NRL Report 6337

# The Damping of Capillary Waves at the Air/Water Interface by Naturally Occurring Surface-Active Material

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**Washington, D.C.**

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## ABSTRACT

The damping of capillary waves was measured on fresh sea water, sampled from the Bay of Panama under various oceanographic conditions. The collected water contained varying quantities of surface-active organic materials capable of adsorbing at the air/water interface and altering the surface properties. In some instances, compression of the adsorbed film was necessary to cause increases in the damping coefficient and the film pressure after a one-hour surface aging period. Other samples contained little surface-active material, and no changes in the surface properties resulted with a 5-to-1 compression of an aged surface.

Agitation, thermal currents, and bubbling were studied as mechanisms for the transport of film-forming material from the bulk water to the surface. Large increases in the rate of film accumulation occurred when these mechanisms were applied. Under static conditions the adsorption rate was quite slow since it was controlled by molecular diffusion.

Simultaneous measurements of damping coefficient and film pressure indicated that wave damping commenced at a film pressure of a few tenths of 1 dyne/cm and increased to a maximum value of from 0.39 to 0.44 $cm^{-1}$ in the neighborhood of 1 dyne/cm. As the film pressure was increased further by compression of the surface film, the damping coefficient decreased to a value of about 0.26 $cm^{-1}$ and became constant when the film pressure had reached 2 dynes/cm. In marked contrast, the damping coefficient measured on the clean sea water surface was 0.08 $cm^{-1}$.

It was postulated that a portion of the wave energy loss was due to a viscous drag of the associated chains of water molecules which were bonded to the molecules of the adsorbed surface film. The drag occurs when the molecules are forced into movement as a result of the alternating compression and expansions of the surface caused by the passing progressive waves. Additional wave energy losses indicated by the maxima in the damping coefficient are attributed to desorption phenomena involving the loss of soluble or weakly adsorbed material from the surface film as surface compressions occur.


## PROBLEM STATUS

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

## AUTHORIZATION


NRL Problem C02-18B
Project RUDC-4B-000/652-1/F001-99-01

Manuscript submitted August 3, 1965.

# THE DAMPING OF CAPILLARY WAVES AT THE AIR/WATER INTERFACE BY NATURALLY OCCURRING SURFACE-ACTIVE MATERIAL

## INTRODUCTION

The presence of a monomolecular layer of adsorbed surface-active organic material on the ocean surface can alter many properties of the air/sea interface. According to Jarvis (1) the adsorbed film may alter the surface temperature of the sea and interrupt the normal mass and thermal convection processes occurring just beneath the water surface. The importance of oceanic surface films to the field of meteorology was discussed by Blanchard (2) who postulated that such films could influence the production of rain-inducing hygroscopic salt nuclei and modify the sea-to-air flux of charged particles. Furthermore, a monomolecular film can cause significant damping of the capillary wave structure, which in turn alters the light reflectance from the film-affected area of the sea.

Two previous NRL reports (3,4) have reviewed the wave-damping literature and reported studies on the effects of insoluble monolayer-forming substances on the decay rate of water waves. It was demonstrated that the amplitude decay rate was more than quadrupled by the presence of an insoluble monolayer at the surface and that this damping effect increased rapidly to a maximum value at about 1 dyne/cm, film pressure. As the surface molecules were compressed, the damping coefficient (k) was found to increase and the compressibility of the monolayer to decrease. Comparisons of damping coefficient vs area with film pressure vs area plots indicated that the greatest increase in k occurred at film pressures of less than 1 dyne/cm where the monolayer was undergoing a transition from a compressible (gaseous) phase to one of less compressibility. After the maximum value of k had been attained, further compression of the film caused little change in the damping rate. All of the various insoluble surface-active compounds behaved in a similar manner with respect to these wave-damping effects even though the compounds differed in chemical structure. The application of these results to the creation of sea slicks and the origin and nature of the responsible organic films have been discussed by Garrett (4,5).

The rate of adsorption of natural surface-active species at the air/sea interface was reported by Jarvis (6) who studied sea water from the Pacific Ocean at La Jolla, California. He measured the increase of film pressure and surface potential as a function of time and found that surface-active material began to adsorb immediately after a surface was swept clean. However, measurable decreases in surface tension were not observed until 10 to 60 minutes after the surface had been cleaned.

A similar study (7) was conducted on water from the Bay of Panama to determine the variability in such measurements between various bodies of water. A companion experiment, which is the subject of this report, was designed to study the wave damping on natural sea water under various conditions. The experiments were planned to yield the following data: simultaneous film pressure (F) and damping coefficient (k) measurements as a function of the compaction of the surface film, the time required for the damping effect to be initiated by the natural surface-active material accumulating at the sea water surface, and the effects of thermal convection and gas bubbling on the rate of surface film accumulation.

