

The fate of soluble and insoluble surfactant monolayers subjected to drop impacts

J.R. Saylor

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Abstract Surfactant monolayers were formed on a water surface and subjected to water drops falling from a nozzle. Surface tension was measured during these experiments to determine the effect of the drop impacts on the surfactant monolayer. The purpose of this work was to determine whether monolayers can be altered by drop impacts without the formation of a splash. Accordingly, a small fall height was used to avoid drop splashes and concomitant surfactant loss by droplet ejection. The relevance of this work pertains to the fate of surfactant monolayers during rain events. Results are presented for a soluble and insoluble surfactant. The results show that the insoluble monolayer is virtually unaffected by the drops, indicating that the monolayer immediately reforms after the drop impact. The soluble monolayer shows significant changes in measured surface tension during droplet impact when the surfactant concentration is high.

Introduction

Surfactant monolayers significantly impact processes which occur at air/water interfaces. Just a few examples are the damping of surface waves (Lucassen and Hansen 1966; Mann and Ahmad 1969; Garrett and Zisman 1970; Noskov 1988; Jiang et al. 1992; Milgram 1998; Szeri et al. 2001), the suppression of evaporation (Rideal 1925; La Mer 1962; Navon and Fenn 1971; Barnes 1986, 1997), the alteration of the surface temperature field during free surface flows (Jarvis 1962; Jarvis and Kargarise 1962; Jarvis et al. 1962; Barnes and Feher 1980; Saylor et al. 2000a, 2000b, 2001), the modulation of dissolved gas transport (Goldman et al. 1988; Frew et al. 1990; Frew 1997; Saylor and Handler 1999), and the reduction of momentum transport from wind to water. Because of their relevance to these processes, an understanding of the factors which influence the formation and elimination of surfactant monolayers is important.

A significant body of literature exists pertaining to the effect of bubbles on surfactant monolayers at an air/water interface. For example, the scavenging of surfactants by rising bubbles and the transport of organic material from the ocean to the atmosphere by bursting bubbles has been investigated in some detail (Szeri et al. 2001; Skop et al. 1991, 1994; Stefan and Szeri 1999; Monahan and Dam 2001).

In contrast, the way in which raindrops affect the fate of surfactant monolayers has been investigated in considerably less detail. Green and Houk (1979) conducted a laboratory study where a water surface covered by hexadecanol (an insoluble monolayer) was subjected to a flux of simulated raindrops. The fate of the monolayer was monitored by measuring surface tension and significant reductions in hexadecanol were observed during the course of the simulated rain events. Upon cessation of rain, some of the eliminated hexadecanol returned to the surface. It was postulated that the hexadecanol was partially mixed into the water bulk by the rain and subsequently diffused back to the surface when the rain stopped. It was also postulated that some hexadecanol had accumulated on the tank walls in the form of drop splashes that subsequently rolled back into the tank. A definitive explanation for these observations has not been provided.

Baier et al. (1974) acquired an extensive set of infrared spectra for monolayers collected from a variety of lakes and oceans. Two of their samples were collected during a rain event. These samples were obtained at opposite ends of a lake, both within an hour of each other. Both samples had a thickness of ~10 nm, suggesting that rain has no effect on surfactant concentration. However, the source of the surfactant and whether this source was producing material during the rain event is not known. Hence, it is difficult to draw any firm conclusions from these data regarding the effect of rain on the fate of monolayers.

Little beyond the aforementioned studies is known about the effect of rain on surfactant monolayers. There are two obvious mechanisms by which rain can reduce the amount of surfactant on a water surface. First, a raindrop splash can eject many small drops, each partially covered with surfactant. These small drops can be transported away from the surface by wind. Secondly, bubbles can be formed during raindrop impacts. These bubbles will rise to the surface and burst, transporting surfactant to the air. While further studies quantifying these two mechanisms are needed, the present work addresses a more subtle question which is suggested by the work of Green and Houk (1979), described above. In discussing the rise in

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J.R. Saylor
Department of Mechanical Engineering,
Clemson University, Clemson, SC 29634-0921, USA
E-mail: jrsaylor@ces.clemson.edu

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surfactant concentration following the simulated rain event, these authors suggest that part of the rise in concentration may have been due to surfactant which had been "...mixed down into the water." (Green and Houk 1979) Since the rise in surface tension occurred over many tens of minutes, and even an hour in some cases, it is unlikely that this would have been due to the relatively large bubbles formed during drop impacts, since these would have rapidly risen to the surface. Hence, it is possible (though not proved in their investigation) that some surfactant was removed from the surface and pushed into the bulk by the clean water drop. 'Insoluble' monolayers do have a small, but finite solubility (Adamson 1990), and so it may be that drop impacts actually increase the dissolution of surfactant into the bulk. Part of the motivation for this study is to determine if this is indeed the case.

