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Damping of Capillary Waves at the Air-sea Interface by Oceanic Surface-active Material¹

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ABSTRACT

The damping rates of capillary waves (wavelength = 0.52 cm) were measured on fresh seawater sampled 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 sea-surface properties. Simultaneous measurements of wave-damping properties and film pressure indicated that the damping coefficient began to rise 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 seawater surface was 0.08 cm^{-1} .

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

Introduction. The accumulation and compression of natural surface-active material at the air-water interface result in the creation of a sea slick. The surface film of organic material is only one molecule thick, and when it is sufficiently compacted it damps the capillary surface waves. The resulting average wave slope is thereby reduced, the light reflectance from the slick area becomes somewhat different from that of the surrounding water, and the film-covered area becomes visible. Sea-surface slicks may also be artificially produced by pouring various oils onto the water. Fish oils and oxidized petroleum products have been commonly used to: calm wind-generated capillary waves, improve the transmission of light through the water surface, and

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reduce the breaking of waves and surf. Interesting accounts of the history of sea slicks and wave-calming oils have been published (Davies 1962, Banting 1932).

Some marine investigators (Dietz and Lafond 1950, Lumby and Folkard 1956, Cox and Munk 1955) have measured the film pressure "in situ" of many naturally occurring sea slicks by using the spreading-oil method of Adam (1937). Film pressures in many slicks were quite low (2 to 10 dynes/cm); this suggested that the damping of wind-generated waves can occur with only partially compressed monolayers of surface-active materials. Ewing (1950) has discussed the mechanism by which internal waves generate surface compressional forces of sufficient magnitude to create slicks by packing the adsorbed organic molecules at the sea surface.

Laboratory studies have demonstrated that capillary waves can be significantly damped by insoluble monolayers at very low film pressures. Garrett and Bultman (1963) found that the damping increased abruptly to a maximum value at a low pressure of 0.5 to 1.0 dyne/cm. Further compression of the surface molecules (increasing film pressure) did not increase the wave-damping effect. On the other hand, damping by soluble surface-active substances passes through a maximum value at higher film pressures of 4 to 6 dynes/cm (Davies and Vose 1965). There has been no direct quantitative measurement of wave-damping characteristics on seawater as a function of the film pressure of natural surface films.

In the present study, the wave attenuation rates for capillary waves on freshly collected seawater have been determined. Simultaneous measurements were made of: The damping rates and film pressure as a function of the compaction of the surface film, the time required for the damping effects to be initiated by the aging surface film, and the effects of thermal convection and air bubbles on the rate of transport of surface-active material into the air-sea interface.

Apparatus. Seawater samples were collected at various depths and locations in the Bay of Panama and returned within 30 minutes to the seaside field laboratory. 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 for the study of processes that transport polar organic material from bulk seawater into the air-sea interface. The experimental system (i) generates linear capillary waves of controlled frequency, (ii) measures their amplitudes, (iii) provides means for the addition and removal of insoluble monolayers from the water surface, and (iv) allows the film pressure (F) to be measured and controlled. The assembly in Fig. 1 is patterned after a device described by Schooley (1949). A 60-cycle signal generated by an audio oscillator was amplified and fed into an electro-mechanical transducer that vibrated a linear knife edge in the surface of the

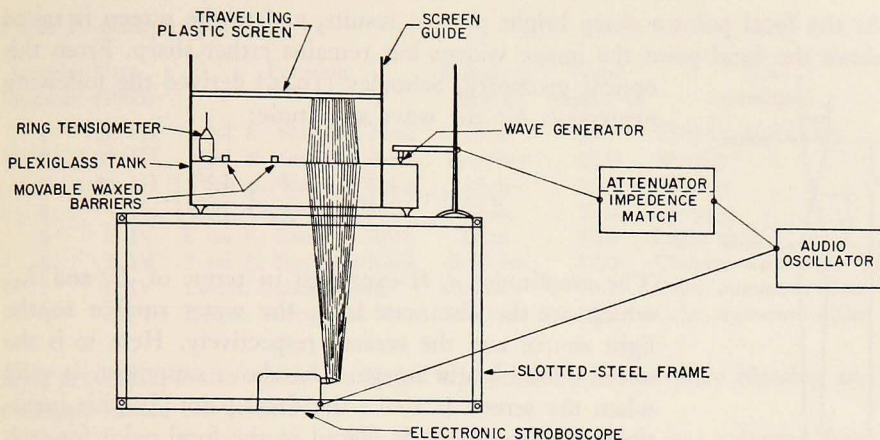


Figure 1. Wave generation and analysis system.

