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Physical and Chemical Parameters Affecting the Damping of Capillary Water Waves by Monomolecular Layers of Organic Materials

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ABSTRACT

The wave-damping action of chemically pure, as well as naturally occurring substances, has been studied under controlled laboratory conditions using mechanically generated transverse water waves. The decay constant or damping coefficient was shown to increase abruptly at film pressures of less than one dyne/cm to a maximum value and to remain relatively constant as film pressure is increased further. The onset of the damping effect has been closely related to major changes in the compressibility of the adsorbed insoluble monolayer which occurred in the neighborhood of the monolayer transition region between the gaseous (compressible) phase and a more condensed (relatively incompressible) phase.

The damping coefficient for insoluble monolayers was independent of the initial wave amplitude but was linearly dependent upon the frequency. Higher frequencies were damped more readily than lower ones. Plots of the damping coefficient (k) versus molecular area at several frequencies indicated that the abrupt damping coefficient increase was a function of monolayer compressibility and not frequency, although k attained a higher maximum value at larger frequencies. Organic surface active compounds of various chemical structures were examined as well as a sample of naturally occurring water-insoluble, monolayer-forming material taken from the ocean surface. All of these materials behaved similarly with respect to the effects of film compressibility and wave-generation frequency on the damping coefficient.

The experimental results were extrapolated to the natural ocean surface taking into account the effects of chemical structure, film pressure, and film compressibility on the damping of capillary ocean waves of different wavelengths.

PROBLEM STATUS

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

AUTHORIZATION

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PHYSICAL AND CHEMICAL PARAMETERS AFFECTING THE DAMPING OF CAPILLARY WATER WAVES BY MONOMOLECULAR LAYERS OF ORGANIC MATERIALS

INTRODUCTION

Ocean waves may be classified as either gravitational or capillary in nature. This is a consequence of the Kelvin equation (1) for the velocity (v) of a wave on a liquid contained in a large deep basin

$$v^2 = \frac{g\lambda}{2\pi} + \frac{2\pi\gamma}{\rho\lambda} \tag{1}$$

where λ is the wavelength, g is the gravitational constant, γ is the surface tension, and ρ the density of the liquid. For values of λ less than 1.7 cm, the first term of Eq. (1), the gravitational term, is small in comparison with the second term, the capillary portion of the expression. The influence of the capillary (or surface tension) effect at various wavelengths is shown in Table 1 with early data cited by Adam (2). At wavelengths less than 1.7 cm, the capillary influence predominates and becomes more important as wavelength decreases. The restoring forces (damping effects) acting at small wavelengths are therefore governed by surface tension and other surface parameters.

Table 1
Wave Properties*

λ (cm)	v (cm/sec)	f(sec^{-1})	Percentage of v^2 Due to Capillary Term
0.1	67.8	678	99.97
0.3	39.4	131	97.0
0.5	31.5	63	92.2
1.0	24.8	24.8	74.5
1.71	23.1	13.5	50.0
2.0	23.2	11.6	42.4
5.0	29.5	5.9	10.5
10.0	40.0	4.0	2.86

*N.K. Adam, The Physics and Chemistry of Surfaces, 3rd ed., Oxford: University Press, p. 386, 1941.

It will be helpful to survey briefly the experimental and theoretical literature concerning this subject. The influence of organic surface active materials adsorbed at the air/water interface upon the damping of capillary waves was presented fully in a previous report (3). It was explained that naturally occurring sea slicks are a manifestation of the process of capillary wave damping caused by the adsorption of naturally occurring oceanic matter from the bulk sea onto the sea surface. It was shown that the wave damping so widely observed can be caused by insoluble organic surface films of monomolecular dimensions at film pressures as low as one dyne/cm or less.

This process was investigated in detail as a function of the film pressure using an experimental system so designed that (a) linear surface waves could be generated at various frequencies and amplitudes, (b) the wave amplitudes could be measured conveniently and accurately, (c) insoluble monomolecular film-forming materials could be added to or removed from the water surface, and (d) the film pressure of the spread monolayer could be controlled and measured. Graphs of film pressure (F) vs the surface area per adsorbed molecule of film (A) were determined in a modified Langmuir-Adam film balance for each pure compound studied and compared with the wave-damping data. The wave-damping coefficient (k) was obtained from the decrease of the wave amplitude with distance from the wave source using the following equation:

$$a = a_o e^{-kx} \tag{2}$$

where a_o is the amplitude of the wave at the source and x is the distance from the source. Equation (2) describes the decay of linear waves on either a clean or a film-covered water surface.