In the present work, water drops traveling at velocities considerably less than terminal velocity are investigated to ascertain their effect on soluble and insoluble surfactant monolayers. Low-velocity drops were specifically chosen to avoid the formation of bubbles and splash drops. Hence, the question addressed here is: can surfactant monolayers be affected without the formation of a bubble or a splash-induced drop? These low-velocity drops also have the benefit of simulating the secondary drops which are formed by the splash of a raindrop. Since each raindrop produces many low-velocity secondary drops, any effect that the secondary drops have on the fate of surfactant monolayers will be enhanced by their large numbers. Moreover, in the absence of rain, spray drops are continually formed on the surface of oceans and large lakes. These spray drops also result in low-velocity impacts. Hence, these experiments do not simulate any dissolution of surfactants which might occur solely as a result of the high kinetic energy of a primary raindrop impact. However, dissolution due to the more numerous low-velocity secondary droplets and spray droplets is addressed.

Small, low-velocity drops have been shown to have a significant effect on mixing of salt and dissolved gases near the air/water interface (Schlüssel et al. 1997; Lange et al. 2000). Indeed, studies of rain-induced mixing near the water surface have shown that the high-velocity impact of the primary raindrop does not significantly contribute to turbulent mixing and transport enhancement. Rather, it is the secondary splash droplets which enhance mixing via the formation of ring vortices (Schlüssel et al. 1997; Rodriguez and Mesler 1988). A similar process may result in the mixing of surfactant monolayers into the bulk. So, while it is clear that bubbles and drop ejections play an important role in the fate of surfactant monolayers during rain events, the question of how low-velocity drops affect monolayers is also relevant.

Related to the above issues is the fundamental question of exactly what sequence of events follows the impact of a drop onto a surfactant-covered surface. The water drop ultimately joins the bulk water beneath the monolayer, but the mechanism whereby it gets past the monolayer is not clear. Perhaps the monolayer separates to permit the drop to join the bulk, and perhaps part of the monolayer is pushed into the bulk. A complete answer to these

questions goes beyond the scope of this work. However, the exploratory study presented herein takes a step toward providing these answers.

Experimental method

The experimental setup used to conduct these experiments is presented in Fig. 1. A drop nozzle made of tapered plastic was connected to a syringe pump via a Teflon tube. The tip of the nozzle was located 32 cm above the water surface. The choice of a 32-cm height was somewhat arbitrary, driven by a desire to attain a high impact velocity, simulating as best as possible the results of Green and Houk (1979) without causing a drop splash.

The syringe pump was set to a flow rate of 21.32 $\mu\text{l}/\text{min}$. The rate at which drops fell at this flow rate varied slightly due to small variations in the drop breakoff dynamics; averaged over 20 drops, the rate was 0.873 drops/min, giving an average separation time of 68.7 s. The average drop diameter was $d=3.6$ mm. Doubly distilled water was used for the drop fluid; surfactants were not introduced in the drop fluid.

The water tank was of glass construction, 98 mm deep and 151 mm by 152 mm on a side. Its volume was 2.25 L. The tank was cleaned and flushed numerous times with doubly distilled water prior to initiation of the experiments presented herein. The inlet and drainage tubes connected to the tank were all made of Teflon and the sealant was RTV silicone rubber which had cured for several weeks prior to these experiments. The entire system was soaked in doubly distilled water for several days before the experiments. The setup was situated in a laminar flow hood, which was kept on during periods when experiments were not being conducted. Doubly distilled

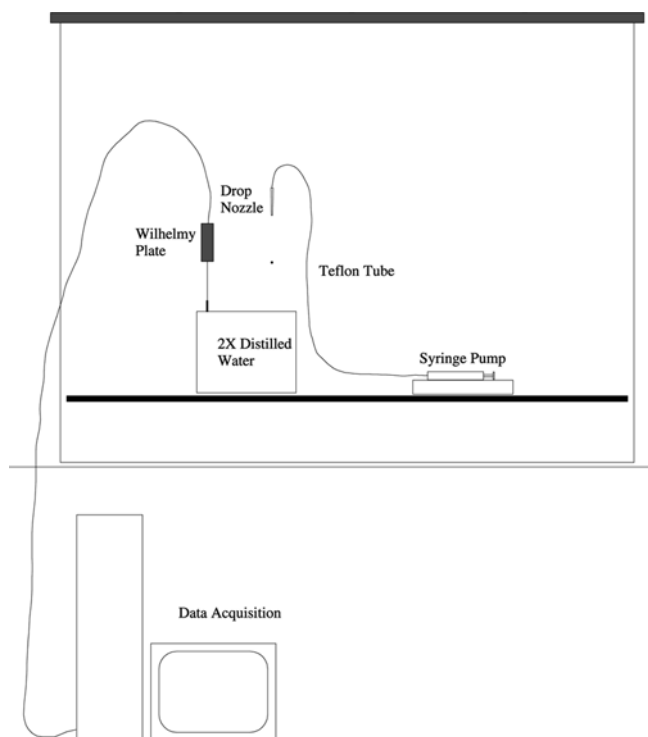


Fig. 1. Experimental setup

water was used in all experiments. Because of these careful procedures, the amount of contaminating surfactants that were inadvertently introduced into the water is expected to be quite small.