## APPARATUS AND PROCEDURES

Sea water samples were collected at various depths and locations in the Bay of Panama and returned within thirty minutes to the seaside field laboratory. Experiments were performed at the Corrosion Laboratory Annex of the Naval Research Laboratory, Naos Island, Canal Zone. The water was transferred immediately to a rectangular Plexiglas tank (72.8 cm long, 12.2 cm wide, and 13 cm deep). The dimensions of the tank were selected to provide sufficient depth of water so that the effects of migration of polar organic material from the subsurface to the surface could be adequately studied.

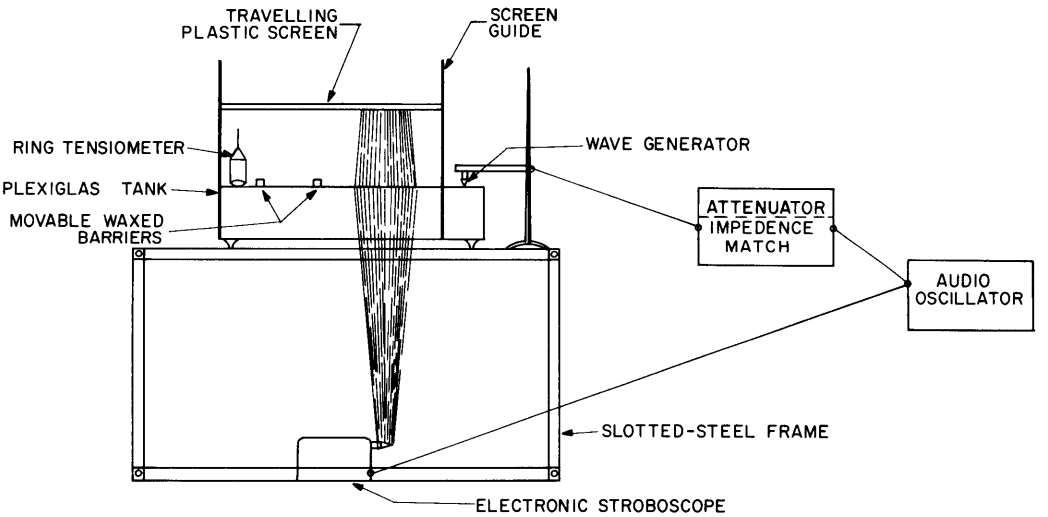


Fig. 1 - Schematic of field laboratory wave-damping system

The experimental system schematized in Fig. 1 was used to generate capillary waves on the sea water, measure the wave amplitudes as a function of distance from the wave source, and determine the film pressure. The fundamental details of this system are discussed in previous NRL reports (3,4). Water waves of small amplitude ($7 \times 10^{-3}$ cm) were generated by a vertically oscillating nylon knife edge attached to a speaker coil driven by an audio oscillator at 60 cps. An electronic stroboscope (General Radio 1531-A) was also triggered by the oscillator and produced light pulses at the same frequency as that of wave generation. Light passing upward through the water surface was refracted by the wave crests and an optical-standing wave pattern was projected onto the screen above the tank. A particular wave image could be brought into sharp focus by moving the traveling screen to the focal point of the light refracted by the wave crest. The height of the screen above the water surface is a function of the wave amplitude. The amplitudes and damping coefficients were calculated by the methods outlined in Ref. 3.

The traveling screen followed metal guides attached to the tank sides. Spring tension was used to hold the screen at a particular height until a reading of the screen height was completed. A millimeter rule attached to one of the guides indicated screen height, and a spirit level mounted on the screen assured that the screen was parallel to the water surface.

Surface tension was measured by the du Nouy ring method. Movable glass film barriers coated with a high-melting paraffin wax to render them hydrophobic were used to compress the adsorbed film. Film area was determined with readings from a millimeter

rule attached to the side of the wave tank. A shelf was provided for the tensiometer along the side of the tank so that the surface tension of the film-covered area between the movable barrier and the fixed end of the tank could be measured.

## EXPERIMENTAL RESULTS

### Time Dependency of Surface Properties

Sampling stations, sample properties, and sea conditions are listed in Table 1. The 0 to 3 in. depth samples were obtained by slowly submerging a 5-gallon bottle to collect water from near the surface. Collections at greater depths were made with a 16-liter