water contained in a transparent ripple tank. Linear water waves (wavelength = 0.52 cm) were generated with a rigid 45-degree knife edge machined from polyethylene. The signal from the oscillator passed through an impedance-matching device and an attenuator that provided a means of varying the wave amplitudes. The same signal source applied to the wave generator was used to trigger an electronic stroboscope (General Radio 1531-A) so that light flashes were produced at the same frequency as that of the water waves generated in the ripple tank. The light rays, upon passing upward through the rippled surface, were converged by the wave crests, and an optical stand-wave pattern was projected onto a translucent plastic screen above the ripple tank.

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 height, 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.

An equation for the calculation of wave amplitude may be derived from the light-path diagram in Fig. 2. Light passing through a wave crest is refracted and focused at a point above the water surface. The greater the wave amplitude, the shorter is the focal length of the transmitted ray. When the plastic screen is placed near the water surface below the focal point, a diffuse pattern is seen.

At the focal point a sharp bright pattern results, and as the screen is raised above the focal point the image widens but remains rather sharp. From this optical geometry, Schooley (1949) derived the following expression for the wave amplitude:

$$a = 0.15 \lambda^2 \left(\frac{1}{L_1} + \frac{1}{L_2} + \frac{3W}{\lambda L_2} \right).$$

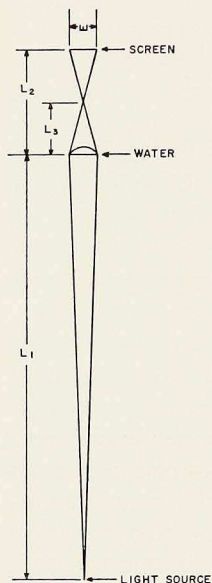


Figure 2. Geometry of ripple focusing.

The amplitude, a , is expressed in terms of L_1 and L_2 , which are the distances from the water surface to the light source and the screen, respectively. Here w is the width of the bright image. The above expression is valid when the screen is above the focal point. In this investigation the screen was placed at the focal point for each wave measured. In this instance, $w = 0$, and the amplitude equation becomes $a = 0.15 \lambda^2 (1/L_1 + 1/L_2)$. Since L_1 is fixed, the amplitudes are an inverse function of the height of the screen at which a wave pattern just becomes sharp and bright.

The amplitudes of linear capillary waves originating from a long source follow an exponential decay expression, $a = a_0 e^{-kx}$, where a_0 is the amplitude of the wave at the source, x is the distance from the source, and k is the decay or damping coefficient. By plotting $\ln a$ versus x , a straight line is obtained, the slope of which is the damping coefficient, k .

In general, the following procedure was followed in handling the collected samples. After the freshly collected seawater was poured into the deep ripple tank, it was usually necessary to allow time for the surface-active constituents to reach the air-sea interface. At the conclusion of the aging period, k and F were measured for various compressions of the surface film. The compressions were made by moving a hydrophobic barrier toward the end of the tank that contained the wave generator, thereby decreasing the area (A) of the surface film that had accumulated during the aging period. As the surface molecules were compacted, the film pressure and the damping coefficient increased.

Experimental Results. Sampling stations, sample properties, and sea conditions are listed in Table I. To collect water from near the surface, the 0-to-10-cm-depth samples were obtained by slowly submerging a 5-gallon bottle. Collections at greater depths were made with a 16-l Van Dorn sampling bottle. Sample 7 was collected by the screen method of Garrett (1965), which removes the upper 0.2 mm of the sea surface. Only samples 7 and 8 were collected under calm sea conditions from a slick-covered area. On all other

Table I. Sampling data.

