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Adsorption of Surface-Active Material at the Surface of Sea-Water Samples from the Bay of Panama

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CONTENTS

Abstract	ii
Problem Status	ii
Authorization	ii
INTRODUCTION	1
MATERIALS AND METHODS	2
EXPERIMENTAL RESULTS	4
ΔF vs Time and ΔV vs Time	4
ΔF vs Area and ΔV vs Area	6
Effect of Stirring on the Rate of Adsorption	10
Effect of Bubbling on the Rate of Adsorption	10
CONCLUSIONS	13
ACKNOWLEDGMENT	17
REFERENCES	18

ABSTRACT

A great variety of surface-active compounds are known to exist in the sea. Under proper environmental conditions, they can adsorb at the surface of the sea, forming the so-called "slicks" that are often observed. The presence of these adsorbed molecules in the interface can cause significant changes in other surface properties besides the damping of capillary waves. Because of their influence on the properties of the sea surface, a study was made of the rate at which these surface-active molecules can accumulate at the water/air interface. Surface tension and surface potential measurements were used to detect the presence of adsorbed material at the surface of sea-water samples. The samples used in the present study were from the Bay of Panama. It was found that periods as long as several hours may be required for sufficient material to adsorb to cause a significant decrease in the surface tension of an undisturbed water sample. The rate of adsorption increased remarkably, however, when a stream of air bubbles was passed through the water, or when the water was stirred vigorously. It was also found that in the Bay of Panama the concentration of surface-active material was rather constant with depth from the surface few inches to a depth of at least 80 ft. Only the very thin layer of water at the interface showed a significantly greater concentration of surface-active material. The results of this study are in good agreement with a similar study of sea-water samples collected near La Jolla, California.

PROBLEM STATUS

This is an interim report; work on this problem is continuing.

AUTHORIZATION

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ADSORPTION OF SURFACE-ACTIVE MATERIAL AT THE SURFACE
OF SEA-WATER SAMPLES FROM THE BAY OF PANAMA

INTRODUCTION

Many phenomena taking place in the sea may be considered as "surface chemical" in nature—for example, damping of capillary waves (1-4), certain changes in surface temperature (5,6), convective movement of surface water (6-8), stability of foams or bubbles at the sea surface (9), and the transport of certain solid particles as well as gases through the interface (10-13). Each of these phenomena may be modified by the adsorption of a film only one molecule thick at the sea/air interface. Such monomolecular films of surface-active material do occur naturally on the surface of the sea, giving rise to the "slicks" that are often observed. Many of the compounds that are present in these slicks have their origin in the broad spectrum of organic materials that occur in the sea. These naturally occurring films arise not only from the living organisms, but also from aggregates of nonliving organic material, and the soluble organic compounds that are present in the sea (11,14,15). The concentration of organic matter in the sea is known to vary considerably with location, but from the results of several studies it is apparent that sufficient organic matter is present in the upper layers of the ocean surface to provide closely packed surface films in most areas under favorable conditions (16,17).

Inasmuch as many properties of the ocean surface are modified by the presence of adsorbed monomolecular films, the rate at which surface-active molecules will accumulate at the interface is of considerable interest. Also of particular interest is the surface concentration of adsorbed molecules that is necessary to modify the various properties of the ocean surface. Two surface-chemistry techniques that can be used to detect the presence of adsorbed molecules at the sea/air interface are surface-tension and surface-potential measurements. The surface-potential measurement will detect any change in the potential of the sea surface that arises from the presence of a permanent dipole moment or a residual charge in an adsorbed molecule. As all surface-active compounds contain one or more polar hydrophilic groups, each molecule will make a contribution to the potential of the sea surface as it adsorbs at the interface. This technique should be well suited for detecting adsorption of the organic materials. We are unable to measure the rate of adsorption at the sea/air interface directly, however, because we do not know the exact composition of the adsorbed monomolecular film, or the specific contribution each molecular specie will make to the surface potential; also we do not know the initial concentration of surface-active material in the sea that is readily available for adsorption.

The surface tension of a sea-water surface is not as sensitive to the presence of small amounts of adsorbed material as is surface potential. In order to have a detectable change in surface tension, a considerable portion of the surface must be covered by adsorbed surface-active molecules. The surface concentration at which a significant change in surface tension is first observed (a change of the order of 0.05 dyne/cm) will be approximately the surface concentration that is necessary to begin modifying other properties of the surface. The two techniques, surface potential and surface tension, thus give somewhat different information regarding the formation of adsorbed films. Surface potential indicates the rate at which molecules are adsorbing at the surface, and surface tension shows approximately when the surface concentration of adsorbed molecules is sufficient to modify many of the properties of the interface.

Not only were changes in the surface potential (ΔV) and surface tension ($\Delta\gamma$) of the adsorbed films observed with time, they were also measured as a function of the area occupied by the film. This measurement was made by first allowing the surface-active molecules in a fresh sample of sea water to adsorb for a certain period of time into a surface of known area. By means of movable barriers the adsorbed molecules were compressed into a progressively smaller area. The changes in surface tension and surface potential were recorded for each compression. From the decrease in area needed to give a significant decrease in surface tension, i.e., to force the adsorbed molecules into an approximately continuous film, one can estimate the amount of film material that had adsorbed into the original area in a specified period of time. The ΔV and $\Delta\gamma$ data obtained upon further compression of the film is useful in characterizing the adsorbed material. It also approximates the changes in ΔV and $\Delta\gamma$ that might occur under natural conditions as the degree of film compression varies. Similar studies were reported earlier (18) for samples of sea water collected from the Pacific Ocean at several locations near Scripps Institution of Oceanography.

MATERIALS AND METHODS

The experimental techniques used in this investigation were the same as those reported in a previous study (18). In the present study, samples were collected from several locations in the Bay of Panama. Upon completion of sampling, the water was transported as rapidly as possible to the laboratory for study. In general the samples were in the laboratory within one hour after sampling. The depth of sampling was varied from the surface to 60 ft. One surface sample was collected using the screen technique of Garrett (19), in which a layer of surface water approximately 0.008 in. thick is isolated. Other surface samples were collected by partly immersing the polyethylene bottles in water 0 to 3 in. deep. The subsurface water samples were collected in 16-liter VanDorn water samplers and transported in clean five-gallon polyethylene bottles. The experiments were carried out at the Canal Zone Corrosion Laboratory of the U.S. Naval Research Laboratory, in facilities located on Naos Island in the Bay of Panama. The sample depth, area of sampling, and the state of the sea surface at the time of sampling are given in Table 1.

The adsorption studies were carried out as described earlier (18). The samples were confined in a Lucite trough 72.8 cm long, 12.3 cm wide, and 15.0 cm deep. Rectangular glass rods were used as barriers to compress the adsorbed film, and a centimeter rule was attached to the side of the tray to record the barrier position. The glass barriers and the upper edges of the Lucite tray were coated with a thin layer of paraffin to produce highly hydrophobic surfaces.