An insoluble and a soluble surfactant were tested in these experiments, oleyl alcohol and Triton X-100. These were chosen primarily because they are very well characterized, having been studied under a broad range of conditions. Oleyl alcohol has the additional advantage of exhibiting characteristics which are not dissimilar from the natural surfactants found on the ocean (Barger 1991). The oleyl alcohol experiments were conducted at surface concentrations ranging from $0.01 \mu\text{g}/\text{cm}^2$ to $0.2 \mu\text{g}/\text{cm}^2$ and the Triton X-100 experiments were conducted at bulk concentrations ranging from 0.52 mg/L to 8.32 mg/L . Experiments were also run with a clean water surface.

Monolayers of oleyl alcohol were formed from a concentrated stock solution of oleyl alcohol in high-performance liquid chromatography (HPLC)-grade heptane. The appropriate quantity of this stock solution was deposited on the water surface using a micrometer syringe. The heptane quickly evaporated upon deposition, leaving a monolayer of oleyl alcohol. It was necessary to deposit several drops from the micrometer syringe to create a monolayer having the appropriate concentration. When doing this, each drop was placed on the surface and the heptane allowed to completely evaporate before applying the next drop.

Triton X-100 monolayers were formed by creating a concentrated solution of Triton X-100 in water and adding the appropriate quantity of this solution to the tank water. Care was taken to avoid the generation of bubbles while mixing Triton X-100 since these can retain and slowly release surfactant, thereby changing the monolayer over time. The stock surfactant solutions were stored in glass flasks having ground-glass stoppers. The joints between the stopper and the flask were sealed with paraffin film when not in use to prevent stock concentration changes via evaporation.

The surfactant monolayer was monitored by measuring surface tension using a Wilhelmy plate. The Wilhelmy plate was located near the tank edge to place it as far as possible from the falling drop. Prior to an experiment the Wilhelmy plate was washed with HPLC-grade methanol and then distilled water. It was then attached to the water surface. Periodically, the Wilhelmy plate was flamed to an orange color to eliminate any organic material. During experimental runs data were acquired from the Wilhelmy plate via a computer at a rate of one measurement per second.

Preliminary experiments revealed that a significant length of time was required for a solution of Triton X-100 to attain a steady-state value for surface tension. An example of the surface tension versus time behavior of a 4.16-mg/L solution of Triton X-100 is presented in Fig. 2 for a period of 16 h after monolayer formation. The plot indicates that an asymptotic value is approached after about 13 h, as was typically the case. Accordingly, each Triton X-100 run was conducted after the tank sat overnight. Surface tension data were acquired during these overnight runs and experiments were only conducted the

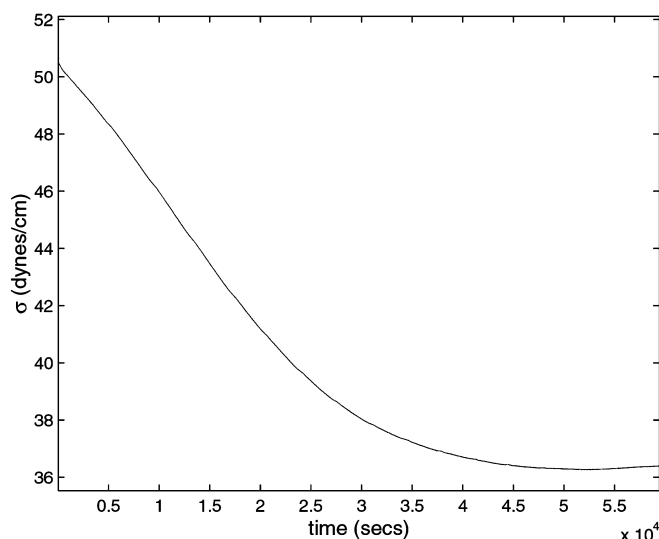


Fig. 2. Long-time stability of Triton X-100. Plot of surface tension σ versus time for a solution having a concentration of 4.16 mg/L

following day if the surface tension had stabilized. Oleyl alcohol achieved stable surface tension values much more rapidly than Triton X-100. For these experiments, the monolayer was deposited and surface tension was typically monitored for an hour. If stable, data acquisition was initiated.