Sample number	Date (1965)	Location	Sampling depth	Water temp. (°C)	Sea condition
1	30 III	4 mi E. San Jose Rock	10 m	21.7	Choppy, white caps
2	31 III	5 mi E. San Jose Rock	0-10 cm	22.0	Choppy
3	31 III	5 mi E. San Jose Rock	15 m	20.3	Choppy
4	1 IV	NRL Corrosion Pier,	2 m	22.0	Choppy
5	2 IV	6 mi E. San Jose Rock	20 m	20.8	Light chop
6	5 IV	3 mi E. San Jose Rock	0-10 cm	22.0	Choppy, white caps
7	6 IV	Lee, S. Taboguilla I.	Surface	26.2	Calm, numerous slicks
8	6 IV	Lee, S. Taboguilla I.	0-10 cm	26.2	Calm, numerous slicks

days, prevailing trade winds associated with the dry season were blowing and a choppy mixed sea resulted.

Typical data are plotted in Fig. 3 for sample 4, which was collected from moderately rich pier water at Naos Island, Bay of Panama. The film pressure and the damping coefficient are 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 F value 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 (1963) for insoluble monomolecular layers of pure organic compounds. That is, during the two-dimensional phase

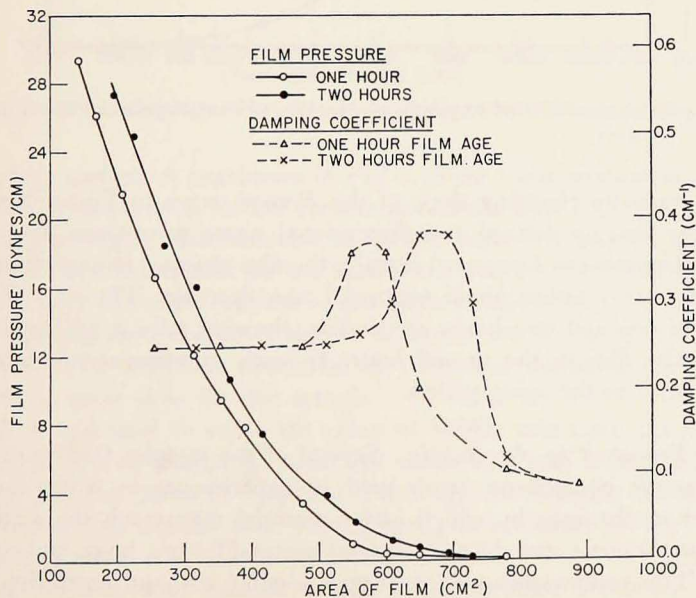


Figure 3. Dependence of k and F upon the area of a naturally formed film at the surface of sample 4.

transition of the monolayer from a gaseous compressible state to one of greater rigidity, k increased abruptly to a maximum value. However, while the pure insoluble monolayers exhibited only a small difference between k_{\max} and the value of k at higher film pressures, the natural surface-active substances from sample 4 caused a pronounced maximum in the k -vs- A plot, which occurred at about 1 dyne/cm, film pressure. As the F value 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} .

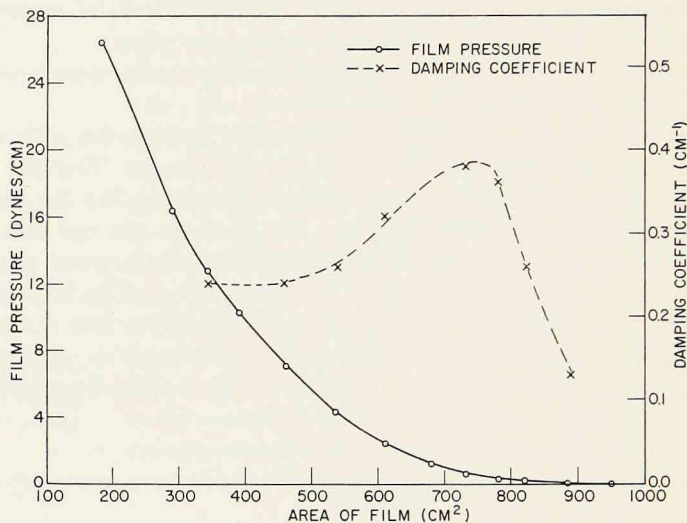


Figure 4. Dependence of k and F upon the area occupied by a bubble-generated film at the surface of sample 1.

