Stagnation in a Fluid Interface: Properties of the Stagnant Film

R. L. MERSON and J. A. QUINN
University of Illinois, Urbana, Illinois

The mechanism whereby surface-active agents cause stagnation in a fluid interface has been extensively studied for water flowing in a horizontal channel. Known surface-active contaminants exhibiting varied surface behavior were added to the water. Distinctly different phenomena were observed with compressible and incompressible films.

There are numerous references in the literature to the spontaneous formation of a semirigid skin near a stagnation point in the moving surface of a liquid. The surface film causes stagnation of the surface and has been observed at the gas-liquid interface in wetted-wall columns (*7, 10, 13*), on laminar liquid jets (*1*), on a rotating drum (*3*), and in flow over solid spheres (*2*). Similar surface stagnation has been reported in liquid-liquid systems with flow over solid spheres (*11*), on falling drops (*4, 6, 12*), and in horizontal radial flow of thin liquid layers (9). The common feature of these contacting arrangements is that the two phases are separated downstream at a stagnation point, usually at a physical barrier placed in the interface.

The observed surface films have been attributed to surface-active impurities which diffuse to the interface from either bulk phase and are swept downstream to the stagnation point where they accumulate, possibly as a monomolecular layer. This is the model examined in the experiments reported here. Fresh interface was continuously formed in a horizontal channel with liquid flowing in contact with air. Surface elements moved freely and steadily downstream until they approached a barrier placed in the interface. Here the surface decelerated to the stagnation point at the edge of the barrier, while the main stream flowed beneath the barrier. Surface-active contaminant molecules were adsorbed from the bulk liquid into the freely moving surface; the adsorbed surface molecules were then abruptly compressed to a high surface concentration at the barrier.

The results presented in this paper are an outgrowth of observations made in a previous study of mass transfer with a moving interface (*8, 9*). In spite of precautions taken to prevent inadvertent contamination, gradual stagnation of the interface occurred for several gas-liquid and liquid-liquid pairs. The purpose of the present work was to examine in detail the stagnation phenomena and, in particular, to ascertain the nature and concentration of the impurities necessary to produce stagnation.

EXPERIMENTAL

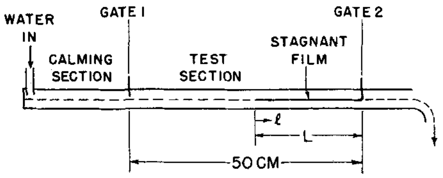

Fig. 1. Schematic side view of channel.

The channel was made of brass and was divided into three sections as shown in Figure 1. Deionized water from the building lines entered the upstream calming section through a distributor perpendicular to the channel. It passed into the test section forming a fresh interface by flowing under gate 1 which could be adjusted to control the thickness of the water layer. Surface velocity measurements were made in the test section by clocking talc particles floating on the surface between two points. At a given time, $t = o$, gate 2 was touched to the interface, thus applying a force to the surface, and the growth of the surface film was measured. The possible effect of gate 2 on the film growth was extensively investigated. Brass, Plexiglas, and Teflon gates were tried. An upward meniscus was produced by pulling the water surface up to the gate with a clean glass slide; Teflon produced a downward meniscus. No difference in the rate of film growth could be detected for the various methods of touching the barrier to the surface.

The position of the film was made apparent by lightly sprinkling talc upstream. The talc indicated the velocity profile in the surface as it was swept downstream. At the edge of the film the talc stopped abruptly in a fine, thin line and then moved to the side of the channel to enter a circulation pattern as shown in Figure 2*a*.

It was observed that the meniscus of water wetting up on the brass sides caused a quite nonuniform depth of liquid across the channel with a maximum surface velocity near the wall. A sketch of the surface velocity profile is shown in Figure 2*a*. This effect was eliminated by clamping glass strips on the sides of the channel, effectively converting the brass channel 3.8 cm. wide to a channel 3.1 cm. wide with a metal bottom and glass sides. The glass was treated with a silicone compound (G. E. Dri-Film SC-87) to eliminate the air-water meniscus, thereby producing the surface velocity profile shown in Figure 2*b*. The direction of circulation in the stagnant film was also reversed because of the relocation of the maximum velocity at the center line of the channel.