At film pressures less than 0.1 dyne/cm, k was found to increase slowly as the monolayer was compressed. Between approximately 0.1 and 0.5 dyne/cm, there was an abrupt rise in k to a maximum value which remained essentially constant with further increases in film pressure. After the film pressure had reached about 0.5 dyne/cm, little additional damping occurred when more surface active material was added to the surface; this being true even when the film was thicker than a monolayer. A comparison of the graph of (k) vs F with that for $\bar{F}$ vs A revealed that the sudden increase in the damping coefficient occurred in the neighborhood of the region of transition of the monolayer from a highly compressible state to a more condensed or less compressible state. All of the various insoluble surface active compounds studied behaved in a similar manner with respect to wave-damping effects even though they differed markedly in chemical structure. These experiments were performed at a wave-generating frequency of 60 cps (wavelength = 0.52 cm) and an initial amplitude of 0.1 mm.

Since ocean waves exist in a broad spectrum of wavelengths and amplitudes which depend upon oceanographic and meteorological conditions, it was the purpose of this investigation to examine the effects of wavelength and wave amplitude on the damping of capillary waves and the pertinence of this information to oceanography.

APPARATUS AND MATERIALS

The apparatus and procedures used to generate linear capillary waves, measure their amplitudes and control, and determine film pressure have been described in a previous report (3). Only one important alteration was made in this system. The light chopper driven by a synchronous motor was replaced by an electronic stroboscope to provide illumination interrupted precisely at the same frequency as that of wave generation. This modification was essential for experiments at high frequencies since the mechanical light chopper could not be synchronized with the wave generator above 90 cps.

The following insoluble monolayer-forming compounds were included in this study: twice-distilled 9, (and 10)-phenylstearic acid (USDA Eastern Regional Research Laboratory) and oleic acid (Hormel Foundation prepared from highly purified methyl oleate by saponification and distillation). These materials were further purified prior to these experiments by passing each through a long adsorption column packed with activated adosrption-grade alumina (80-200 mesh). Sea-slick sample P-13 was taken from the top 0.15 mm of the ocean, 8 miles west of San Diego, California, using an aluminum screen technique (4) developed at this Laboratory. This sample contained organic constituents of the sampled sea slick which had been extracted with chloroform and isolated by vacuum distillation. All monolayers were spread from dilute freshly distilled stock solutions of chloroform or petroleum ether.

Aqueous substrates used were distilled water, sulfuric acid solution in distilled water (pH2), and synthetic sea water (5).

WAVELENGTH EFFECT

The damping coefficient (k) is a function of frequency of the ripples (6) and can be calculated from the theoretical relationship

$$k = \frac{8\pi^2 \eta}{\rho V \lambda^2} \tag{3}$$

or as an approximation

$$k = \frac{8\pi\eta f}{3\gamma} \tag{4}$$

where V is the group velocity of the wave train, f is the ripple frequency, and η is the bulk viscosity expressed in poises. Equation (4) is valid only for water and short wavelengths (0.5 cm or less).

Figure 1 is presented as background and demonstrates the relationship between k and A for a typical insoluble organic monolayer of the type reported earlier (3). Also plotted is the corresponding plot of F vs A for the same monolayer under the identical condition. As the area per molecule decreased, the isothermal surface compressibility of the monolayer decreased slowly. When A reached approximately $100A^2$, the compressibility decreased rapidly. In surface chemical terminology, the monolayer has gone through a two-dimensional phase change from a more diffuse (gaslike) surface state to a more condensed (liquidlike) state. In a similar manner, as A decreased, k at first increased slowly, then increased