The gradually changing slope of the F -vs- A curve in Fig. 3 does not indicate any sharply defined two-dimensional phase transitions. Even though the initial increase in k occurred sharply, the film changed its state from gaseous to liquid over a rather broad region of area decrease. The data for surface films aged one and two hours are similar, showing 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. Several of the samples that were dilute in surface-active components were used in experiments to study the various transport mechanisms by which active material may reach the surface. The surface of sample 1 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. Since this sample contained only small amounts of surface-

active material, 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 were determined at intervals of decreasing area. The resulting data, plotted in Fig. 4, show that, at a film area of 890 cm² (the area of the entire tank surface), the damping coefficient had increased to 0.13 cm⁻¹ as compared with a value of 0.08 cm⁻¹

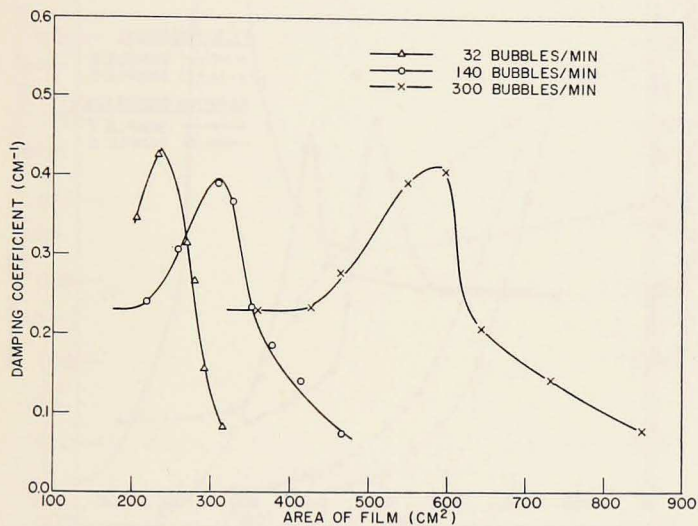


Figure 5. Damping coefficient vs surface-film area for bubble-generated films at various bubble rates.

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 1 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 that proved to be quite slow for this sample.

Sample 6 was used to study the effect of bubble rate upon the accumulation of surface film. Damping coefficient versus film area is plotted in Fig. 5 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 about the efficiency of the bubbling process would be presumptuous because of the highly variable conditions and unknown chemical constituents involved in this experiment. However, note

the similarity in the shapes of the k -vs- A curves as well as the pronounced maxima of k in each.

Thermal Effects. The transport of organic matter by thermal convective cells was examined by placing a 1500-w rod-shaped immersion heater along the bottom of the tank. 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-

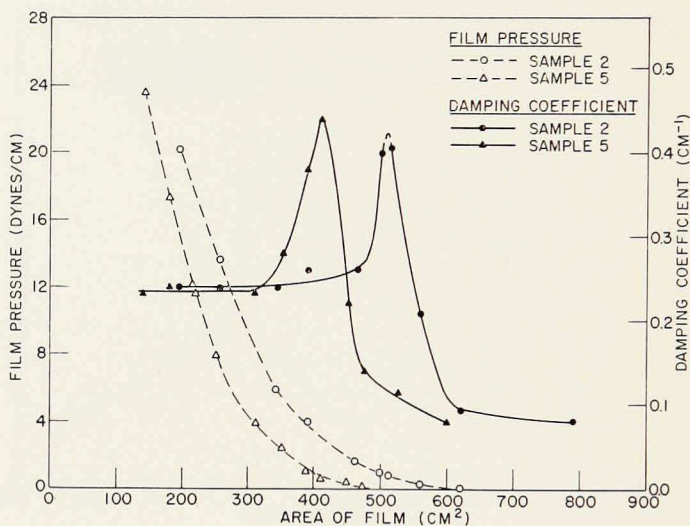


Figure 6. Dependence of k and F upon the area occupied by films generated by thermal convection.

water column decreased near the surface because of mixing with cooler water. With 30 v applied to the 115-v heater, the column rose at a rate of 4 mm/sec.

Thermal convection cells were generated in samples 2 and 5 for 20 minutes by means of 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 at about 1 dyne/cm, film pressure, for both samples. The surface properties of the thermally transported film material were like those of the natural and bubble-generated films.