Table I
Sampling Data

| Sample Number | Date (1965) | Sampling Station | Sample Depth | Sample Temperature | Sea Condition | Relative Surface Activity |
|---|---|---|---|---|---|---|
| 1 | 28 March | NRL Corrosion Pier Naos Island, Bay of Panama | 5 ft | 22.5°C | Choppy, white caps | 2 |
| 2 | 29 March | 4 mi E. San Jose Rock Bay of Panama | 30 ft | 21.0 | Choppy, no visible slicks | 2 |
| 3 | 29 March | 4 mi E. San Jose Rock | 0-3 in. | 21.8 | Choppy, no visible slicks | 3 |
| 4 | 30 March | 4 mi E. San Jose Rock | 30 ft | 21.7 | Choppy, white caps | 3 |
| 5 | 31 March | 5 mi E. San Jose Rock | 0-3 in. | 22.0 | Choppy | 3 |
| 6 | 31 March | 5 mi E. San Jose Rock | 50 ft | 20.3 | Choppy | 3 |
| 7 | 1 April | NRL Corrosion Pier Naos Island | 5 ft | 22.0 | Choppy | 2 |
| 8 | 2 April | 6 mi E. San Jose Rock | 60 ft | 20.8 | Light chop | 3 |
| 9 | 3 April | 6 mi E. San Jose Rock | 10 ft | 24.0 | Light chop | 2 |
| 10 | 3 April | 6 mi E. San Jose Rock | 60 ft | 21.3 | Light chop | 3 |
| 11 | 5 April | 3 mi E. San Jose Rock | 0-3 in. | 22.0 | White caps, waves 1-2 ft | 2 |
| 12 | 5 April | 3 mi E. San Jose Rock | 40 ft | 20.3 | White caps, waves 1-2 ft | 2 |
| 13 | 6 April | Lee, S. Taboguilla Island | Surface | 26.2 | Calm, numerous slicks | 1 |
| 14 | 6 April | Lee, S. Taboguilla Island | 0-3 in. | 26.2 | Calm, numerous slicks | 3 |

Van Dorn sampling bottle. Sample 13 was collected by the screen method of Garrett (8) which removes the upper 0.2 mm of the sea surface. Only sample 13 was collected under calm sea conditions from a slick-covered area. On all other days, prevailing trade winds associated with the dry season were blowing, and a choppy mixed sea resulted. In spite of the rather steady winds, small temperature gradients existed. This can be seen from a comparison of the temperatures of the samples taken at different depths on March 31, April 3, and April 5, 1965.

The relative surface activities of the collected water samples (Table 1) were indicated by an arbitrary grouping in three classes. Sample 13, collected from the sea surface and by far the most surface active, was placed in the first class. Since the screen method concentrates surface-active materials to a large degree, the collected sample was quite surface active. The adsorption of the surface-active material at the surface of this sample was rapid, and film pressure and the damping coefficient both changed rapidly with time as the surface aged. Barriers were not needed to compress the adsorbed film in order to increase F and k.

A relative surface-activity value of class 2 was given to those samples whose surface film attained a measurable film pressure with barrier-compression after a surface-aging period of one hour. After the sample was poured into the tank, its surface was swept a number of times with the barrier to remove all surface-active substances. One hour after the cleaning there was no measurable changes in either F or k. However, upon compression of the surface with the wax-coated barrier, increases in k and F were recorded for class 2 samples since some surface-active material had reached the surface during the aging period. When no changes in F or k were developed by a 5-to-1 compression of the surface after the one-hour period, the sample was considered dilute and given a surface-activity rating of class 3.

Typical data are plotted in Fig. 2 for sample 7, which was collected from moderately rich pier water at Naos Island. The film pressure and the damping coefficient are

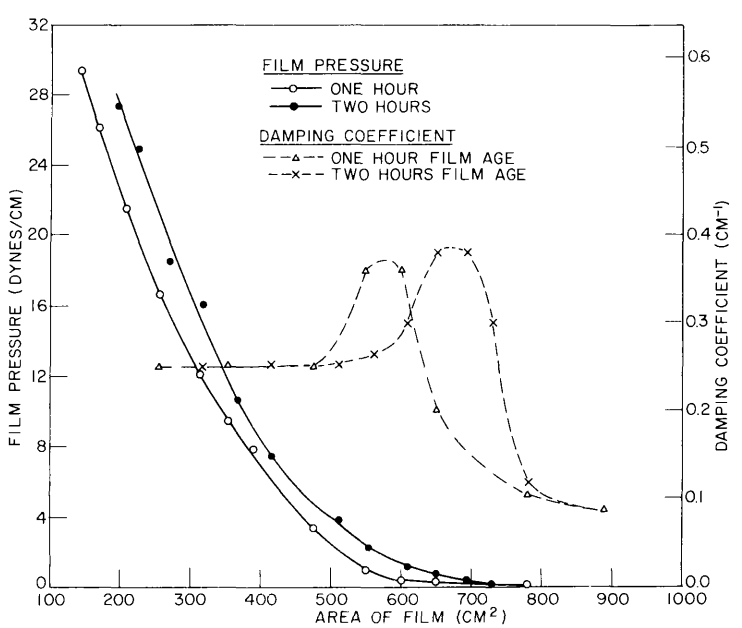


Fig. 2 - Dependence of k and F upon the area occupied by a naturally-formed film at the surface of sample 7