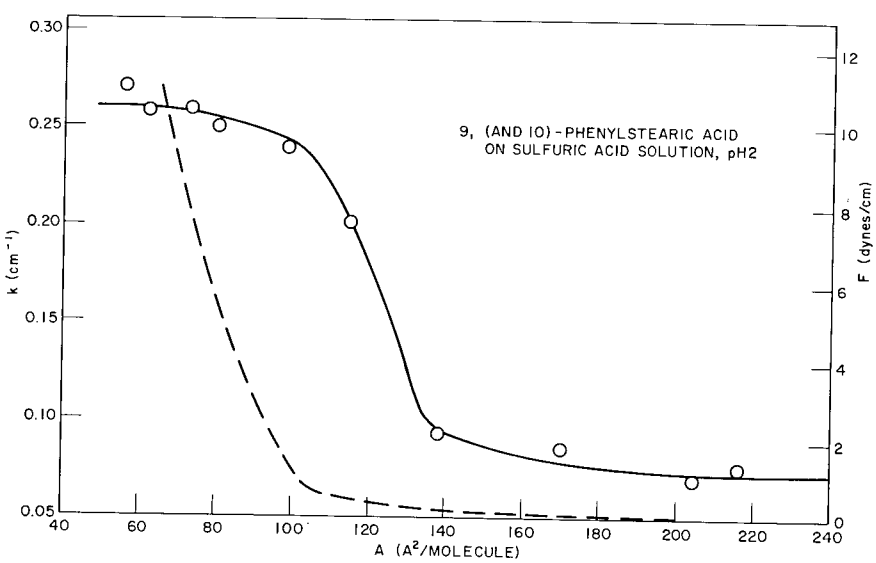

Fig. 1 - Dependence of the damping coefficient (k) upon the area (square angstroms) per molecule of a phenylstearic acid monolayer (solid line). Corresponding film pressure (F) vs area (A) curve (dashed line).

abruptly in the neighborhood of the transition region where the monolayer compressibility was decreasing rapidly. After k has reached a maximum value, further decrease in A did not appreciably change the value of the damping coefficient.

Similar experiments were performed at 35, 60, and 150 cps using a standard monolayer and substrate system to determine effect of frequency upon the damping coefficient-area and force-area interrelationship. The initial wave amplitude was held constant in this experiment to avoid a possible competing amplitude effect. These data are summarized in Fig. 2 and show that the onset of the damping effect occurs at about the transition region of the F vs A curve for all frequencies studied. In each case k increased to a maximum value as A decreased and remained about constant with further decrease in molecular area. Figure 2, therefore, shows that for any wavelength of capillary waves within the range studied, commencement of the damping effect was independent of frequency and dependent only on the properties of the monolayer. Although the molecular area at which the damping effect became large was not frequency dependent, the maximum value of k for the incompressible surface was a function of the frequency of wave generation. As frequency is increased (wavelength decreased), the damping effect exerted by a monomolecular surface layer becomes significantly greater.

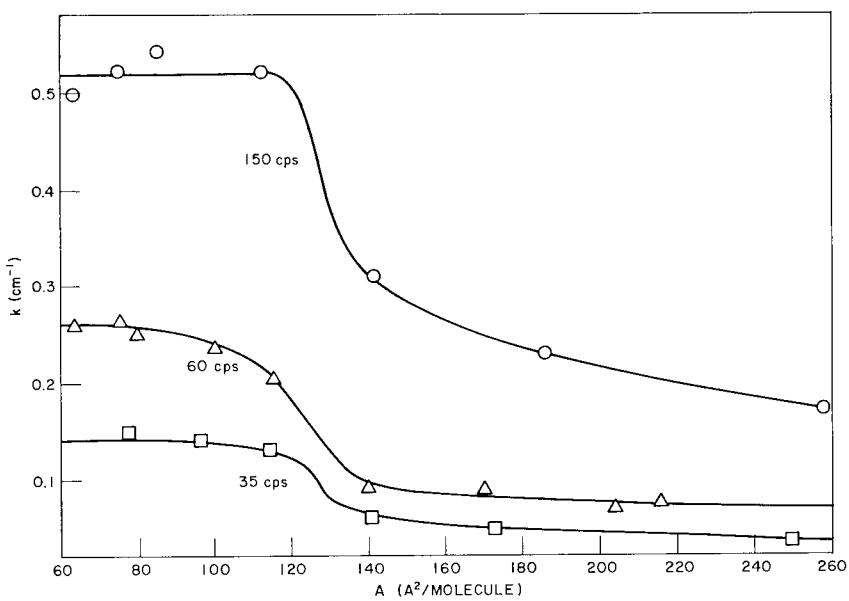

Fig. 2 - Dependence of the damping coefficient (k) upon the molecular area (A) for a phenylstearic monolayer on sulfuric acid solution (pH2) at three frequencies. Amplitude (a_o) = 0.05 mm.