Screen-collected Sample. Sample 7, 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

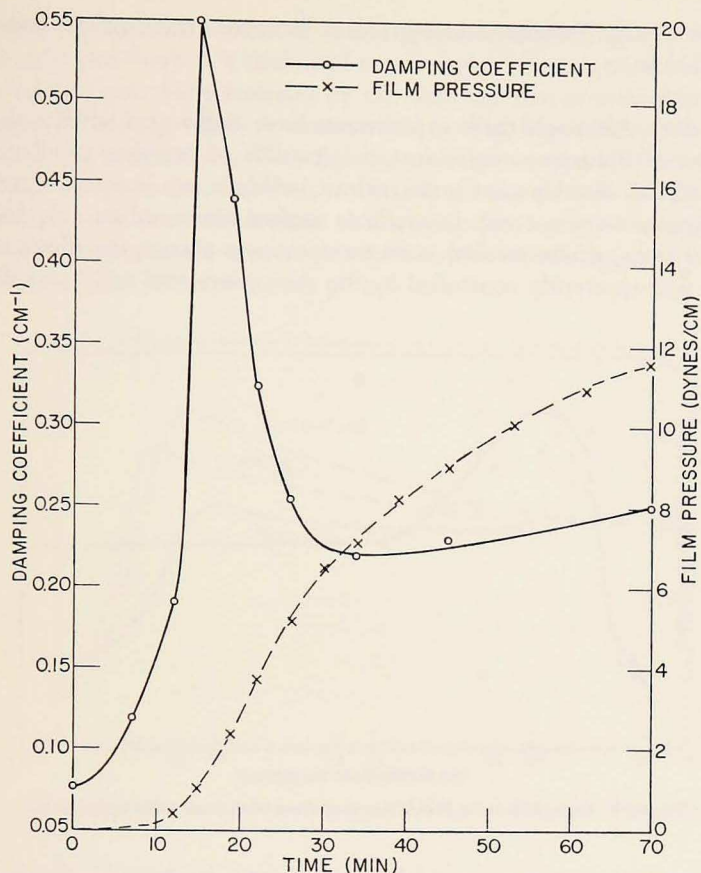


Figure 7. Increase in k and F with time for the surface film from screen-collected sample 7.

fashion. There was a small decrease in the rate of film accumulation during the subsequent experiments, but the maximum damping coefficient (k_{\max}) remained at the high values 0.68 and 0.60 cm^{-1} .

A second sample (No. 8) was collected by submerging a five-gallon bottle at the same location as that used for the screen-collected water. Although near-surface water was collected in this manner, the sample was quite dilute in surface-active organic matter. Since the screen method obtained samples 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 using 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 is to be expected that there

would be a large concentration gradient between the surface and a short distance below.

Discussion. Although these experiments have demonstrated that the water in 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 the slow process of molecular diffusion.

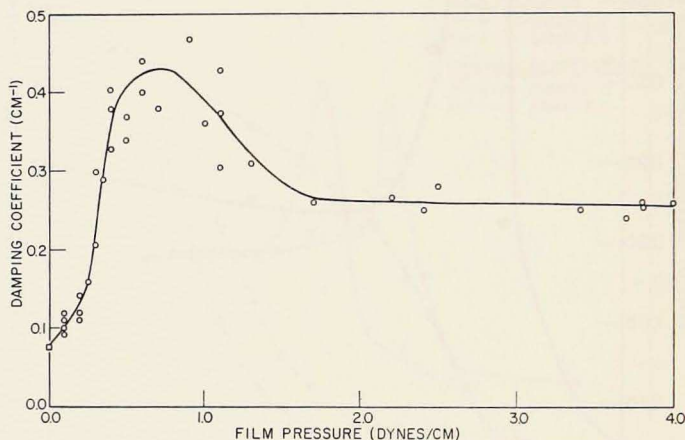


Figure 8. Composite k -vs- F plot for data from seven seawater experiments.