For the experiments presented here, drop impacts were initiated approximately 1 h after data acquisition began. When the syringe pump was turned on, a beaker was used to capture the first several drops so that any contaminants that may have deposited on the water interface at the nozzle tip did not fall on the water surface. Once the drop impacts began, they were maintained for an hour or two and then turned off. Data was acquired for approximately one more hour after the drops were turned off. In this way the behavior of the monolayer was recorded before, during, and after drop impacts, all in a single time trace.

Ripples due to drop impacts on the water surface caused the Wilhelmy plate to oscillate in the vertical direction for a time after each impact. The time between drops was sufficiently long that these ripples dissipated during the intervening period. A larger tank could have been used to conduct these experiments, permitting relocation of the Wilhelmy plate sufficiently far from the drop impact site so that any plate oscillations would be negligible. However, such a setup would not record the behavior of the monolayer near the impact site which, as will be shown below, reveals interesting and different behaviors for the soluble and insoluble monolayer investigated here.

Results

Plots of the long-time behavior of the oleyl alcohol and Triton X-100 monolayers are presented in Figs. 3 and 4, respectively. These plots contain data for the monolayer before, during, and after the drop impact period. Some of the oleyl alcohol plots in Fig. 3 have start times different from zero. These are runs for which a greater period of time was necessary to achieve stability. Data acquired

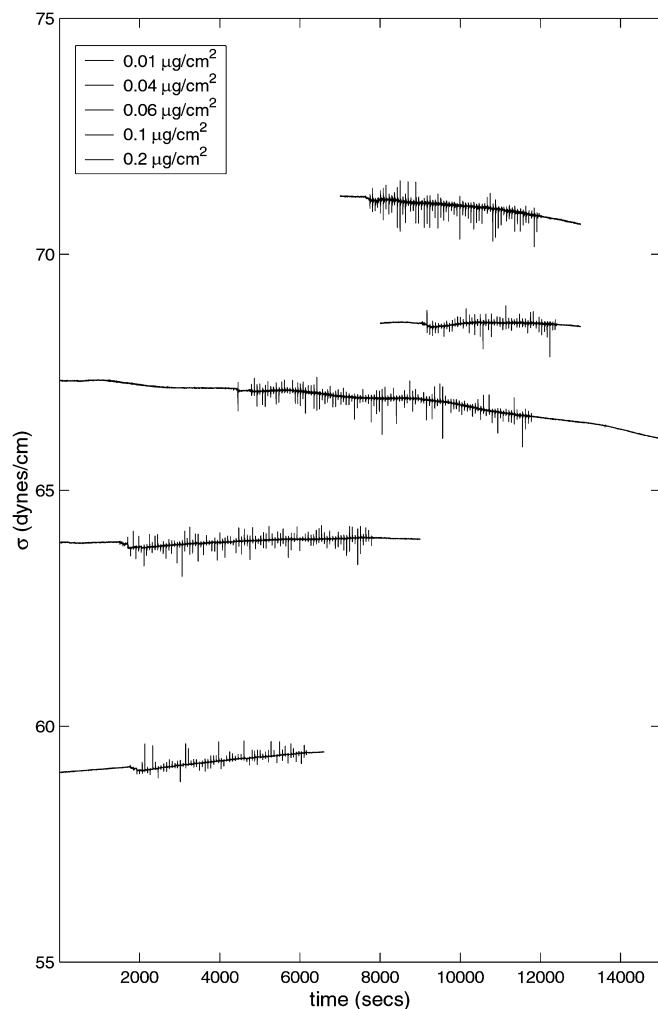


Fig. 3. Plot of surface tension versus time for five different oleyl alcohol monolayers. The concentrations decrease from $0.2 \mu\text{g}/\text{cm}^2$ for the *bottom plot* to $0.01 \mu\text{g}/\text{cm}^2$ for the *top plot*. Data prior, during, and after the initiation of drops is included in each time trace

while significant surface tension changes occurred are omitted in these plots.

For Triton X-100, the monolayer was allowed to stabilize overnight, so $t=0$ s in Fig. 4 occurs after this overnight wait period. For some of the high-concentration Triton X-100 runs, there was still a slow change in surface tension even after the overnight wait period. Waiting for significantly longer periods of time to achieve stability in these cases was not deemed prudent, since changes in the water level due to evaporation and the concomitant change in the Wilhelmy plate reading would have created errors.