The surface tensions of the sea-water samples were determined by the Wilhelmy plate method (20), the platinum plate being suspended from a lever arm attached to a calibrated torsion wire. Changes in surface tension were determined by noting the rotation of the torsion wire necessary to maintain the platinum plate at a constant depth in the water. To insure that the plate would be completely wetted by the sea water, it was rinsed with distilled water after each run and heated to red heat. By using this technique, surface tensions could be measured to within ± 0.05 dyne/cm. Surface potential measurements were made with the ionizing electrode method (21,22) using a 2×2 in. brass plate having one surface covered with thin strips of polonium 210. The alpha radiation from the polonium ionized the air gap between the electrode and water and permitted a small current to flow between the two surfaces. The difference in potential between the water and the electrode was measured with a Keithley electrometer to a precision of ± 1 millivolt. The surface potential was recorded continuously with a Varian recorder. During these experiments the laboratory temperature was $20^\circ \pm 1^\circ \text{C}$.

In the laboratory, each sample of sea water was placed in a Lucite film trough, and the surface was cleaned by sweeping with the glass barriers. Usually five or six passes

Table 1
Sea-Water Samples, March and April 1965

Sample No.	Date	Sampling Location in Bay of Panama	Sample Depth	Sea Surface Condition
1	Mar. 29	12 mi south Panama City, R.P. 4 mi east San Jose Rock	20 ft	No visible slicks, water choppy
2	Mar. 29	Same as 1	30 ft	Same as 1
3	Mar. 30	Same as 1	30 ft	No visible slicks, white caps visible
4	Mar. 30	Same as 1	0-3 in.	Same as 3
5	Mar. 31	12 mi south Panama City, R.P. 5 mi east San Jose Rock	50 ft	Same as 3
6	Mar. 31	Same as 5	0-3 in.	Same as 3
7	Apr. 1	NRL Corrosion Pier	5 ft	Slicks in area, water calm
8	Apr. 2	12 mi south Panama City, R.P. 6 mi east San Jose Rock	60 ft	No visible slicks, occasional white caps
9	Apr. 3	Same as 8	10 ft	Some slicks visible, occasional white caps
10	Apr. 3	Same as 8	10 ft	Same as 9
11	Apr. 5	10 mi south Panama City, R.P. 3 mi south San Jose Rock	0-3 in.	No visible slicks, water choppy, white caps
12	Apr. 5	Same as 11	40 ft	Same as 11
13	Apr. 6	In lee of Taboguilla Island (1/2 mi south)	Surface screen sample (0.008 in.)	Slicks in area, surface very calm
14	Apr. 6	Same as 13	0-3 in.	Same as 13

with the barrier were sufficient to clean the surface; i.e., there was no further increase in surface tension with subsequent sweeping. At this point the surface tension was that of clean sea water. As the initially adsorbed film was swept from the water surface, the surface-potential difference between the electrode and the water surface approached a constant value. This initial surface potential was assumed to be that of a clean surface and was used as the zero or reference potential, V_0 . After the surface tension and surface potential were determined for the clean surfaces, the samples were allowed to stand, and changes in surface tension ($\Delta\gamma = \gamma_0 - \gamma$) and surface potential difference ($\Delta V = V - V_0$) were recorded as a function of time. The decreases in surface tension were

plotted as changes in film pressure ($\Delta F = \gamma_0 - \gamma$). During the measurements, the film-balance troughs were enclosed in clean Lucite covers to prevent contamination of the water surfaces by airborne particles. When the ΔF -vs-time and ΔV -vs-time curves were completed, the surface-active materials adsorbed at the interface were compressed to progressively smaller areas, and ΔF and ΔV were recorded as functions of the area occupied by the film. The adsorbed film was allowed to equilibrate for one to two minutes after each movement of the barrier.

In the procedures outlined above for studying changes in ΔF and ΔV with time, the samples were allowed to stand undisturbed, and presumably diffusion was the primary means by which surface-active material accumulated at the interface. In practice, however, the surface of the ocean seldom remains undisturbed for any length of time. Due to the action of the wind and waves, there can be considerable turbulence in the surface layer. To simulate this condition in a simple laboratory experiment, several of the samples were stirred mechanically while ΔV and ΔF were recorded as a function of time. The stirring rod was a 1/4-in. stainless steel rod with a V-shaped bend near the bottom. The rate of stirring was controlled by a variable-speed motor. In addition to diffusion, it has also been postulated that surface-active material can be brought to the interface by gas bubbles rising to the surface. Experiments were therefore carried out to see what effect air bubbles might have on the rate of accumulation of the surface-active material. A glass tube was attached to a small air pump and was immersed in the sea water sample. A stream of air bubbles was released into the sample as ΔF and ΔV were recorded as a function of time. The rate of bubbling was closely controlled.

EXPERIMENTAL RESULTS

ΔF vs Time and ΔV vs Time

Changes in surface tension and surface potential with time were determined for most of the samples as they were allowed to stand undisturbed. Figure 1 gives the ΔF -vs-time and ΔV -vs-time curves for samples collected at various depths beneath the sea surface. All samples listed in Fig. 1, with the exception of No. 7, were from approximately the same location in the Bay of Panama, 12 mi south of Panama City, R.P., and from 4 to 6 mi east of San Jose Rock. This is 6 to 8 mi upwind and upcurrent from the area normally used by ships transiting the Panama Canal, and should be relatively free of man-made contamination. The water was of rather uniform temperature, the water at 80 ft being only one to two degrees cooler than the surface water. The water appeared to contain a large number of planktonic organisms and was quite turbid, generally giving a Secchi disc reading of approximately 15 ft. The condition of the sea surface at the time of sampling was about the same for each sample listed in Fig. 1, with the exception of No. 7. The wind varied from about 5 to 15 knots and generally small white caps were visible. No slicks were observed in the sampling area.

The ΔF -vs-time curves in Fig. 1a show little variation among the samples. None of the samples gave a film pressure of even 0.2 dyne/cm after two hours, and only after about three hours did two of the samples show film pressures approaching 0.3 dyne/cm. These data indicate that there is definitely surface-active material present in bulk sea water, but that on standing undisturbed, it can take anywhere from 20 min to several hours before a significant reduction in surface tension will be observed. In view of the large number of organisms present in the water of the Bay of Panama, it is surprising that close-packed films of highly, surface-active material did not occur more rapidly. It is possible that many of the highly surface-active molecules have been previously adsorbed on the particulate material in the sea and are not available for adsorption at the sea/air interface. It is also possible that much of the material initially adsorbed at the sea surface is somewhat soluble and therefore is not highly surface active. If this is the case, a certain amount of time may be required for those materials to be replaced at the interface by the more surface-active compounds.