plotted simultaneously against the area of the film expressed in square centimeters. As the film area was first decreased by advancing the barrier, both F and k increased, and k increased rapidly to a maximum value at the low value of F of about 1 dyne/cm. The correspondence between the film pressure and the damping coefficient at low F was similar to that reported by Garrett and Bultman (9) for insoluble monomolecular layers of pure organic compounds. That is, k increased abruptly to a maximum value during the two-dimensional phase transition of the monolayer from a gaseous compressible state to one of greater rigidity. However, insoluble monolayers exhibited only a small difference between $k_{max}$ and the value of k at higher film pressures, while the natural surface-active substances from sample 7 caused a pronounced maximum in the k vs A plot, which occurred at about 1 dyne/cm, film pressure. As the value of F of this sample was increased above 1 dyne/cm, k decreased from its maximum value of 0.39 $cm^{-1}$ to a nearly constant value of 0.25 $cm^{-1}$.

The gradually changing slope of the F vs A curve from Fig. 2 does not indicate any sharply defined phase transitions. Even though the initial increase in k occurred sharply, the film changed state from gaseous to a liquid phase over a rather broad region of area decrease. This type of F vs A curve is representative of a highly mixed film, and it probably indicates the presence of both soluble and insoluble constituents. The data for surface films aged one and two hours are similar and show only a 17% gain in area coverage by film in the second hour. In each experiment, the surface was cleaned prior to the aging period.

## Film Transport by Air Bubbles

Since the class 3 samples were dilute in surface-active components, many of these samples were used in experiments which were designed to study the various transport mechanisms by which active material reached the surface. The surface of sample 4 was cleaned, allowed to stand for one hour, and compressed 5 to 1. This compression was as large as possible without interfering with the wave generator. No measurable increases occurred in either k or F. The surface was again cleaned and the bulk sample was bubbled with air for 30 minutes with 6-mm-diameter bubbles at a rate of 240 bubbles per minute. The bubbles were released near the bottom of the 13-cm-deep tank. At the conclusion of the bubbling operation, the surface was compressed and F and k determined at intervals of decreasing area. The resulting data, plotted in Fig. 3, show that at a film area of 890 $cm^2$, which was the area of the entire tank surface, the damping coefficient had increased to 0.13 $cm^{-1}$ as compared to a value of 0.08 $cm^{-1}$ for the clean surface. A maximum in k of 0.38 $cm^{-1}$ was attained at 0.8 dyne/cm, and it decreased upon further compression of the film. Even though sample 4 contained relatively small amounts of surface-active components, the bubbles acted as efficient scavengers for the active material in the subsurface water, for they greatly increased the rate of film accumulation. Without an artificial transport mechanism, the development of a monomolecular film under quiescent conditions would be controlled by molecular diffusion, a process which proved to be quite slow for this sample.

Sample 11, containing small amounts of surface-active components, was used to study the effect of bubble rate upon the accumulation of surface film. Damping coefficient versus film area is plotted in Fig. 4 for three different rates of bubbling. Although an increase in the bubble rate increased the rate of film development, as indicated by the k values, an attempt to draw conclusions as to the efficiency of the bubbling process would be presumptious due to the highly variable conditions and unknown chemical constituents involved in this experiment. However, it is worth noting the similarity of the shapes of the k vs A curves as well as the pronounced maxima of k in each.

A further experiment was conducted to determine the role of bubbles in the transport of surface-active material from the bulk water to the surface. The objective was to determine whether the bubble/water interface was simply a rising adsorptive medium or

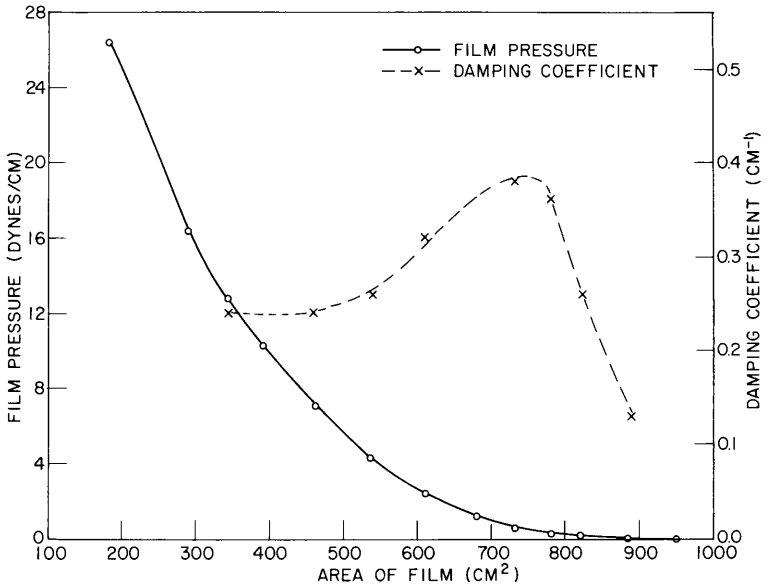


Fig. 3 - Dependence of k and F upon the area occupied by a bubble-generated film at the surface of sample 4

