tension data are predicted to within  $\pm 10\%$ .  $p$ -values ranging from 2.00 to 4.00 were found.

One reason to expect discrepancies between the measured and computed velocities in the inner region is the assumed power-law form (2.12) for the constitutive equation. Such a form is to be expected for coherently spreading pure oils, but there is no independent reason to expect it to hold for those oils which exhibit a lens-monolayer configuration. The generally good agreement obtained for the oil-surfactant mixtures suggests the validity of the assumptions made in §3 for such systems.

A more critical evaluation of the constitutive relation requires a quantitative comparison between the predicted and measured  $\sigma^*(h)$  behaviour of the spreading mixtures. The predicted constitutive relations for the 0.02 and 0.2 M oleic acid-tetradecane systems have been evaluated by substitution of the independently-measured interfacial tension equation,  $\sigma_{ow} = \sigma_{ow}(c)$ , into (3.1). Since fatty acids are known to exist as dimers in hydrocarbon solvents, the activity coefficient term in (3.1),  $d \ln \gamma / d \ln C$  becomes  $-0.5$  for the low surfactant concentrations of interest here (cf. Prausnitz *et al.* 1986). The resulting predicted constitutive relationships are plotted in figure 16 in comparison with measurements. The experimental curves were obtained by cross-plotting thickness data (of the type in figure 15) with film-tension data (of the type in figure 14). The agreement between calculated and experimental curves is good.

The spreading data obtained in this study, together with the analysis of Foda & Cox, were sufficient to construct an easily-used semi-empirical model for the prediction of spreading behaviour. This model is detailed elsewhere (Camp 1985).

## 7. Conclusions

A data base of sufficient depth and breadth for the spreading of small amounts of pure oils and oil-surfactant mixtures on water has been presented to permit a definitive check of theoretical hydrodynamic descriptions of the process in the



surface-tension regime. The data include leading-edge position as a function of time, and internal spreading velocity, film tension and effective film thickness as functions of time and position. The measurement of film-tension profiles required the development of a new technique, and these hitherto unavailable data permitted the first decisive check of the internal consistency of hydrodynamic models. Dimensionless film tension was found to decrease continuously from the leading edge to the origin, contradicting the assumptions of some earlier investigators.

The similarity analysis of Foda & Cox (1980) was found to provide an internally consistent description of the spreading of both pure oils and oil-surfactant mixtures. The application to mixtures required the development of an effective format for the constitutive equation for such systems.

The leading-edge spreading law, (2.11), was followed by all oils with a universal value of  $k = 1.40 \pm 0.04$ . The appropriate value to use for the spreading coefficient  $S$  is  $(\sigma_w - \sigma_o - \sigma_{ow})$  for oil-surfactant mixtures and single-component oils for which the equilibrium spreading pressure, ESP, is nearly equal to  $(\sigma_w - \sigma_o - \sigma_{ow})$ . These systems exhibited a configuration near the origin of a continuous bulk oil film. The ESP should be used for  $S$  when it exceeds  $(\sigma_w - \sigma_o - \sigma_{ow})$ . The asymptotic solution of Foda & Cox for the near-origin region of the film is in reasonable agreement with spreading data, provided an appropriate, independently determined constitutive relation is employed.

Despite the internal consistency of the Foda & Cox analysis, the overall spreading behaviour of the single-component oils was markedly different from that anticipated by Foda & Cox and others. Specifically, the velocity data showed a sharp acceleration zone connecting a slowly moving inner region of bulk configuration (if  $\text{ESP} = \sigma_w - \sigma_o - \sigma_{ow}$ ) or monolayer with lenses (if  $\text{ESP} > \sigma_w - \sigma_o - \sigma_{ow}$ ) with a leading monolayer of uniform velocity equal to that of the leading edge. The existence of the distinct acceleration zone has not been predicted or reported previously. In contrast, dilute surfactant-oil mixtures showed no sharp acceleration zones in the velocity profile. Film thicknesses were of the order of tenths of micrometers, decreasing with increasing surfactant concentration. The pure oils for which the ESP was much larger than  $\sigma_w - \sigma_o - \sigma_{ow}$  displayed a pattern of small lenses shedding outward from the advancing film in the inner region. These included the fatty acids and alcohols studied. Oils for which the ESP was effectively equal to  $\sigma_w - \sigma_o - \sigma_{ow}$ , including the silicones and the oil-surfactant mixtures studied, showed coherent films of continuously decreasing thicknesses from the origin to the leading edge.

The usefulness of the Foda & Cox analysis for making theoretical predictions of spreading behaviour is severely limited in practice by the difficulty of accurately specifying the constitutive relation for many oils. These difficulties arise both for the oils yielding the lens-monolayer configuration during spreading and those which remain coherent. The latter are generally unstable with respect to the lens-monolayer state but are unable to execute the transformation during the time of an ordinary spread. These are examples of the constitutive relation for a spreading oil differing from that which pertains to equilibrium.

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