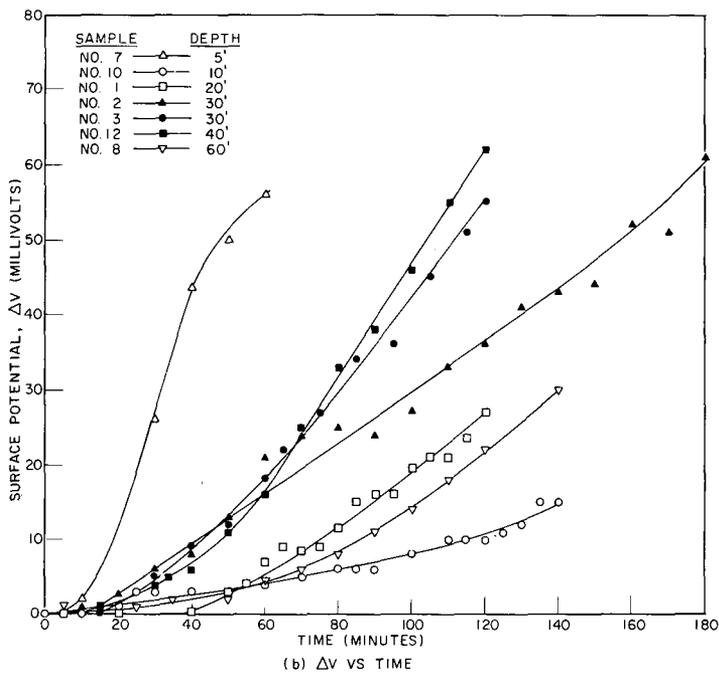
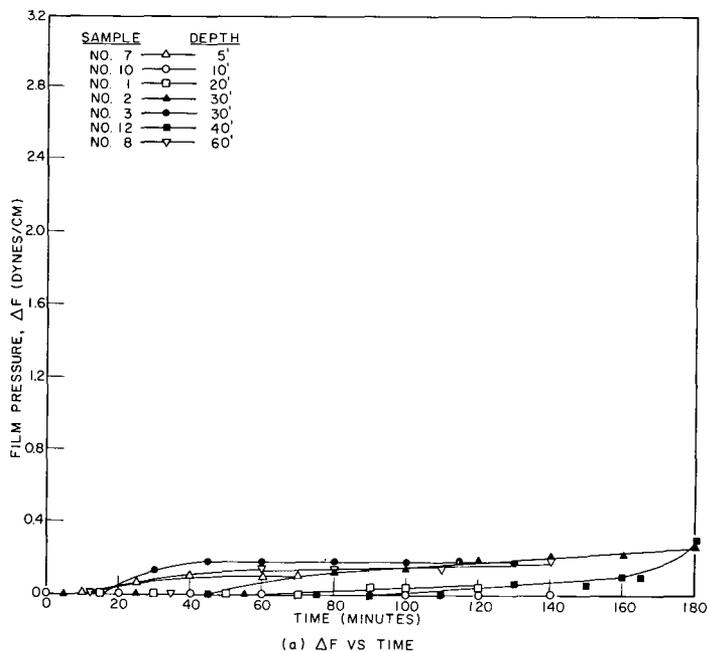


Fig. 1 - Change in film pressure (a) and surface potential (b) of a sea-water surface with time as surface-active contaminants adsorb at the interface. Samples collected at various depths beneath the surface.

Figure 1b indicates that surface potential is more sensitive to the presence of small amounts of adsorbed material than is surface tension and also shows an apparent correlation with depth. Although each of the samples had a ΔF of less than 0.2 dyne/cm after two hours, ΔV changes as high as 60 millivolts were observed. The ΔV of sample 7 appears to be abnormally high. As this sample was collected from the NRL corrosion pier very near shore, it quite possibly could be contaminated, or at least could contain somewhat different materials than the samples collected further away from shore.

In Fig. 2a the F -vs-time curves are given for the samples collected near the interface. The curves for the surface samples collected by partly immersing a sample bottle (the 0 to 3 in. samples) are generally indistinguishable from the ΔF -vs-time curves for the deeper samples given in Fig. 1a. This fact indicates that the concentration of surface-active material that is readily available for adsorption is rather constant with depth, up to very near the surface. The composition of the surface layer itself, however, may be quite different. Sample 13, obtained using Garrett's screen technique, which isolates a thin layer of surface water (less than 0.008 in.) including the adsorbed film, gave a much different ΔF -vs-time curve. After standing 20 min, it had developed a film pressure of 2.6 dynes/cm, and at the end of an hour, a film pressure over 12 dynes/cm. This high value demonstrates the selectivity of adsorption at an interface, the less surface-active materials that were initially adsorbed at the surface having been replaced by those which are more strongly adsorbed. This action is particularly evident when comparing sample 13 with sample 14, a 0 to 3 in. sample collected in the same location and at the same time as the screen sample. The ΔV -vs-time curves in Fig. 2b are also quite similar to those given in Fig. 1b for the subsurface samples, with the exception of sample 13.

ΔF vs Area and ΔV vs Area

The sea-water samples remained undisturbed in the film trays while ΔV and ΔF were recorded as a function of time. During this time the surface-active materials were allowed to adsorb into an area of approximately 800 sq cm. The adsorbed film was then gradually compressed into an area of only 204 sq cm, while film pressure and surface potential were measured as a function of the area occupied by the film. Figure 3 gives the ΔF and ΔV values determined for films of sample 5 as they were compressed. The adsorbed film was not swept from the surface after each run; rather it was expanded and allowed to age until the next compression. The data in Fig. 3 show that when an adsorption time of 25 min was allowed, relatively little stable, film-forming material was present. Even after being compressed to 204 sq cm, a film pressure of only 0.5 dyne/cm and a surface potential difference of only 80 millivolts were observed. The longer the surface face of the sample was allowed to stand undisturbed, the greater were the measured values of surface potential and surface tension. The ΔV -vs-area curves in Fig. 3b appear to be approaching a limiting value of about 320 millivolts after 120 min, although the film pressure is still rather low. It should be recognized that as the adsorbed molecules approach close-packing, small changes in area per molecule can cause large changes in ΔF without altering ΔV appreciably.

The data given in Fig. 3 for sample 5 are for water from a depth of 50 ft. Figure 4 shows analogous data for a sample of water from the surface 0 to 3 in. The curves in each case are quite similar with the subsurface sample in Fig. 3a showing a slightly greater concentration of readily adsorbable material. In Figs. 3 and 4, each of the ΔF -vs-area curves gave approximately the same film pressure at 800 sq cm. Not until the films were compressed did the differences in film concentration become apparent. This fact suggests that the initially adsorbed films were mixtures of a number of surface-active species, varying from soluble, slightly surface-active components to highly surface-active insoluble ones. As the films were compressed, the somewhat soluble and less stable materials were forced out of the interface. This action left the surface rich in the more surface-active components. It was also observed that the relative amount of stable film-forming material at the interface increased with film age, indicating that the initially adsorbed soluble or slightly soluble material was gradually being replaced.