The dependency of the damping coefficient on frequency for a clean distilled water surface is expressed by Eqs. (3) and (4). This relationship is plotted in Fig. 3. The data points were determined to verify the purity of the distilled water used in these experiments and all fall near the theoretical line. Small amounts of surface active impurity would have caused positive errors in k for clean water. The data points below 35 cps were taken from Roberts (7) and represent a wavelength range of from 0.866 to 3.77 cm. This range extended from the capillary wave region into the gravity wave spectrum where the dominating restoring force is gravity rather than surface tension.

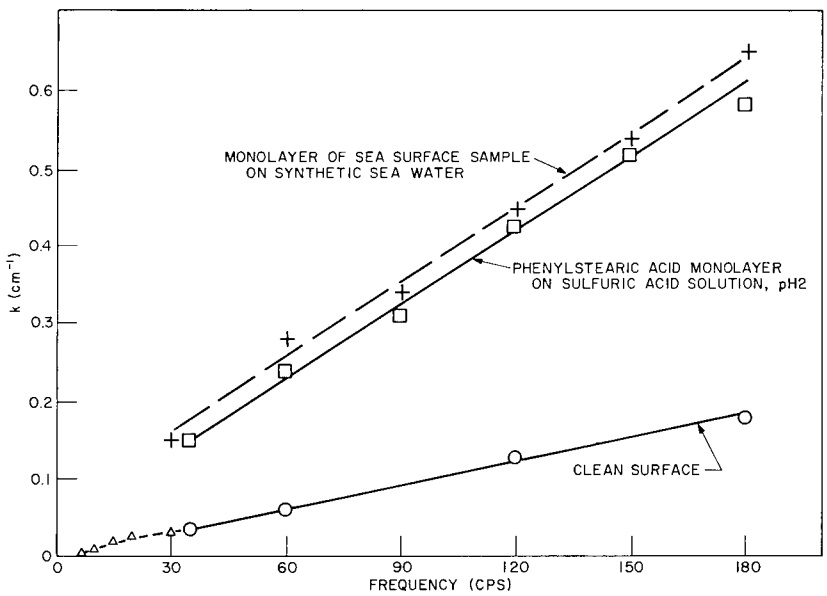

Fig. 3 - Effect of wave-generation frequency on the damping coefficient (k) for various monolayers. (Δ) data of Roberts (7).

In Fig. 3, the damping coefficient (k) versus wave frequency for an acid-water surface (pH2) covered with a phenylstearic acid monolayer is plotted. The film pressure of the monolayer was held constant at 2.3 dynes/cm and a constant initial amplitude of 0.05 mm was generated at each frequency studied. The film pressure of the monolayer was sufficiently high so that it was at the damping maximum on the plateau of the k vs F curve depicted in Fig. 1. Consequently, small changes in F resulting from increased surface area during wave formation could not cause significant changes in k during the experiment. Note that the slope of the damping coefficient vs frequency plot for the film-covered surface is steeper than that for the clean water. Thus, the damping effect is much greater on a film-covered surface than on clean water at high frequencies.

Data showing the variation of k with frequency for a sample of insoluble sea-slick constituents (P-13) are also included in Fig. 3. This sample was handled experimentally like the phenylstearic acid. It was spread on water from a dilute chloroform solution to form a monomolecular layer to establish a film pressure of 10.0 dynes/cm. Although analytical data reported elsewhere (8) reveal that the insoluble organic matter in the sea is a complex mixture of fatty acids, fatty esters, hydrocarbons, and traces of other materials, the data points in Fig. 3 fall near those for the monolayer of phenylstearic acid. The k vs A and F vs A curves for P-13 were determined on sea water (Fig. 4). Because the molecular weight of this monolayer was not known, the value of A is expressed as square meters per milligram of film. The relationship between the two curves is similar to that depicted in Fig. 1 and described by Garrett and Bultman (3) for pure monolayers.