The talc used in the experiments was ignited at red heat for several hours to remove organic impurities. Repeated trials in which the surface film was allowed to grow to a considerable length before the first particles of talc were introduced proved that the talc itself was not a source of contamination, nor did it materially affect the behavior of the existing film.

Precautions taken to prevent spurious contamination were numerous. The water storage tank and conveying lines were of Pyrex glass thoroughly cleaned in hot chromic acid cleaning solution and flushed with deionized water. Cleaned Teflon stopcocks were used exclusively, and where flexible joints were

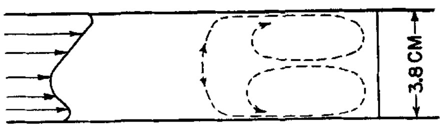

Fig. 2a. Typical velocity profile in the free surface and circulation pattern in the film-metal walls.

R. L. Merson is with Western Regional Research Laboratory, Albany, California.

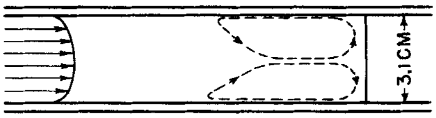

Fig. 2b. Typical velocity profile in the free surface and circulation pattern in the film-glass walls.

necessary in the lines, they were made by wrapping the joint between glass pieces with Teflon pipe sealant tape and were subsequently cleaned. A Plexiglas cover was placed over the channel to exclude air-borne contaminants. Each measurement of the rate of film buildup was repeated until entraneous contamination had been eliminated and the data were reproducible.

PROPERTIES OF THE ADSORBED LAYER

Surface-active agents may be subdivided into three broad classes (*4*) in accordance with the compressional behavior which their monolayers exhibit at an interface. So-called *condensed films*, for example, films formed from stearic acid, are quite incompressible, and only a small surface force is required to pack the molecules of the film into a spacing very close to 20 Å^2/molecule, the limiting area which approximates the cross-sectional area of hydrocarbon chains in the crystalline state. Gaseous films, such as those of ionized dodecyltrimethylammonium chloride, are compressible over a wide range of surface pressures.

In the limit of no repulsion or cohesion among the surface molecules, gaseous films follow a force-area relationship

$$\Pi A = kT \tag{1}$$

Intermediate in compressibility to condensed and gaseous films are the slightly compressible expanded films typified by monolayers of oleic acid.

Assume as a model a laminar stream of liquid with bulk concentration of surface-active impurities C_o. If adsorption equilibrium is rapidly established between the freely moving surface and the bulk, the surface concentration upstream of the stagnant film will be constant at Γ_o. The surface concentration in the stagnant film itself depends on the compressibility of the film. For the incompressible case the film concentration Γ_s is constant with time and uniform throughout the film. Conservation of the adsorbed material in the surface of the liquid in the channel is given by

$$\frac{d}{dt}\{(\Gamma_s-\Gamma_o)\,L\} = u_i\Gamma_o \tag{2}$$

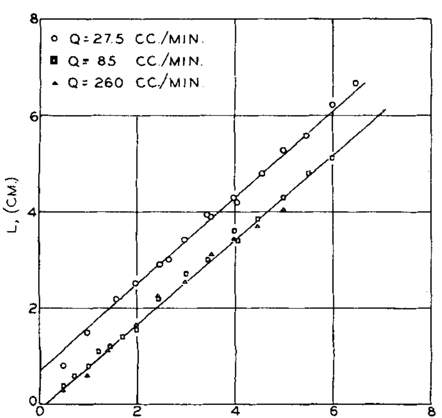

Fig. 3. Film growth on deionized water surface.

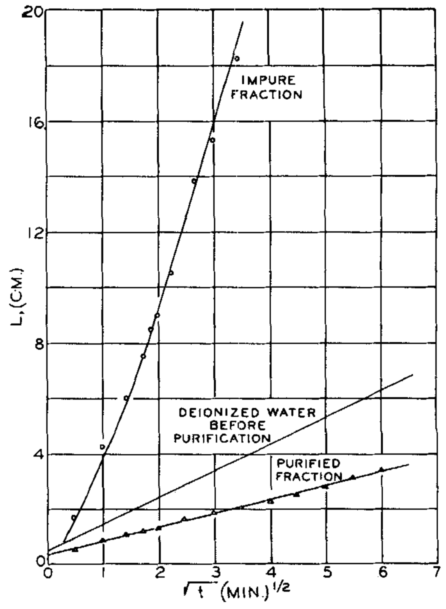

Fig. 4. Film growth on water from bubble column, $Q = 27.5$ cc./min.