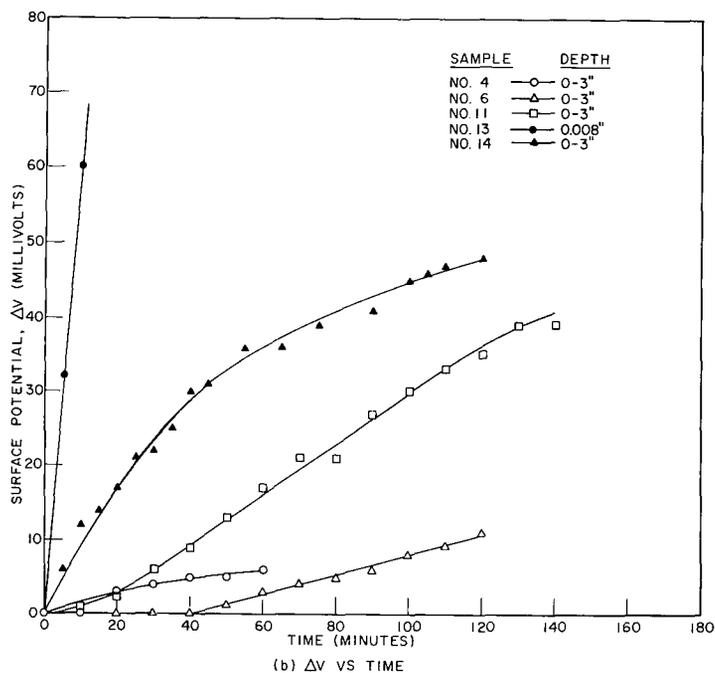
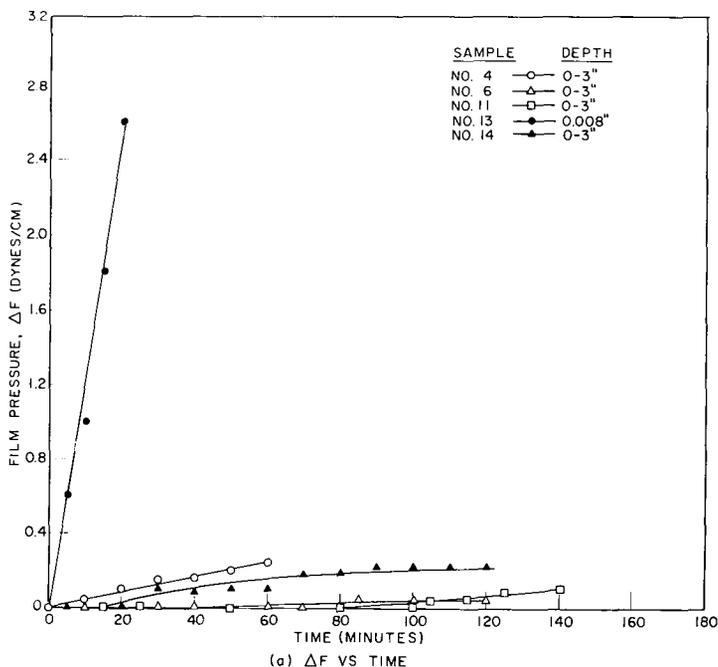


Fig. 2 - Change in film pressure (a) and surface potential (b) of a sea-water surface with time as surface-active contaminants adsorb at the interface. Samples collected from sea surface.

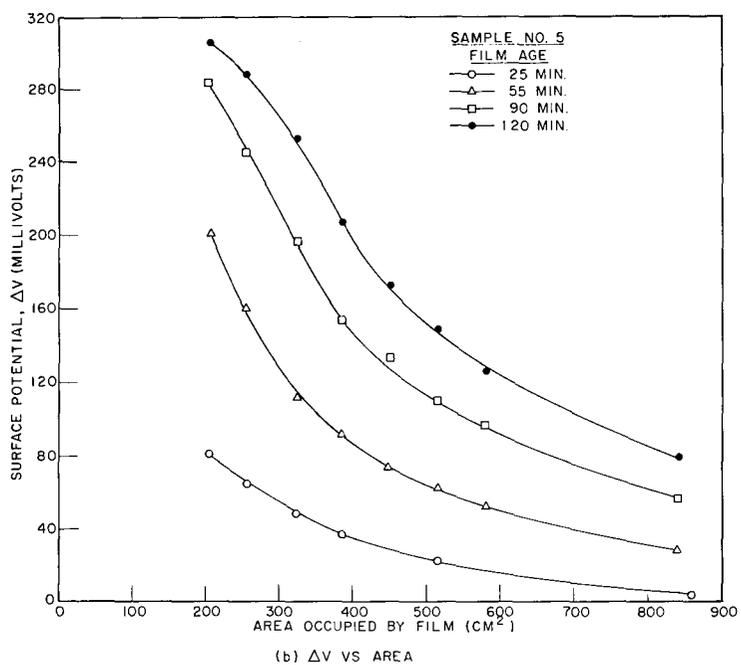
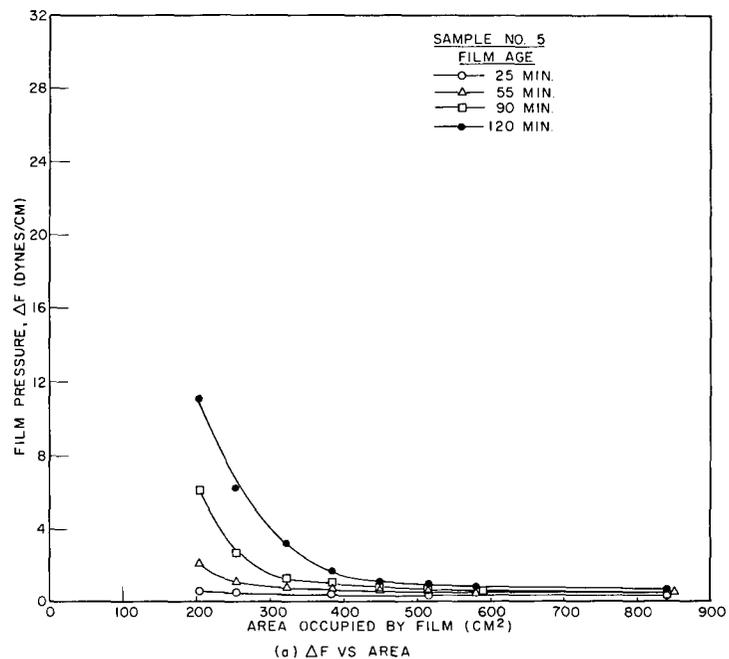


Fig. 3 - Film pressure (a) and surface potential (b) as a function of film age and the area occupied by the adsorbed molecules (sample 5)