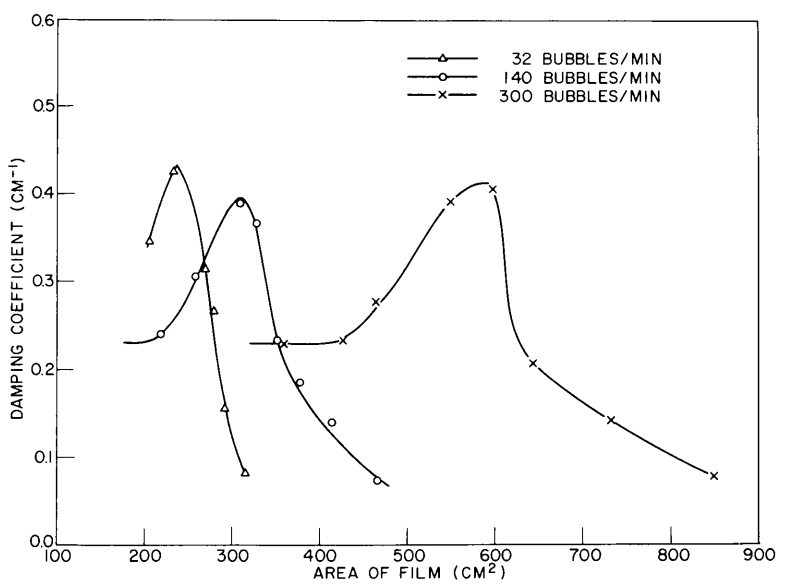


Fig. 4 - Damping coefficient vs surface film area for bubble-generated films at various bubble rates (sample 11)

whether the turbulence generated by the bubbling was causing destruction of organic aggregates into a number of surface-active fragments. Organic aggregates are found generally in sea water and consist of both organic and inorganic matter with inclusions of plankton and bacteria (10). Sample 8 was treated experimentally like sample 4, and almost identical F vs A and k vs A plots were obtained. After the bubbling procedure and the measurement of the film properties, the surface was cleaned and the water was

siphoned from the tank into a clean vessel and poured again into the tank to redistribute the organic material throughout the bulk water. The surface was recleaned and aged for one hour. No increase in either F or k occurred when the surface was then compressed 5 to 1. If the organic-inorganic complexes had been fragmented by the bubbling, a number of surface-active species would have been released, and an acceleration in the rate of film formation would have occurred. Since no such increase in the accumulation rate of the surface film was found in the final phase of the experiment, no significant fragmentation of the aggregates by bubbling had occurred.

The surface properties of several of the samples were measured one hour after the tank was filled but without a prior cleaning of the surface by sweeping with the hydrophobic barriers. The results indicated that there was a moderate amount of film present at the surface. After a 2-to-1 compression of the surface film, F was 0.7 dyne/cm and k measured 0.23 $cm^{-1}$. The surface was then carefully cleaned and the water allowed to stand for one additional hour, after which a 5-to-1 surface compression yielded no increases in either F or k. The initial pouring of the sample had mechanically generated currents which had transported material into the newly created surface. In the second phase of the experiment, following the cleaning of the surface under static conditions, the rate of surface film accumulation was due largely to the slow process of molecular diffusion.

## Thermal Effects

The transport of organic matter by thermal convectional cells was examined by placing a 1500-w rod-shaped immersion heater along the bottom of the tank. The thermal cell created by this heater is depicted in Fig. 5. The heated water rose in a narrow band about the width of the heating element almost to the surface, dispersed somewhat at the surface, and descended along the sides of the tank. The sharpness of the warm water column decreased near the surface due to mixing with cooler water. With 30 v applied to the 115-v heater the column rose at a rate of 4 mm/sec.

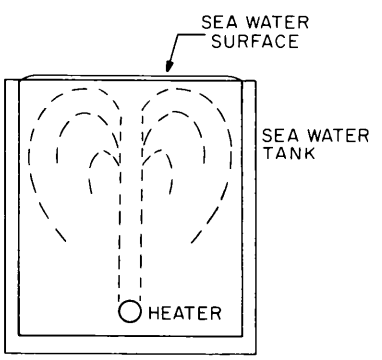


Fig. 5 - Thermal convection cells generated by cylindrical immersion heater.

Thermal convection cells were generated in samples 5 and 8 for 20 minutes by the foregoing procedure. The surface properties of the generated films were measured at the conclusion of the heating period. These data, plotted in Fig. 6, show a sharp maximum in k which occurs at about 1 dyne/cm, film pressure, for both samples. In most respects the surface properties of the thermally transported film material are like those of the natural and bubble-generated films.