The length of stagnant film at any time after a barrier is placed in the surface is therefore

$$L = \left(\frac{u_i\,\Gamma_o}{\Gamma_s-\Gamma_o}\right)t \tag{3}$$

If the surface-active material forms a compressible film, a concentration gradient will exist within the film. A force balance on the film combined with the surface equation of state, Equation (1), gives

$$\Gamma_s - \Gamma_o = \frac{\tau\, l}{k\,T} \tag{4}$$

Thus, for a constant shear stress τ the concentration in the monolayer increases linearly with distance l along the stagnant film. For the compressible case the rate of film growth becomes

$$L = \left(\frac{2u_i\,\Gamma_o\,kT}{\tau}\right)^{1/2}\sqrt{t} \tag{5}$$

In Equations (3) and (5) it has been assumed that there is no desorption from the stagnant film. If desorption is important, its effect may be approximated by using Langmuir desorption kinetics. The net rate of film growth then takes the form

$$L = \left(\frac{2u_i\,\Gamma_o kT}{\tau b}\right)^{1/2}(1-e^{-bt})^{1/2} \tag{6}$$

The above expressions for L are but three examples from a large class of plausible models for the stagnation process. Here the flow field and the adsorption kinetics have been greatly simplified. However, as discussed below, these elementary models appear adequate to account for the gross features of the channel experiments.

RESULTS AND DISCUSSION

The results for the natural contaminant in the deionized water are presented in Figure 3 for three flow rates. The length of the stagnant film grew as the square root of time, as predicted for a gaseous film in accordance with Equation (5). The variation of intercept with flow rate is due to the shape of the leading edge of the film as it was distorted by the surface velocity gradient. At the lowest flow rate the shape of the film was similar to the sketch in Figure 2*a*; at the higher rates the shape was similar to that in Figure 2*b*. In the length measurements the edge of the film was taken to be the center-line position of the film, hence the flow rate variation of the intercept. As long as a consistent method of measuring the position of the film was used, the slope of the film growth curves was constant for all flow rates and for the higher flow rates the intercept was also constant.

Several methods of further purifying the deionized water were attempted (including repeated distillation and distillation from an alkaline permanganate solution). The purest water was obtained by sparging in a glass column. Deionized water was admitted at a low rate to the center of a 100-cm. column of water. Water-pumped air was introduced to the bottom of the column through a fritted bubbler. As the bubbles rose through the liquid, surface-active impurities were adsorbed on the surface of the bubbles and were carried to the top of the column producing a concentration gradient in the column. Purified water was drawn off just above the fritted sparger in the region of the nascent bubbles, and the remaining water, enriched in impurities, steadily overflowed at the top of the column, thus effecting a separation. Typical results of this purification scheme are shown in Figure 4. In the case depicted the water has undergone a single pass through the sparging column, and the concentration of contaminants in the purified water has been reduced by a factor of 4.

In an attempt to characterize the natural contaminant, pure surface-active agents exhibiting different surface properties were added to deionized or purified water. A saturated solution of stearic acid, representative of an incompressible monolayer, gave the results shown in Figure 5. The curvature of these data is due to the compressible film of the natural contaminant present in the deionized water. By subtracting out the natural background one can obtain a linear plot of the net film length vs. time (8). The ratio of the slopes of the lines at different flow rates is in excellent agreement with the ratio of the measured surface velocities, in accord with Equation (3). Similar results were obtained for solutions of calcium oleate.

Data for oleic acid solutions are shown in Figure 6. This substance forms adsorbed surface films which are slightly compressible. For this reason even the net film growth curves show appreciable curvature when plotted in accordance with Equation (3).