To indicate the probable chemical relationship of the sea sample to that of a pure monolayer system, pure oleic acid was studied on synthetic sea water and k vs A and F vs A curves were plotted in Fig. 5 with A expressed in square meters per milligram. Oleic acid was chosen since an earlier report (8) had shown that it is one of the common fatty acids found in natural sea slicks. The outstanding difference between Figs. 4 and 5 is that the oleic acid occupied a much larger area per milligram of spread material than did the sea sample. This can be interpreted to indicate that the sea surface material contained a

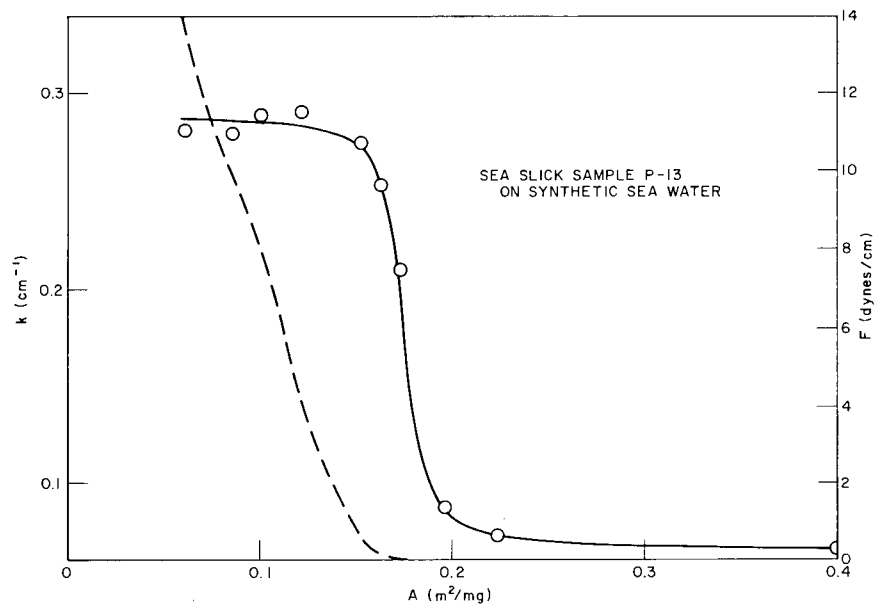

Fig. 4 - Dependence of the damping coefficient (k) upon the film area (square meters per milligram) of a monolayer of sea-slick constituents (solid line). Corresponding film pressure (F) vs area (A) curve (dashed line).

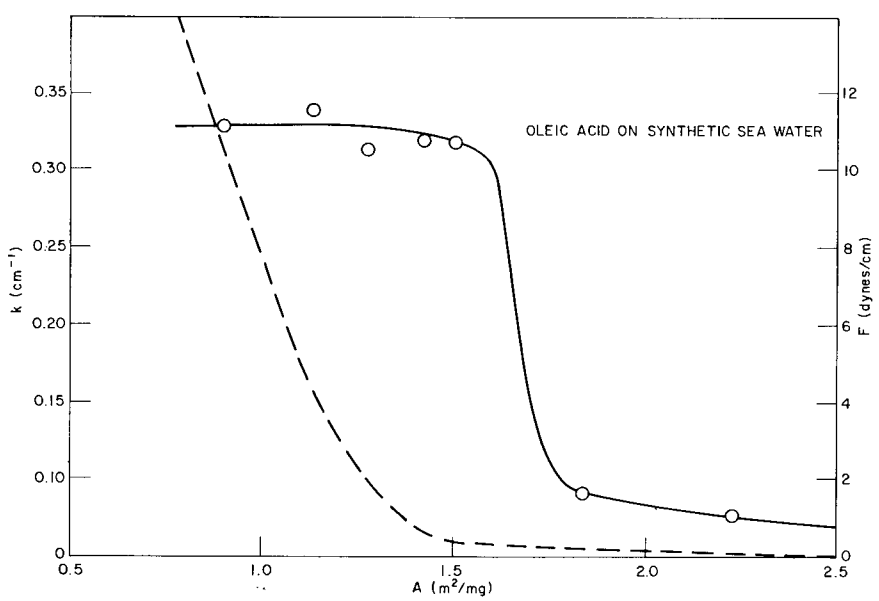

Fig. 5 - Dependence of the damping coefficient (k) upon the area (square meters per milligram) of an oleic acid monolayer (solid line). Corresponding film pressure (F) vs area (A) curve (dashed line).

relatively large quantity of nonpolar material which was not surface active and did not contribute to either the damping effect or the F vs A curve. This nonpolar material was presumably forced out of the monolayer by the surface active constituents as they are compressed. Neglecting the differences in specific areas, however, the relationship between k and F is similar for both the sea sample and the pure oleic acid, i.e., large increases in k occurred with the decrease in compressibility accompanying the change of state of the monolayer.