In Figs. 3 and 4, drop impacts occur in the central portion of the plots, indicated by spikes in the data. These spikes are a result of Wilhelmy plate oscillation caused by the initial drop impact. The individual oscillations are not observable at the temporal resolution of these plots; however, they can be seen in Figs. 5 and 6, where 1,000-s segments of the drop-containing data are replotted for oleyl alcohol and Triton X-100, respectively. In these two plots, an initial spike in the data is seen at the point in time corresponding to each drop impact. These initial spikes

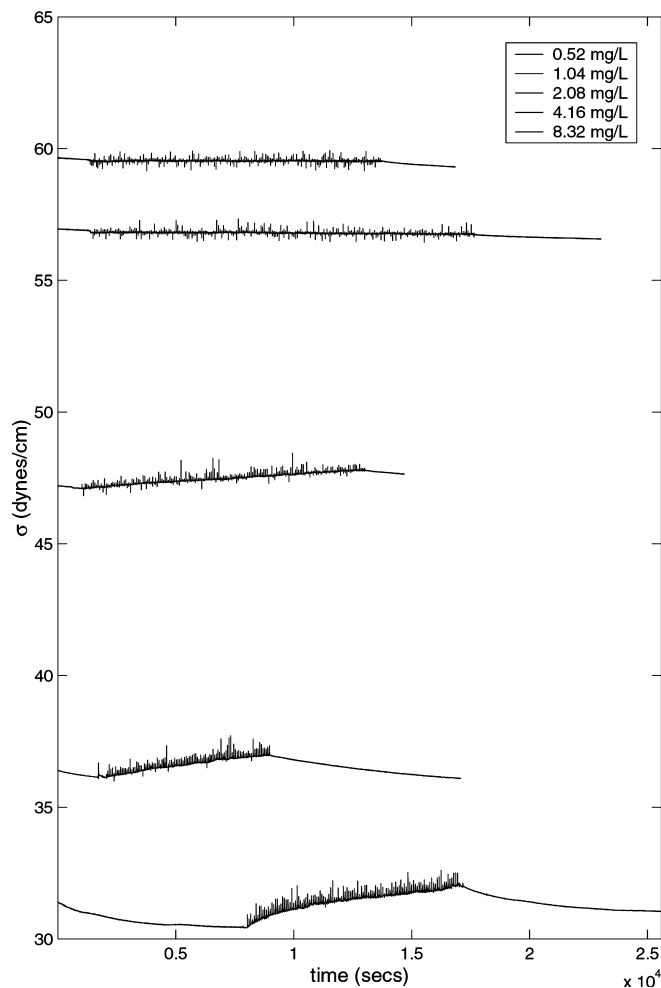


Fig. 4. Plot of surface tension versus time for Triton X-100. Five different concentrations are plotted. The concentrations decrease from 8.32 mg/L for the *bottom plot* to 0.52 mg/L for the *top plot*. Data prior, during, and after the initiation of drops is included in each time trace

are very quick and are not fully resolved at the 1-Hz data acquisition rate employed here. Hence, the spikes are sometimes larger than the mean value and sometimes less than the mean value. A higher sampling rate would most likely reveal a rapid initial oscillation caused by the initial drop impact. For present purposes, these initial spikes serve to identify the point in time at which the drop impact occurred.

After the initial spike in the data, subsequent oscillations of the Wilhelmy plate are reasonably well resolved, as can be seen in the time traces of Figs. 5 and 6. These oscillations are caused by the capillary waves which propagate away from the impact site, causing the Wilhelmy plate to rise and fall. Note that the y-axes presented in these figures are exactly 1 dyne/cm in extent for all plots, allowing easy quantitative comparison of the surface tension variation. The oscillations seen in these figures reveal that the type and concentration of surfactant affects the oscillations. The oleyl alcohol data plotted in Fig. 5 show a progressive reduction in the oscillation amplitude of the plate as the surfactant concentration is increased from 0.0 to $0.2 \mu\text{g}/\text{cm}^2$. For the Triton X-100 data,