## Screen-Collected Sample

Sample 13, which was collected by the screen method, was extremely surface active. Both F and k changed rapidly with time without the need of barrier compression. The surface properties plotted against time in Fig. 7 show a maximum in k of 0.55 $cm^{-1}$ at 1 dyne/cm, film pressure. The surface was cleaned and the experiment was repeated twice in an identical fashion. There was a decrease in the rate of film accumulation for the subsequent experiments, but the maximum damping coefficient ($k_{max}$) remained at the high values 0.68 and 0.60 $cm^{-1}$. The damping coefficient maxima of 0.55 to 0.68 $cm^{-1}$ are the largest values known to this author for a film-covered surface using 60-cps waves.

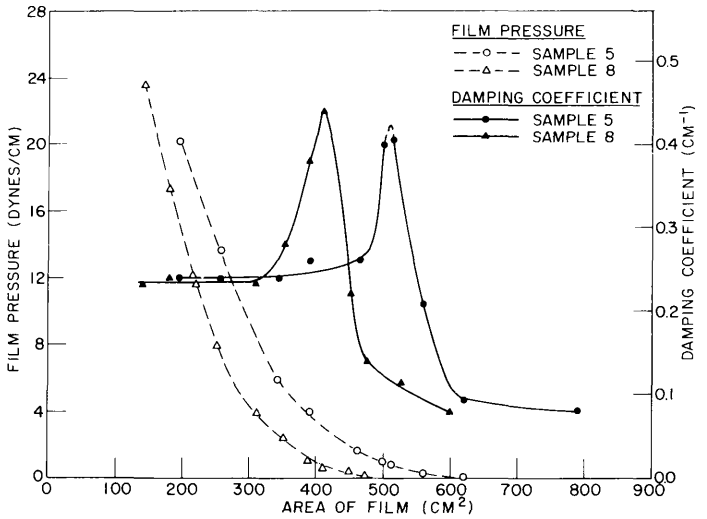


Fig. 6 - Dependence of k and F upon the area occupied by films generated by thermal convection at the surface of samples 5 and 8

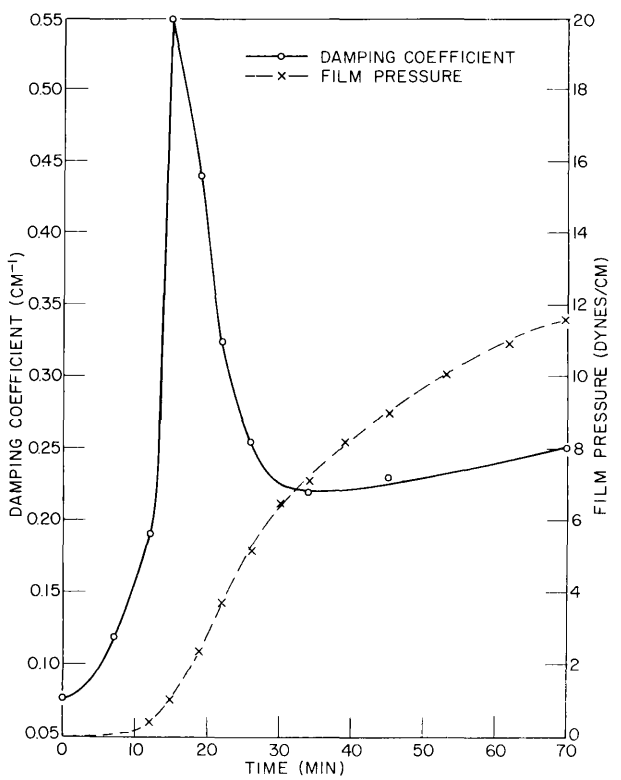


Fig. 7 - Increase of k and F with time due to the surface film from screen-collected sample 13

A second sample (No. 14) was collected by submerging a five-gallon bottle at the same location as that for the screen-collected water. Although near-surface water was collected in this manner, the sample fell into the class 3 or dilute surface-activity category. Since the screen method sampled much closer to the water surface (0.2 mm), the screen-collected water was much richer in surface-active constituents. The large differences in amounts of material collected by these two techniques were especially exaggerated by the calm condition of the bay at the time of sampling. The sampled area was slick-covered, indicating that many of the natural active components had reached the surface. Under such conditions, it was to be expected that there would be a large concentration gradient between the surface and a short distance below.

## DISCUSSION

The major objective of these field experiments was to survey the wave damping properties of naturally-contained surface-active materials adsorbed at a sea water surface. Due to the similarity of much of the wave damping and film pressure data, not all of the samples listed in Table 1 are discussed in this report. The rate of adsorption of the surface-active constituents and the effects of sea conditions are discussed by Jarvis (7), who performed simultaneous experiments on the samples listed in this report.