Dodecyltrimethylammonium chloride is an ionized surface-active agent used as an example of a substance which forms a compressible, gaseous surface film. Film growth curves for solutions of this substance are plotted in Figure 7. After the film length had reached 8 to 10 cm., the rate of growth followed Equation (5), derived for a gaseous film. In accordance with Equation (5), if the thickness of the water layer δ remains constant, then the rate of formation of gaseous films should be independent of flow rate since

$$\tau = \frac{4 \mu u_i}{\delta} \tag{7}$$

In the operation of the channel the film thickness increased slightly with flow rate. The increase in the slope of the curves in Figure 7 for dodecyltrimethylammonium chloride is in close agreement with the observed increase in the average δ from 2 mm. at the low flow rate to 2.5 mm. at the higher one.

Figure 8 represents an example of the formation of a stagnant film when desorption from the film is important. An unknown contaminant in reagent grade benzene pro-

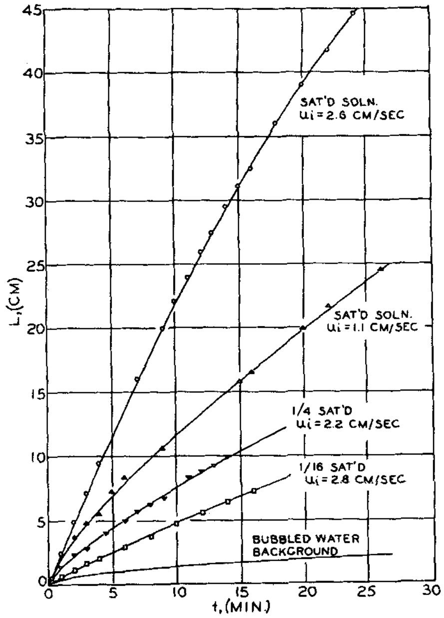

Fig. 6. Film growth on oleic acid solutions.

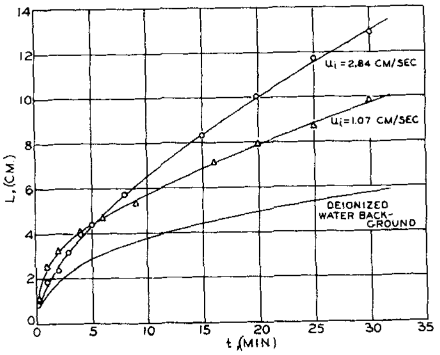

Fig. 5. Film growth on saturated solution of stearic acid.

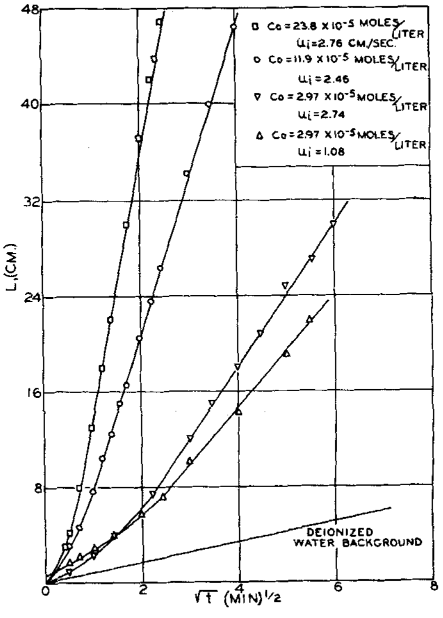

Fig. 7. Film growth on solutions of dodecyltrimethylammonium chloride.

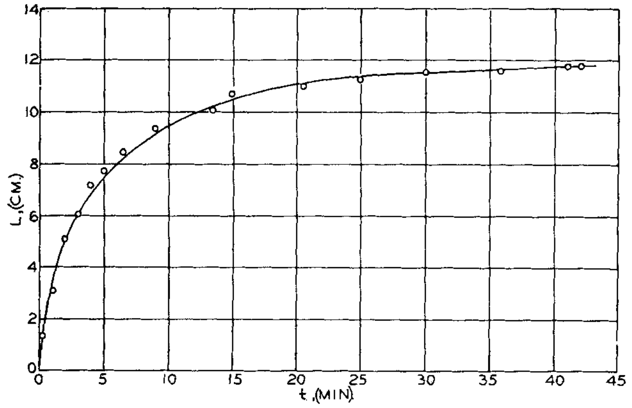

Fig. 8. Stagnation at the benzene-air interface. The data are fitted with a curve of the form $L = a(1-e^{-bt})^{1/2}$ with $a = 11.9$ cm., $b = 0.103$ min^{-1}.

duced a surface film which grew to an equilibrium length of about 12 cm. at a flow rate of 54 cc./min. A curve of the form of Equation (6) has been fitted to the data. This example illustrates that the stagnation phenomena are not restricted to aqueous systems and may be encountered with organic substrates as well.