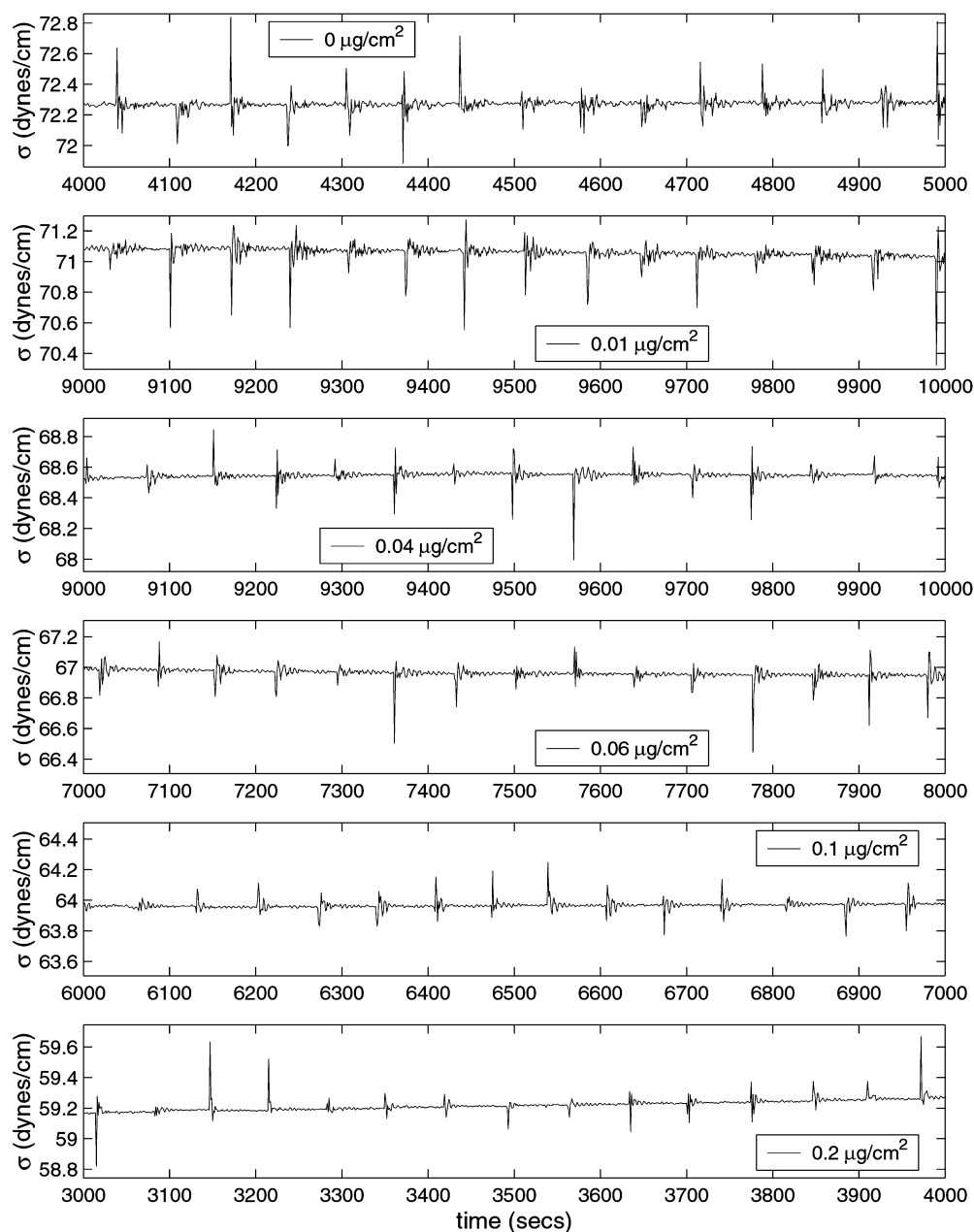


Fig. 5. Plot of surface tension versus time for oleyl alcohol monolayers showing the short-time behavior due to the drop impact. Each plot is a 1,000-s segment taken from the data plotted in Fig. 3. The concentrations are the same as for Fig. 3

presented in Fig. 6, the oscillation amplitude decreases as the concentration increases from 0.00 to about 1.04 mg/L. However, further increases in the concentration result in an increase in the oscillation and a qualitative change in the oscillation pattern, showing an exponential drop in surface tension. Careful observation of these plots, particularly at concentrations of 4.16 mg/L and 8.32 mg/L, reveals that the exponential decay in surface tension displays sudden decrements or downward steps superimposed on the decay. The cause and significance of these results are now discussed.

Discussion

The behavior of each of the two surfactants investigated here is discussed in turn. The surface tension versus time behavior of the oleyl alcohol monolayers presented in Fig. 3 reveal no significant change in surface tension that

can be confidently attributed to the impact of water drops. In these plots, the surface tension changes are slow before, during, and after the drop impacts. The rate of change of surface tension holds constant in sign and magnitude when the drops begin to fall. In some cases, there appears to be a small decrease in surface tension immediately after the first drop strikes the surface, albeit this effect is small. The drop impacts have no effect on the measured surface tension, and hence it seems that the oleyl alcohol monolayer is unaffected by the drop impact. At least for the case of this insoluble monolayer and this height, the drop is somehow able to push the monolayer aside allowing the drop fluid to join the water bulk without pushing the monolayer into the bulk. As mentioned earlier, these experiments were conducted at low impact velocity. It is possible that there would have been dissolution of oleyl alcohol into the bulk had the drop impacts occurred at