Although these experiments have demonstrated that the water of the Bay of Panama contains materials capable of damping capillary waves, the rate of film development under calm conditions can be quite slow. Many of the samples were not rich in available surface-active substances, and under calm conditions where vertical mass transport was absent the film accumulation rate was apparently controlled by molecular diffusion. However, when vertical transport by rising bubbles or thermal or mass convections occurred, active material reached the surface rapidly. But even under these accelerated conditions lateral surface compressional forces were still necessary to compress the surface components sufficiently to cause wave damping.

Processes similar to those demonstrated in the laboratory operate in the ocean and serve to modify the air/sea interface. For example, a Langmuir circulation cell (13) could not only transport surface-active material vertically to the surface, but also would provide lateral surface compressions necessary to increase film pressure and generate sea slicks by the wave-damping process. In the absence of convection cells of this kind organic film-forming material could be carried upward by rising bubbles, organisms or particulate matter.

In every experiment, the relationship between film pressure and the damping coefficient at low F was in qualitative agreement with that discussed in earlier works (3,4). At about F = 1 dyne/cm for most of the fresh sea water samples, however, a maximum k occurred at a value of from 0.39 to 0.44 $cm^{-1}$. As the film pressure was increased further, k decreased to a value of from 0.24 to 0.28 $cm^{-1}$ where it became essentially constant by the time the film pressure had reached 2 dynes/cm. This $k_{max}$ effect is summarized in Fig. 8, a composite plot of k vs F for seven experiments on natural sea water. Figure 8 represents samples treated in a number of ways; i.e., bubbled, heated, or simply allowed to age without the application of external devices to increase the surface-adsorption rate. Not included in the plot were the highly active screen sample data where $k_{max}$ equalled 0.55 to 0.68 $cm^{-1}$.

Damping coefficient maxima for many insoluble monolayers are somewhat smaller than those found for the natural sea components and often are not obvious experimentally. From Fig. 8, $k_{max}$ is 0.17 units greater than the plateau region of the k vs F curve at about 0.26 $cm^{-1}$. For comparison, the damping properties of an insoluble monolayer of purified oleic acid are plotted in Fig. 9. Only a small difference (0.03 $cm^{-1}$) existed between the $k_{max}$ and the plateau value of 0.27 $cm^{-1}$.