However, when vertical transport by rising bubbles or by thermal convections occurred, active material reached the surface more rapidly. But even under these accelerated conditions, lateral surface compressional forces were 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 could not only transport surface-active material vertically to the surface, but it would also provide lateral surface compressions necessary to increase film pressure and generate sea slicks by the wave-damping process (Langmuir 1938). In the absence of convection cells of this kind, organic film-forming material could also be carried upward by upwellings, rising bubbles, or buoyant organisms and particulate matter.

In every experiment the relationship between film pressure and the damping coefficient at low F was in qualitative agreement with data for insoluble monolayers (Garrett and Bultman 1963). For all of the seawater samples there was a maximum in the damping-coefficient-vs-film-pressure-plot at

about one dyne/cm, with 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. The k_{max} effect is summarized in Fig. 8—a composite plot of k -vs- F for seven experiments. The figure represents samples that were 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. Data for the highly active screen-collected sample whose k_{max} was 0.55 to 0.68 have not been included in the plot.

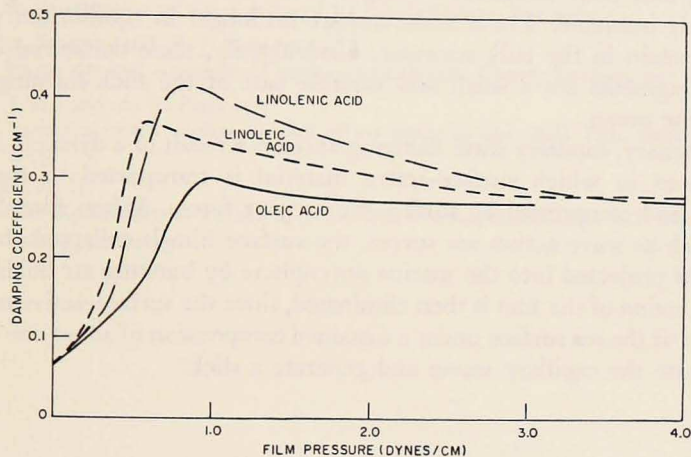


Figure 9. Relationship between damping coefficient and film pressure for oleic, linoleic, and linolenic acids.

A possible explanation for the pronounced k_{max} caused by the natural sea-water films may be derived from the data (Fig. 9) for a number of pure insoluble monolayers measured in a laboratory wave-damping system. Although only a small difference (0.03 cm^{-1}) existed between the k_{max} and the plateau value of 0.27 cm^{-1} for oleic acid, the difference became somewhat greater for the more unsaturated fatty acids. The shapes of the curves in Figs. 8 and 9 suggest that unsaturated fatty acids may be important contributors to the damping by natural sea-surface films. According to Garrett (1967), the unsaturated acids are commonly found in the sea surface along with the saturated fatty acids and alcohols. In Fig. 8 there is an additional feature— k_{max} occurs at about one dyne/cm film pressure. This fact indicates that the film is composed primarily of water-insoluble surface-active substances, since k_{max} would be expected at larger values if the damping were the result of very soluble surface-active materials (Davies 1965).

As lateral compressions occur in the ocean surface, the adsorbed water-insoluble substances exclude the more soluble and less permanent molecules,

so that the surface film becomes increasingly more insoluble. This result is accelerated by the alternating compactions and dilations of the surface film caused by passing waves. These compressions and expansions in the surface progressively decrease the concentration of soluble entities (Jarvis et al. 1967).

Proteinaceous material, though generally soluble in water, may adsorb at the sea surface and contribute to surface effects. Protein monolayers also give pronounced k_{\max} when k is plotted against F (Davies and Vose 1965). According to Langmuir and Schaffer (1939), most proteins are denatured when adsorbed, and their molecular configuration is altered so that they become irreversibly insoluble. These molecules are no longer in equilibrium with the soluble protein in the bulk seawater. Undoubtedly, these denatured insoluble protein fragments are a small and variable part of the slick-forming surface film on the ocean.

In summary, capillary wave damping at sea is a result of a dynamic interplay of processes in which surface-active material is transported to the air-sea interface and compressed by surface convergent forces. When film-dispersive forces such as wave action are severe, the surface film is collapsed and resubmerged or projected into the marine atmosphere by bursting air bubbles. The damping action of the film is then eliminated, since the surface-active molecules must exist at the sea surface under a sustained compression of about one dyne/cm to attenuate the capillary waves and generate a slick.

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