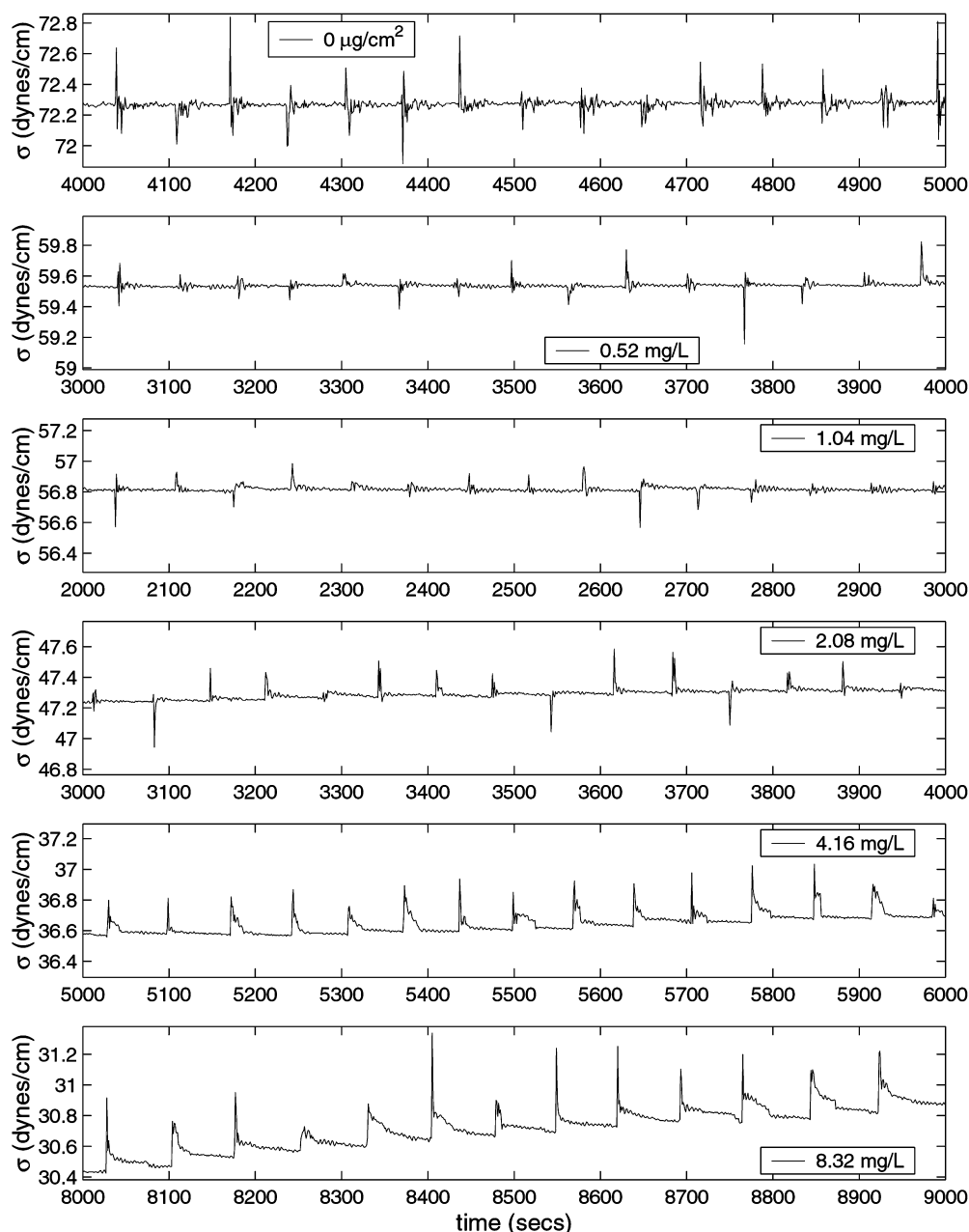


Fig. 6. Plot of surface tension versus time for Triton X-100 monolayers showing the short-time behavior due to the drop impact. Each plot is a 1,000-s segment from the data plotted in Fig. 4. The concentrations are the same as for Fig. 4

terminal velocity; however, this extends beyond the scope of the present work.

The short-time behavior presented in Fig. 5 shows that the presence of the oleyl alcohol monolayer damps out the oscillations of the Wilhelmy plate as the surfactant concentration increases. What is being observed are the well-known wave-damping properties of surfactants (Adamson 1990; Gaines Jr 1966). As the surfactant concentration increases, the waves formed by the drop impact are more effectively damped and the Wilhelmy plate oscillation decreases in magnitude. This is consistent with wave-damping data presented by Henderson (1998), who shows almost no wave damping by oleyl alcohol up until a concentration of 0.08 $\mu\text{g}/\text{cm}^2$, where the damping rises suddenly. In the present data, there appears to be no change in the oscillation of the Wilhelmy plate for concentrations less than 0.06 $\mu\text{g}/\text{cm}^2$. At concentrations greater than

0.06 $\mu\text{g}/\text{cm}^2$, the Wilhelmy plate oscillations decrease significantly, in agreement with Henderson (1998).