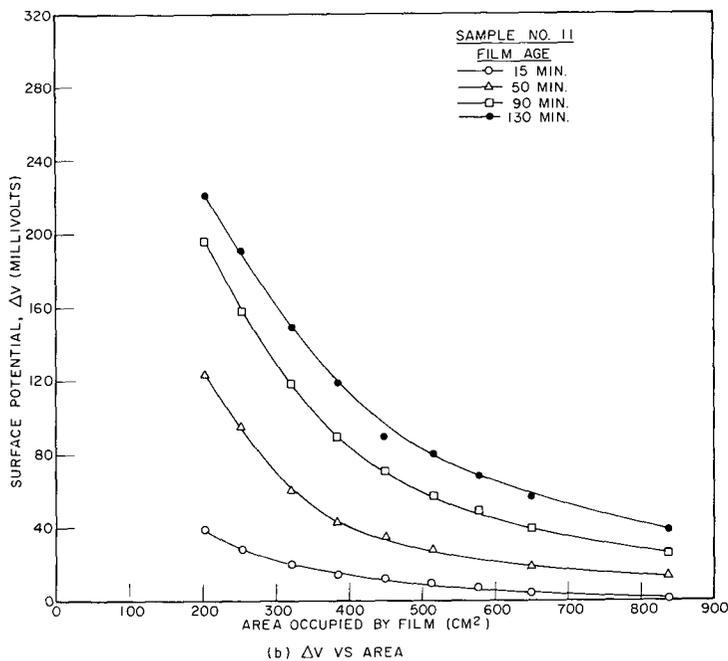
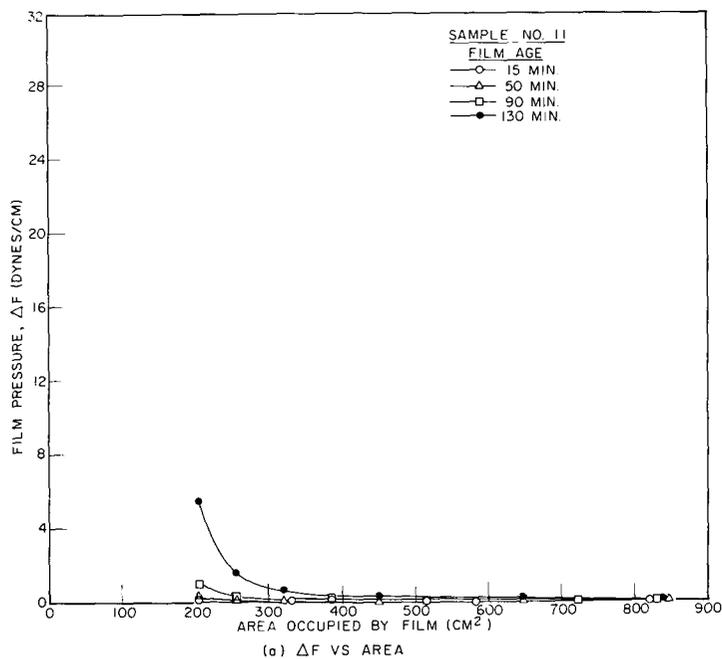


Fig. 4 - Film pressure (a) and surface potential (b) as a function of film age and the area occupied by the adsorbed molecules (sample 11)

Curves of ΔF vs area and ΔV vs area are given in Figs. 5 and 6 for the films adsorbed at the surfaces of several water samples after standing undisturbed for two hours. It is apparent in Fig. 5 that each subsurface sample, except No. 10 and perhaps No. 8, gave about the same ΔF and ΔV behavior upon compression. Sample 10 had significantly less material adsorbed at the interface. Analogous data for the surface samples, 6, 11, and 14 in Fig. 6, were similar to the data for the subsurface water samples. The exception is the surface screen sample, No. 13, which was shown in previous figures to have a substantially higher concentration of film-forming material. In general it can be concluded that there is little difference in concentration of surface-active material between the subsurface samples and those collected from the few inches below the surface; a significantly higher concentration occurs at the interface itself.

Effect of Stirring on the Rate of Adsorption

The stirrer was mounted at the opposite end of the film tray from the tensiometer and surface-potential electrode. This arrangement was to minimize the effect of surface waves created by the movement of the stirring rod. The stirring action caused a general circulation of water away from the stirrer along the bottom of the trough, and toward the stirrer near the surface. In addition to this general flow of water, there was considerable turbulence observed in the bulk water. The average rate of movement of the water increased with increasing rate of stirring. At 1500 rpm the general rate of movement of particles suspended in the water was of the order of 5 to 10 cm/sec, while at 200 rpm, the particles were observed to move more slowly, on the order of 0.1 cm/sec. At 1500 rpm particles very near the interface seemed to be in rapid motion, whereas at the slower rates of speed, they moved sluggishly.

In the absence of stirring, there was no measurable film pressure for sample 9 after 30 min, as recorded in Fig. 7. The surface potential, however, increased 20 millivolts in the same period of time, indicating that some adsorption had taken place. Increasing the rate of stirring to 200, 540, or 800 rpm did not make an appreciable change in the ΔV -vs-time curves, although it did cause an increase in ΔF to about 0.2 dyne/cm at the end of 30 min. Only at the stirring rate of 1500 rpm were marked changes in the ΔF and ΔV curves observed. This increase at 1500 rpm could be due to some of the larger suspended particles being broken up by the rapid agitation. It is also possible that the rapid rate of stirring is influencing the surface-boundary layer thickness, effectively reducing the length of time necessary for the molecules to diffuse to the surface. Figures 8a and 8b shows the effect of different stirring rates on the ΔF -vs-area and ΔV -vs-area curves of sample 6. Again only at the higher rates of stirring were there indications of a significant increase in surface-active material at the interface.

Effect of Bubbling on the Rate of Adsorption

Previous studies have shown that surface-active material present in sea water will adsorb at the surface of air bubbles (10,11,12,15). As these air bubbles burst upon reaching the surface, they should release much of their adsorbed surface-active material to the interface. If this is true, then one would expect that when a stream of air bubbles is passed through a water sample, the rate at which the surface-active materials accumulate at the interface should be much greater than when simple diffusion is the only means of molecular transport. Figure 9 shows the effect of bubbling on surface tension and surface potential. The bubbling rate was varied from 0 to 200 bubbles per minute. In the absence of bubbling, ΔF and ΔV were only 0.1 dyne/cm and 3 millivolts, respectively, at the end of 30 min. Each increase in bubble rate caused an increase in the rate of change of surface potential, a rate of 200 bubbles per minute giving rise to a ΔV of more than 100 millivolts in less than 20 min. The changes in ΔF vs time with bubble rate were less pronounced, although they did show a regular increase with increasing rate of bubbling.