From the rate of film formation it is possible to calculate surface concentrations and thus deduce the level of contamination necessary to produce the observed stagnation of the interface. For stearic acid, the surface concentration Γ_s in the incompressible film can safely be assumed to be that corresponding to the limiting area per molecule, 20 Å^2/molecule (*4*) or 5×10^{14} molecules/sq.cm. When one uses measured surface velocities in Equation (3), the value of Γ_o calculated from the slopes of the net stearic acid data is 7×10^{11} molecules/sq.cm. Based on a surface population of 10^{15} molecules/sq.cm. for pure water, only one molecule in a thousand is stearic acid in the free surface. These molecules are compacted seven hundred-fold to produce the semirigid skin which causes stagnation. Similarly for saturated oleic acid and for dilutions to one-eighth and one-sixteenth saturation (Figure 6), surface concentrations in the free surface based on the initial net slopes are 2.3×10^{12}, 1×10^{12}, and 0.3×10^{12} molecules/sq.cm. Free-stream surface concentrations of dodecyltrimethylammonium chloride can be calculated from the slopes of the straight portions of the curves in Figure 7. For bulk concentrations of 2.38×10^{-4}, 1.19×10^{-4}, and 0.30×10^{-4} moles/liter, the surface concentrations upstream from the stagnant film are 2.1×10^{11}, 0.70×10^{11}, and 0.11×10^{11} molecules/sq.cm., respectively. From the slope of the curve for the natural contaminant, the surface concentration for this unknown substance was between 3.6×10^{8} and 5.4×10^{8} molecules/sq.cm. When one extrapolates from the data for the known additive, this corresponds to a bulk concentration of approximately 0.3 wt. part per million as dodecyltrimethylammonium chloride.

CONCLUDING REMARKS

1. The rate of film buildup depends upon the compressibility of the film which in turn is a function of the cohesive forces between the adsorbed molecules. It has been shown that an incompressible film in which cohesive forces are high grows linearly with time, the growth being simply an accumulation of the surface-active molecules at the leading edge of the film. If cohesive forces are absent, the resulting film is compressible, and each additional molecule carried into the film compresses the preceding ones so that the film grows as the square root of time. It is this latter type of behavior which characterizes the natural contaminant present in the deionized water used here.

2. Extremely small amounts of surface-active materials suffice to contaminate a fluid interface. Since dynamic experiments in general require large quantities of the interacting fluids, the normal tendency is to neglect the exacting purification necessary to remove the impurities from the ordinary supply. Furthermore, the most common purification method used, namely, deionization, often employs quaternary ammonium salts as the anion exchanger (*5*) and may itself be a source of contamination. Consequently, it is not surprising that many researchers have observed the formation of stagnant interfacial films.

3. There are three notable differences between the conditions in the present work and those of other systems in which surface films have been observed. The films in other work have been formed on nearly vertical surfaces as opposed to the horizontal interface used here. The surface velocities have been from 10 to 100 times higher in other systems. Also, the stagnant films in other work have appeared to reach an equilibrium height, less than 2 cm. in most cases. In the present work the monolayers on the water surface did not reach an equilibrium length but continued to form steadily up to the full 50 cm. length of the channel. Possible explanations for the finite film lengths which have been reported are that the shear stress in most systems exceeds the surface pressure necessary to collapse the surface films into a multimolecular third phase or, less likely, there is desorption from the film as shown here for benzene in Figure 8. Obviously, for surface velocities an order of magnitude larger than those used here and for film lengths of 2 cm. or less, the film formation would appear to be instantaneous.

4. A possible explanation may also be offered concerning the controversial nature of contaminant films on falling drops. The stagnant cap photographed by Savic (*12*) at the rear of a falling drop may be caused by contaminant which forms an incompressible film that has reached an equilibrium length. On the other hand, the theories of Levich (*6*) and others, intended to explain the reduction in terminal velocity and internal circulation of falling drops, may apply to compressible films which envelope the entire drop.