Summarizing, the insoluble oleyl alcohol monolayers investigated here are robust. Any slow dissolution of oleyl alcohol into the water was not measurably enhanced by the drop impacts. It would be interesting to repeat these experiments with solid-phase monolayers. These monolayers can collapse when over-compressed. Some solid-phase monolayers like stearic acid show visible striations on the surface when they collapse (Gaines Jr 1966). An experiment with such a monolayer would visually reveal whether drop impacts result in collapse and whether this collapse is permanent or temporary.

These oleyl alcohol results also suggest that the rise in concentration of the insoluble surfactant investigated in the simulated rain event of Green and Houk (1979) was most likely due to splash drops which returned surfactant

to the bulk after rolling down the tank walls. This conclusion cannot be stated with certainty, as the present experiments were conducted using a surfactant different from that used by Green and Houk (1979), although both were of the insoluble type.

The behavior for the soluble surfactant Triton X-100 presented in Figs. 4 and 6 is different from that of oleyl alcohol. Figure 4 shows an increase in the measured surface tension as the clean water drops strike the water surface. When the drops stop, the surface tension returns to its original value or returns to its original rate of change for those high-concentration cases where the surface tension was changing slightly prior to initiation of the experiment. This behavior seems to imply that the clean water drops dilute the soluble surfactant near the water surface. Presumably, diffusion of surfactant from the bulk solution subsequently eliminates any increase in surface tension caused by dilution.

The short-time behavior of Triton X-100 observed in Fig. 6 shows a damping of the Wilhelmy plate motion with increasing concentration for the concentration range 0.0–1.04 mg/L. However, in the concentration range 2.08–8.32 mg/L, a different behavior is observed. Instead of decreasing with increasing concentration, the amplitude of the pulse corresponding to each drop impact increases with concentration. This behavior is consistent with damping of water waves by Triton X-100 (Lapham et al. 2001).

In addition to changes in the Wilhelmy plate oscillation, there is also a qualitative difference in the way the surface tension returns to the pre-drop value for the high-concentration Triton X-100 runs. After the drop impact, the surface tension does not immediately return to the pre-drop value. Instead, the value drops slowly in an exponential fashion. Also, sudden downward steps in the post-drop surface tension decay are observed after some drops, but not after others. The sudden rise and exponential decay in the Wilhelmy plate signal seems to indicate that the Wilhelmy plate is measuring, in that brief interval, an actual rise in surface tension due to dilution of the water near the plate, followed by a diffusive replenishing of Triton X-100 from the bulk. At the highest concentration, it is clear that this diffusive decay does not bring the surface tension to its pre-drop value prior to the next drop impact. This accounts for the net increase in surface tension observed in the long-duration time traces of Fig. 4. Obviously, at a higher drop flux (i.e., more drops per unit area), this rise in surface tension would be even greater.

For some of the high-concentration Triton X-100 runs, bubbles were occasionally observed beneath the drop impact site. This bubble formation did not always occur but was considered a nuisance, since the goal of these experiments was to study the fate of surfactant monolayers without bubbles or drops. These bubbles may explain the step-like decrements in surface tension which are observed during some of the high-concentration runs in the following manner. Any bubble which is formed is certain to bring some of the monolayer into the bulk. The observed bubbles were large and quickly rose back to the water surface. Upon bursting at the surface, the surfactant on the bubble surface should return to the surface, quickly

decreasing the surface tension and explaining the sudden drop in surface tension.

Taken as a whole, these results suggest that for the soluble surfactant Triton X-100, the clean water drops striking the surface increase the local surface tension measurement. This increase is sudden and is followed by a slow decrease in surface tension, which can be explained by diffusion of Triton X-100 from the bulk toward the surface. Hence, these soluble monolayers do not 'spring back' and reform like the insoluble oleyl alcohol monolayers. However, they do seem to reform, albeit by a slower diffusive process.

Conclusion

The experiments presented herein, while preliminary in nature, reveal several interesting results concerning the fate of surfactant monolayers subjected to drop impacts. First, without the formation of bubbles or drops, the insoluble monolayers studied here were robust. After a drop impact, the monolayer seemed to quickly reform, returning the surface tension to pre-drop values. Clean water drops are somehow able to pass through the insoluble monolayer without pushing any of it into the water bulk. In contrast, the soluble monolayer investigated here was affected by the drop impacts. The surface tension increased when clean drops struck the surface, apparently due to a dilution of the near-surface water. When the drops ceased, the surface tension slowly returned to its value prior to the initiation of the experiment. The short-time behavior of the surface tension versus time plots for the soluble surfactant showed an interesting exponential decay, indicating an immediate increase of the surface tension in the region of the drop impact due to dilution, followed by diffusion of surfactant from the bulk to the surface. Further experiments are necessary to more directly relate these results to monolayers subjected to rain on oceans and lakes.

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