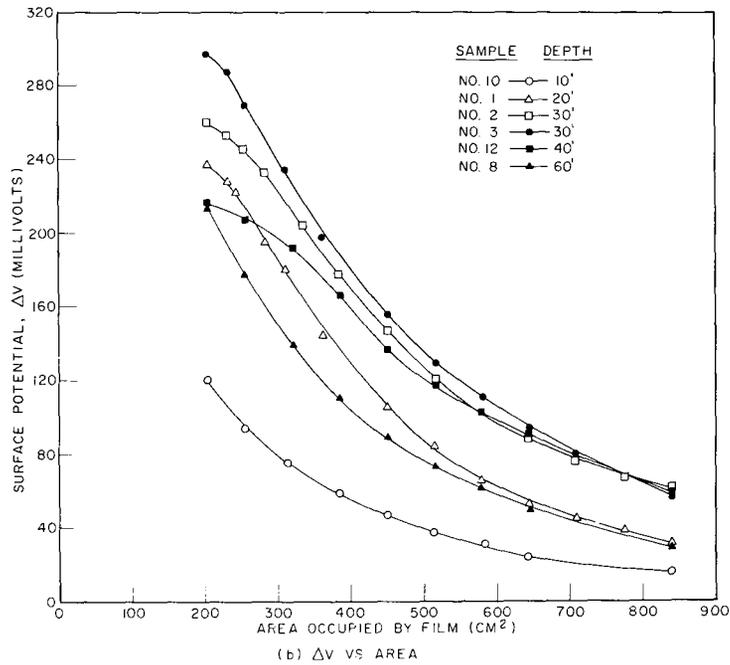
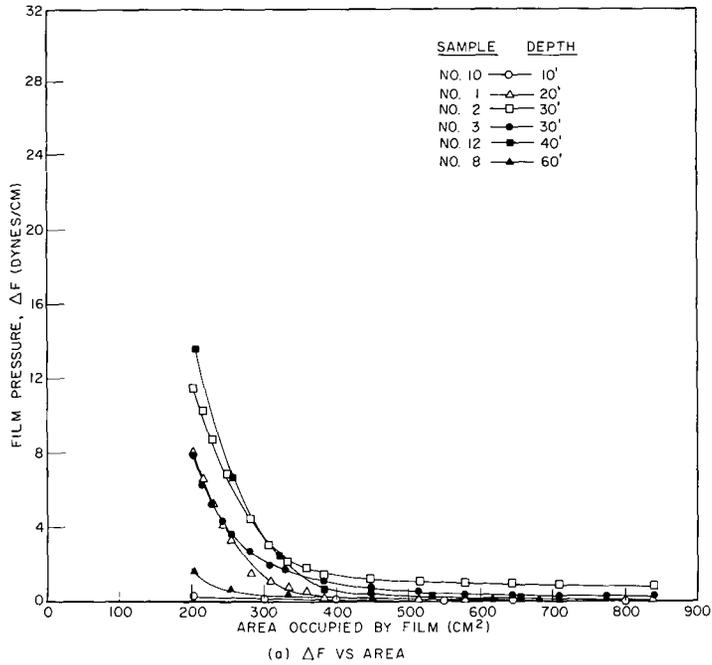


Fig. 5 - Film pressure (a) and surface potential (b) as a function of the area occupied by the adsorbed monomolecular film. Sea-water samples collected at various depth (film age two hours).

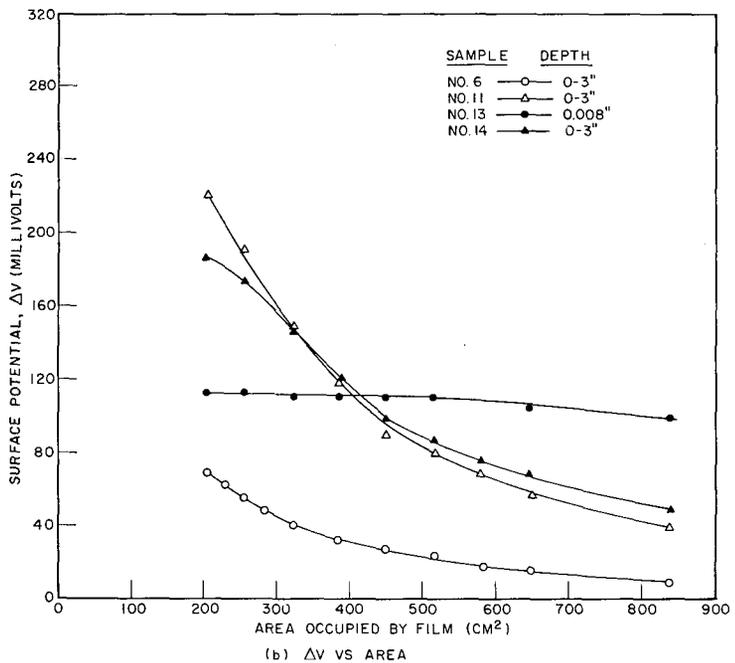
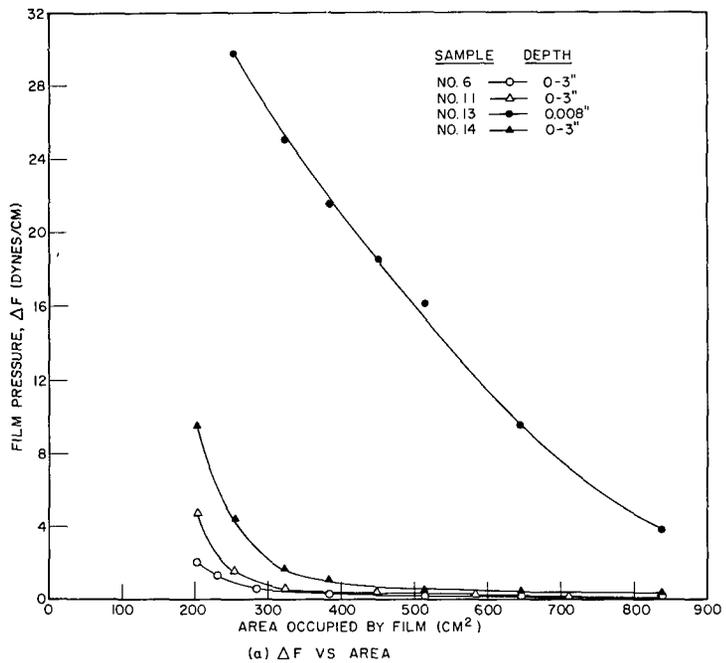


Fig. 6 - Film pressure (a) and surface potential (b) as a function of the area occupied by the adsorbed monomolecular film. Sea-water samples collected from sea surface (film age two hours).

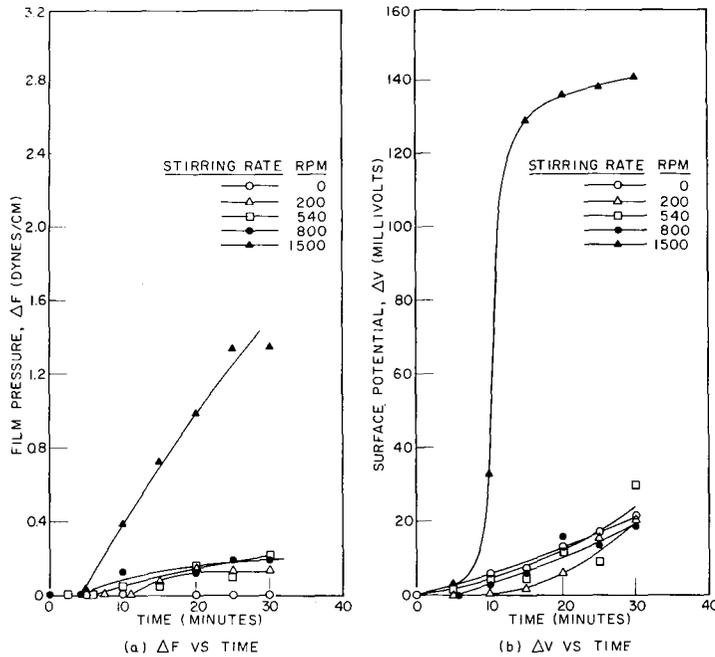


Fig. 7 - Effect of stirring upon the rate of adsorption of surface-active material at the surface of sample 6. ΔF -vs-time (a) and ΔV -vs-time (b) curves as a function of rate of stirring.