SOLUBLE SURFACE ACTIVE COMPOUNDS

Soluble as well as insoluble materials adsorbed at the air/water interface are effective in attenuating capillary waves. The contribution to the damping effect from soluble and highly surface active compounds can be appreciable. Davies and Vose (9) studied the effects of frequency and concentration on damping of aqueous solutions of sodium lauryl sulphate and found that at high concentrations (0.01 M) and frequencies greater than 100 cps the concentration of adsorbed surface active laurate ions tended toward a constant maximum value and k increased linearly with frequency just as would an insoluble monolayer spread on the same surface. At frequencies less than 100 cps, deviations from linearity were explained by postulating that the surface concentration of adsorbed ions was decreased, thereby lowering the damping effectiveness of the film.

AMPLITUDE EFFECT

Experiments were performed to determine the effect of varying the initial wave height a_o (or the amplitude at $x = 0$) on the damping coefficient for a surface covered with a phenylstearic acid monolayer. The value of k on clean water surfaces was found to be independent of wave amplitude. Various initial amplitudes were generated on an acid-water surface covered with a monolayer of phenylstearic acid, and the damping coefficient was determined for each amplitude studied. These measurements were made at three different monolayer film pressures: (a) low film pressure of 0.1 dynes/cm where the film compressibility was high and there was little damping, (b) a film pressure of 0.8 dynes/cm where the compressibility was moderate and the damping maximum had been reached, and (c) a relatively high film pressure of 14.0 dynes/cm. The results presented in Table 2 show no effect at

Table 2
Effect of Initial Amplitude on k*

Film Pressure (dynes/cm)	Initial Amplitude (mm)	k (cm^{-1})
Clean Surface		0.13
0.1	0.054	0.15±0.01
	0.035	0.16±0.01
	0.016	0.15±0.01
	0.009	0.17±0.01
0.8	0.023	0.43±0.02
	0.010	0.42±0.02
	0.006	0.42±0.02
	0.003	0.39±0.02
14.0	0.011	0.41±0.02
	0.008	0.40±0.02
	0.006	0.44±0.02
	0.003	0.44±0.02

*Monolayer - 9, (and 10)-phenylstearic acid. Substrate - acid water, pH2. Wave generation frequency - 120 cps.

any of the three film pressures of initial amplitude on the damping coefficient within the limits of the ±5% experimental uncertainty in determining k.

DISCUSSION

The "sea slick" is an area of the ocean surface in which capillary waves have been damped by the presence of an adsorbed film of surface active substance. The spectrum of capillary waves on the sea includes wavelengths from a few centimeters down to a few tenths of a centimeter. They are found under almost all sea conditions except in an absolute calm or in areas which are entirely slick covered. Since the experimental wavelength range in this study was 0.24 to 0.87 cm and these wavelengths are common in the capillary wave spectrum of the sea, the laboratory results reported here are applicable to explaining the observed wave damping of the ocean surface.

The ocean contains a widely distributed complex mixture of organic matter, especially in or near the surface with much of this material being surface active and capable of adsorbing at the surface. Constituents of the sea surface film described earlier (8) were found in laboratory experiments to form insoluble monolayers which could be compressed to high film pressures. These films were also shown to be capable of causing the wave-damping effect at low film pressures in a manner similar to that of the pure monolayer-forming materials included in this report. Since k increases to a maximum value at rather low values of film compressibility, only small surface compressional forces are required to create and sustain a sea slick. Such forces are supplied by the wind and water movements which affect the sea surface. Under ideal conditions, as shown by the laboratory experiments, it should be possible for a slick to form at film pressures less than one dyne/cm. From the study of the effect of frequency, it was demonstrated that when a critical compressibility of the film was attained all wavelengths were affected but to different degrees of damping. That is, the shorter the wavelength, the greater was the damping coefficient for any particular set of conditions.