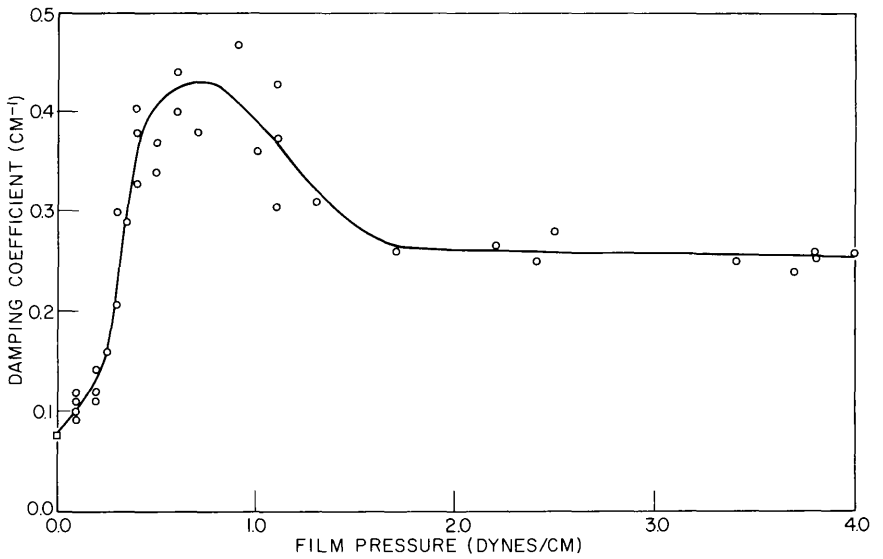


Fig. 8 - Composite k vs F plot for data from seven experiments

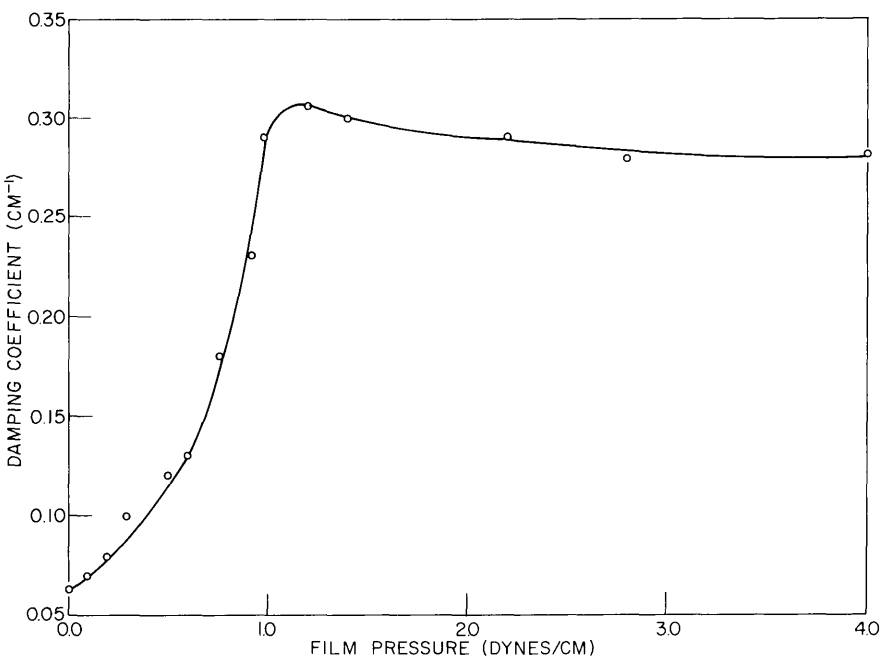


Fig. 9 - Dependence between k and F for an oleic acid monolayer on distilled water

The plateau value of k, approximately 0.26 $cm^{-1}$ for 60-cps waves on water at 20°C, may be attributed to energy losses associated with a viscous drag of the underlying hydrogen-bonded chains of water molecules. These molecular chains are in turn bonded to the adsorbed surface molecules. When the surface molecules have been compressed to a point where the water surface is "immobilized," wave amplitude losses occur as the progressive expansions and contractions of the surface works against the viscous drag of

the associated chains of water molecules. The increase of k to its plateau value occurs, therefore, in the neighborhood of a monolayer-phase change from a compressible state to one of greater rigidity.

When a maximum in k occurs greater than that of the plateau value, it must represent an additional wave-energy loss. Such a maximum in the damping coefficient as the solute concentration was increased has been reported recently by others studying soluble surface-active substances (11,12). It is likely that the large damping maxima which were found for the highly complex mixed monolayers of natural oceanic substances may be due to a desorption energy requirement. This energy is expended when the more soluble or less surface-active components are forced out of the surface by the alternate compressions and expansions of the film caused by the passing progressive waves. That this effect occurs at low film pressures can be explained as follows. As the film pressure is first increased by compression of the surface molecules, the more soluble species are submerged into the bulk water or, in the case of nonpolar substances, are forced upward out of the surface. Consequently, the surface becomes more exclusively populated by the water-insoluble fatty alcohols, acids, and esters, which do not leave the surface upon further compression. For example, proteins, carbohydrates, and low-molecular-weight fatty compounds would be lost from a surface and a more insoluble film would be formed as the surface is compressed. Thus, it is possible that such mixed films would damp waves by desorption energy losses at low film pressures, as well as by viscous drag processes attributable to the insoluble components.

## ACKNOWLEDGMENT

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13. ABSTRACT


The damping of capillary waves was measured on fresh sea water, sampled from the Bay of Panama under various oceanographic conditions. The collected water contained varying quantities of surface-active organic materials capable of adsorbing at the air/water interface and altering the surface properties. In some instances, compression of the adsorbed film was necessary to cause increases in the damping coefficient and the film pressure after a one-hour surface aging period. Other samples contained little surface-active material, and no changes in the surface properties resulted with a 5-to-1 compression of an aged surface.

Agitation, thermal currents, and bubbling were studied as mechanisms for the transport of film-forming material from the bulk water to the surface. Large increases in the rate of film accumulation occurred when these mechanisms were applied. Under static conditions the adsorption rate was quite slow since it was controlled by molecular diffusion.

Simultaneous measurements of damping coefficient and film pressure indicated that wave damping commenced at a film pressure of few tenths of 1 dyne/cm and increased to a maximum value of from 0.39 to 0.44 $cm^{-1}$ in the neighborhood of 1 dyne/cm. As the film pressure was increased further by compression of the surface film, the damping coefficient decreased to a value of about 0.26 $cm^{-1}$ and became constant when the film pressure had reached 2 dynes/cm. In marked contrast, the damping coefficient measured on the clean sea water surface was 0.08 $cm^{-1}$.

It was postulated that a portion of the wave energy loss was due to a viscous drag of the associated chains of water molecules which were bonded to the molecules of the adsorbed surface film. The drag occurs when the molecules are forced into movement as a result of the alternating compression and expansions of the surface caused by the passing progressive waves. Additional wave energy losses indicated by the maxima in the damping coefficient are attributed to desorption phenomena involving the loss of soluble or weakly adsorbed material from the surface film as surface compressions occur.


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Security Classification

| 14. KEY WORDS | LINK A ROLE | LINK A WT | LINK B ROLE | LINK B WT | LINK C ROLE | LINK C WT |
|---|---|---|---|---|---|---|
| Wave damping | | | | | | |
| Air/Water Interface properties | | | | | | |
| Surface active material | | | | | | |
| Film pressure | | | | | | |
| Capillary waves | | | | | | |
| Oceanography | | | | | | |

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