Figure 10a and 10b indicates the amounts of material adsorbed at the surface of sample 9 when air bubbles are passed through the sample at various rates. After 30 min with no bubbling, the surface area could be reduced from over 800 sq cm to about 200 sq cm with no marked change in ΔF , and an increase in ΔV of about 115 millivolts. As the bubbling rate increased to 200 per minute, a similar decrease in area gave rise to ΔF and ΔV changes of 9 dynes/cm and 250 millivolts respectively. It appears that ΔV is actually approaching a maximum somewhere near 250 millivolts, even though the ΔF -vs-area curves do not indicate that the adsorbed film has reached its closest molecular packing. Comparable ΔF -vs-area and ΔV -vs-area data in Fig. 8 for different rates of stirring indicate that the surface films generated by bubbling and stirring may have somewhat different compositions. The ΔF values obtained in the stirred samples were higher than those measured after bubbling, but their maximum surface potentials were considerably less. The surface potential of the stirred sample 6 appeared to reach a maximum of 180 to 190 millivolts, well below the apparent maximum value of 250 to 320 millivolts observed with all but the surface screen sample.

CONCLUSIONS

The results of this study show that sufficient surface-active material was present in the water of the Bay of Panama to form continuous close-packed monomolecular films at the sea surface, provided sufficient time was allowed for the material to accumulate at the interface. The surface-potential data indicate that detectable amounts of surface-active materials began adsorbing at the interface within minutes after the surface was cleaned. Detectable changes in film pressure occurred more slowly; often more than 60 min elapsed before significant film pressures were observed. The one surface-water sample collected by the screen technique apparently contained a considerably higher concentration of surface-active material than the other samples, since its surface potential

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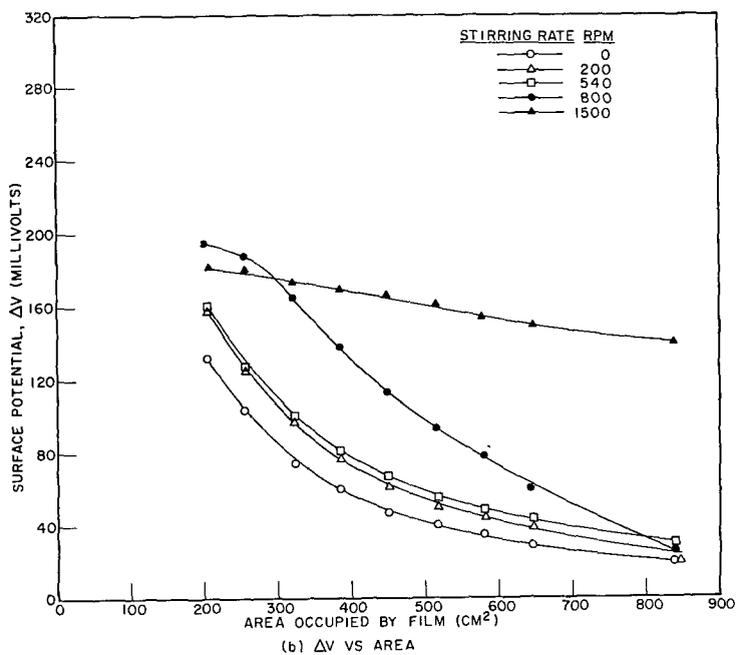
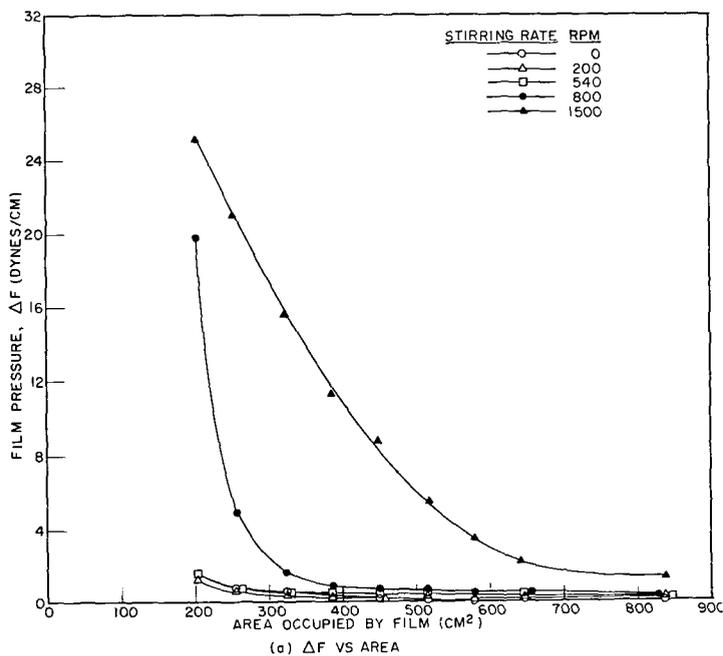


Fig. 8 - Effect of stirring upon the rate of adsorption of surface-active material at the surface of sample 6. ΔF -vs-area (a) and ΔV -vs-area (b) curves as a function of rate of stirring (film age 30 min).

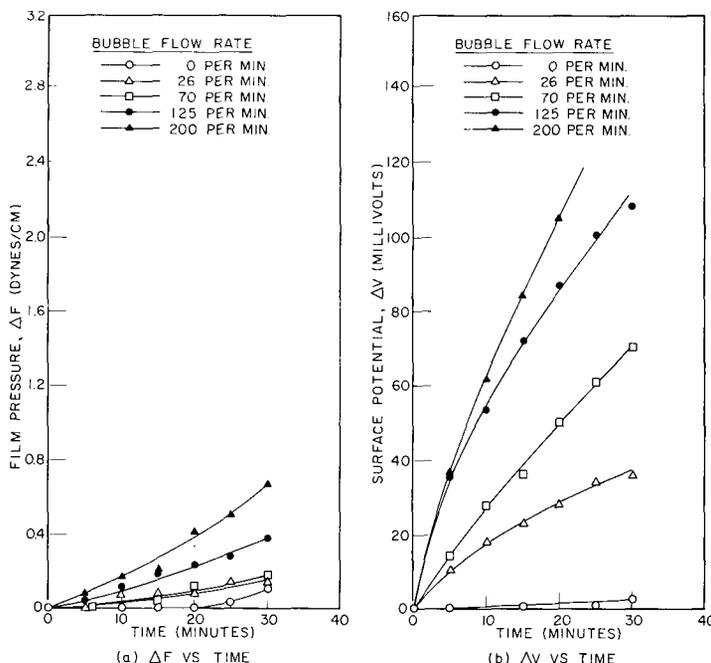


Fig. 9 - Effect of bursting bubbles on the rate of adsorption of surface-active material at the surface of sample 9. ΔF -vs-time (a) and ΔV -vs-time (b) curves as a function of the rate of bubbling.