ACKNOWLEDGMENT

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NOTATION

A = mean molecular area, Å^2/molecule
b = desorption rate constant, min.$^{-1}$
C_o = initial concentration in substrate, moles/liter
k = Boltzmann's constant, 1.380×10^{-16} erg./molecule-°K.
l = distance measured from the leading edge of the stagnant film, cm.
L = length of the stagnant film, cm.
Q = volumetric flow rate, cc./min.
t = time, min.
T = absolute temperature, °K.
u_i = free surface velocity, cm./sec.

Greek Letters

Γ = surface concentration, moles/sq.cm.
Γ_o = surface concentration in equilibrium with C_o, moles/sq.cm.

Γ_s = surface concentration in stagnant film, moles/sq.cm.
δ = thickness of the water layer, cm.
μ = liquid viscosity, g./cm. sec.
Π = film pressure, dynes/cm.
τ = shear stress at surface, dynes/sq.cm.

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Longitudinal Dispersion in Pulsed Perforated-Plate Columns

TERUKATSU MIYAUCHI and HARUHIKO OYA
University of Tokyo, Tokyo, Japan

Experimental measurements have been performed for pulsed perforated-plate columns of different sizes and geometry to obtain longitudinal dispersion coefficients for continuous and dispersed phases and size and holdup of liquid droplets dispersed in the columns. These quantities are correlated with operating conditions and column design, including the data published by different authors. Longitudinal dispersion coefficients for the continuous phase are shown to follow the backflow model. A superficial number of stages in series in each compartment is shown to come from inherent instability of fluid motion in the compartment. The longitudinal dispersion coefficient of the dispersed phase approaches that of the continuous phase with increasing pulse velocity. Holdup and mean size of droplets are correlated mainly on the basis of the rate of energy dissipation in the column fluid. Inclusion of dispersed-phase viscosity is shown to correlate the holdup data successfully for different liquid-liquid systems.

Many investigations have been presented for pulsed perforated-plate columns since Van Dijck's first presentation of this type of extractor (*35*) and successful application of it to the reprocessing of spent reactor fuel at Idaho and Oak Ridge. Of these, some experimental works (*4, 5, 26*) have revealed that column HTU takes a minimum value with increasing pulse frequency and amplitude. Influence of longitudinal dispersion on column behavior is mentioned in the works by Thornton (32) and others.

This paper presents the column behavior along the theoretical treatment presented recently (*17, 18, 20, 21,* 29) for two-phase counterflow operations with longitudinal dispersion. The theory seems particularly helpful to interpret extraction-rate data obtained in continuous countercurrent extraction columns. Dimensionless parameters are included to characterize the behavior: individual column Peclet numbers for each phase to specify the extent of longitudinal dispersion, true overall NTU to characterize the rate of local mass transfer, and capacity ratio (extraction factor). Of these parameters longitudinal dispersion behavior of pulsed perforated-plate columns is presented here on the basis of experimentally measured dispersion coefficients. Burger and Swift (*3*) and Mar and Babb (*16*) have reported longitudinal dispersion coefficients obtained by measuring concentration pattern of steadily injected tracer material, and Eguchi and Nagata (*7*) have presented those calculated from extraction runs. Miyauchi and Vermeulen (*22*) show that the coefficients are well correlated on the basis of backflow.

Correlation of the dispersed-phase holdup is also included here, since this quantity has an intimate relation with longitudinal dispersion coefficient and local mass transfer behavior of this phase. Experimentally measured holdup data are also available from Cohen and Beyer (*5*), Thornton (*32*), and Sehmel and Babb (*25, 27*).

EXPERIMENTAL APPARATUS AND PROCEDURES

Experimental Apparatus

The assembly of the entire apparatus is shown in Figure 1. It consists of constant level feed vessels for water, methyl isobutyl keton (MIBK), and 0.1 N aqueous solution of potassium chloride as tracer electrolyte; and a pulse perforated-plate

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Haruhiko Oya is with Shōwa Denko Company, Ltd., Tokyo, Japan.