Soluble surface active substances adsorbed at the air/water interface are also effective in damping water waves in the capillary portion of the ocean wave spectrum, but they will not contribute greatly to wave damping in the natural oceanic environment when there are insoluble monolayer-forming components present. The less surface active and more soluble materials such as amino acids, polypeptides, and carbohydrates will ordinarily be minor contributors to the wave damping observed, since they would be displaced or excluded from the surface through competitive adsorption by the less soluble surface active materials, such as the higher fatty acids, alcohols, and esters which are usually present in or near the surface.

The ocean is a reservoir rich in naturally occurring surface active organic substances. At any portion of its surface it can quickly be covered with natural slicks whenever suitable oceanographic and meteorological conditions exist. In fact, it is usually observed that when the sea is calm for a long time so that the surface film is not collapsed or blown away by wind or dissipated by a strong wave action, the entire surface appears to be covered with a slick. Although gravity-influenced swells may persist under these conditions, the capillary wave structure has been damped out. As the film disrupting conditions (usually wind) reappear, the surface slick is broken into windrows and much of it is collapsed and resubmerged. Through such processes the active organic sea constituents enter into a dynamic equilibrium with the ocean surface, and when these materials can be laterally compressed so that they form an incompressible film, they create a sea slick through the wave-damping process.

SUMMARY

The damping of mechanically generated capillary waves has been investigated on clean water and on water surfaces covered by monomolecular films at various film pressures. The damping coefficient (k) was shown to obey Eq. (4) for a very clean water surface. As insoluble surface active materials were spread onto the surface, k increased above that for the clean surface indicating that the capillary waves were decaying at an increasing rate. A comparison of F vs A with k vs A graphs for the same monolayer showed that k increased rapidly at values of F of less than one dyne/cm. The large increase in k occurred when the compressibility was decreasing during the phase transition of the monolayer from a gaseous to a liquid or liquid-expanded state. Once the maximum value of k had been attained, further increases in F caused no further significant changes in k. All of the materials studied behaved in this manner including both pure compounds and natural surface active substances taken from the ocean surface.

Equation (4) shows that for a clean surface, k is directly proportional to the ripple frequency (f) for wavelengths less than 0.5 cm. Thus, if the frequency is doubled there is a twofold increase in the damping coefficient on clean water. On the other hand, the slope of the f vs k curve (Fig. 3) for a film-covered surface is steeper than that for the clean water surface. For example, k was large (0.65 cm^{-1}) for 180-cps waves on a surface covered with film-forming material taken from the ocean surface, while for a clean surface k = 0.18 at the same frequency.

The molecular area at which the abrupt increase in k occurred did not appear to be a function of the frequency of wave generation (as shown by Fig. 2). The damping coefficient was found to be independent of the initial amplitude for both clean and monolayer-covered surfaces.

In general, it has been demonstrated that both soluble and insoluble surface active materials, when adsorbed at the air/water interface, are capable of damping capillary waves to a maximum value of k at film pressures of less than one dyne/cm. Since k increases greatly while the monolayer compressibility is relatively high, only small lateral forces on the ocean surface are necessary to initiate capillary wave damping and create sea slicks when surface active materials are present.

REFERENCES

1. Lord Kelvin, Phil. Mag. 4th Series 42:368 (1871)

2. Adam, N. K., "The Physics and Chemistry of Surfaces," 3rd ed., Oxford: University Press, p. 386, 1941

3. Garrett, W. D., and Bultman, J. D., "The Damping of Water Waves by Insoluble Organic Monolayers," NRL Report 6003, Oct. 17, 1963

4. Garrett, W. D., "Collection of Slick-Forming Materials from the Sea," NRL Report 5761, Mar. 5, 1962

5. "Lubricants, Liquid Fuels and Related Products; Methods of Inspection, Sampling and Testing," Federal Test Method Standard, Method 4011.3, May 12, 1958

6. Goodrich, F. C., Proc. Roy. Soc. A260:503 (1961)

7. Roberts, W. L., "Study of Waves in a Small Tank," NRL Report 6097, June 1964

8. Garrett, W. D., Timmons, C. O., and Jarvis, N. L., "Constitution and Surface Chemical Properties of Sea Slicks," NRL Report 5925, May 23, 1963

9. Davies, J. T., and Vose, R. W., Birmingham Univ. Chem. Engr. 14:29 (1963)