and surface tension increased rapidly with time. There appeared to be no important differences in ΔF and ΔV between the subsurface water samples and those collected from the surface 0 to 3 in. The present data on the changes in ΔF and ΔV as functions of time and area are also in good agreement with the results of similar experiments performed on sea-water samples collected near Scripps Institution of Oceanography. This agreement would indicate that the amounts of readily adsorbable material present in the water at each location are not greatly different.

Experiments also indicated that agitation of the water samples, either by rapid stirring or by bubbling air through them, would markedly increase the rate of accumulation of surface-active material at the interface. An increase in ΔF and ΔV due to stirring was observed, however, only when the water was stirred rather vigorously (a stirring rate of about 1500 rpm). The increase in adsorbed material with stirring rate may possibly arise from the physical dissociation of particles in the water due to the rapid agitation, or to an apparent thinning of the unstirred water layer very near the surface. Even low rates of bubble formation, however, caused significant increases in the appearance of surface films. The ΔF -vs-area and ΔV -vs-area curves for films obtained using these two techniques were quite dissimilar, those formed by bubbling giving higher ΔV values and lower ΔF values with compression of the film.

Garrett and Bultman (1) have shown, from studies of insoluble monomolecular films, that the damping of capillary waves by such films is related to the compressibilities of the adsorbed film, and that the necessary compressibility is reached at rather low film pressures, approximately 0.2 dyne/cm. On this basis, it is estimated that most of the samples studied would not have given rise to films capable of damping capillary waves even after standing undisturbed for upwards of two hours. In most cases, a certain compression of the film would have been necessary, the degree of compression required varying with the concentration of material adsorbed at each surface.

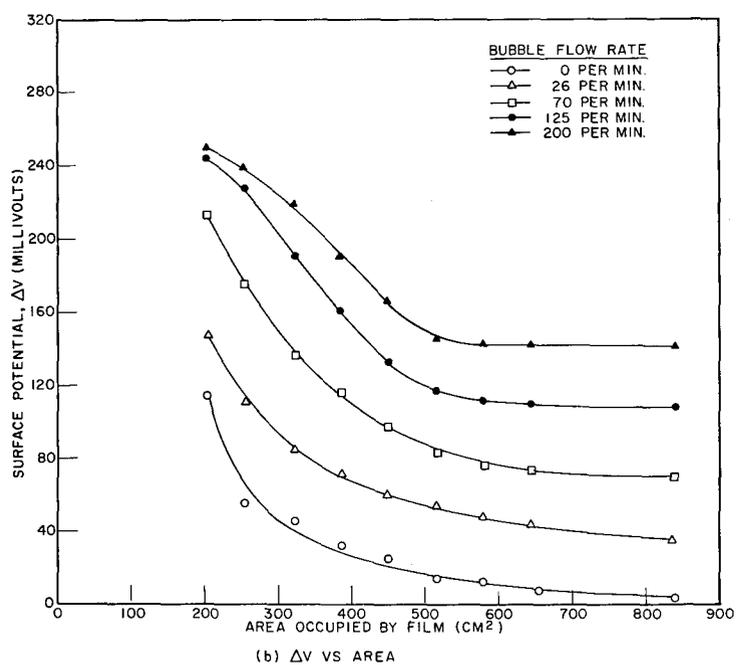
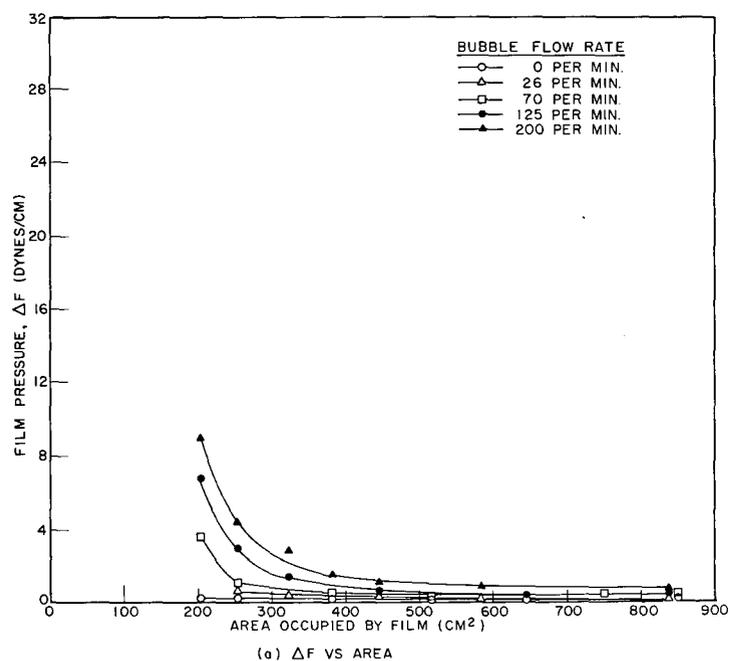


Fig. 10 - Effect of bursting bubbles on the adsorption of surface-active material at the surface of sample 9. ΔF -vs-area (a) and ΔV -vs-area (b) curves as a function of the rate of bubbling (film age 30 min).

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13. ABSTRACT A great variety of surface-active compounds are known to exist in the sea. Under proper environmental conditions, they can adsorb at the surface of the sea, forming the so-called "slicks" that are often observed. The presence of these adsorbed molecules in the interface can cause significant changes in other surface properties besides the damping of capillary waves. Because of their influence on the properties of the sea surface, a study was made of the rate at which these surface-active molecules can accumulate at the water/air interface. Surface tension and surface potential measurements were used to detect the presence of adsorbed material at the surface of sea-water samples. The samples used in the present study were from the Bay of Panama. It was found that periods as long as several hours may be required for sufficient material to adsorb to cause a significant decrease in the surface tension of an undisturbed water sample. The rate of adsorption increased remarkably, however, when a stream of air bubbles was passed through the water, or when the water was stirred vigorously. It was also found that in the Bay of Panama the concentration of surface-active material was rather constant with depth from the surface few inches to a depth of at least 80 ft. Only the very thin layer of water at the interface showed a significantly greater concentration of surface-active material. The results of this study are in good agreement with a similar study of sea-water samples collected near La Jolla, California.			

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Adsorption Surface-active substances Air-sea interface Monomolecular films Sea water Surface tension Surface potential						

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