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Wave damping by monomolecular surface films and their chemical structure. Part II: Variation of the hydrophilic part of the film molecules including natural substances

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ABSTRACT

The direct wave attenuation influence of surface active compounds on plunger-generated water waves (1.0, 1.3, 1.8, 2.0, 2.3, and 2.5 Hz) was investigated in the Hamburg wind-wave tunnel by systematic variation of the hydrophilic group. Long-chain alcohols, acids, and amines exhibit a considerable wave damping effect. An additional wave energy dissipation term is active in the presence of carboxylic acid ester (E/Z-isomerization). It is concluded from the experimental results that hydrophobic interactions between the hydrophobic alkyl chains and the adjacent water layer play a dominant role by inducing "ice-like clathrate structures." Some hydrophilic groups (mono- and di-oxyethylenated alcohols) may also promote formation of these structures, whereas other hydrophilic groups (sodium sulfonates; poly-oxyethylenated alcohols with $n_{glycol} \geq 3$) are counteracting against this effect ("structure breakers"), which results in a considerably lower wave attenuation effect. Proteins and triglycerides exhibit no significant wave damping ability, while sterols, and hydrophobized amino acids and carbohydrates in part show wave damping characteristics similar to those of long-chain alcohols. The experimental results are discussed in the framework of theories developed by Cini *et al.* (1983) and by Lucassen-Reynders and Lucassen (1969) with emphasis upon the so-called "Marangoni-effect," which appears to be of highly dissipative character.

1. Introduction

Natural polar organic substances consisting of a hydrophobic alkyl chain ("tail") and a hydrophilic "head group" are known to accumulate at the air/sea interface due to their ambiphilic character thus forming monomolecular surface films ("slicks"). The most influential factors limiting the formation and existence of these slicks are the biological activity and air-sea dynamics (breaking waves, bursting bubbles) within the upper water layer of the ocean surface (Hühnerfuss *et al.,* 1977; Garrett and Hühnerfuss, 1984).

One of the most notable effects of surface films is their ability to dampen water waves, thus modifying several characteristics of the sea surface; e.g., the electromag-

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netic emission in the visible and microwave bands as well as scattering of these spectral bands, and gas exchange rates (Hühnerfuss and Garrett, 1981). In recent experiments, the attenuation of wind waves by surface films has been investigated by simulating natural slicks by well-defined pure artificial monomolecular surface films both in large-scale experiments on the open sea (Hühnerfuss and Garrett, 1981; Hühnerfuss *et al.*, 1978, 1981a, 1983) and in wind wave tunnel experiments (Hühnerfuss *et al.*, 1981b). It has been shown that the surface films exhibit a direct wave damping influence on the water waves ("viscous damping effect") and as a consequence of the thus modified sea-surface roughness indirect influences on the wind/wave and the long wave/short wave interactions (Hühnerfuss *et al.*, 1981a). Furthermore, a distinct dependence of the wave attenuation intensity on the chemical character of the film forming substances has been concluded from these pioneering experiments (Hühnerfuss *et al.*, 1981b, 1983). Therefore, since natural surface films are known to consist of a variety of organic chemical compounds, the composition of which may vary considerably with the seasonal occurrence of different planktonic species and with day-night cycles, it has been postulated that they may very differently interfere with air-sea interaction processes depending on the chemical structure of the film forming substances. In order to gain insight into the correlation between the chemical structure of surface films and their wave damping ability, systematic wind-wave tunnel experiments have been performed with pure surface active compounds.

In a first set of experiments [see Part I of this work, (Hühnerfuss *et al.*, 1982) hereafter referred to as Part I] the direct influence of slicks on wave damping has been investigated by varying systematically the hydrophobic part of the film molecules. On account of the widespread occurrence of carboxylic acid derivatives in natural surface films the hydrophilic part of the surface active substances has been an ester group. It turned out that stepwise prolongation of the carboxylic acid alkyl chain between C_{14} and C_{22} showed a maximum in wave damping to occur at C_{16} (palmitic acid methyl ester). Introduction of one to three $C\!=\!C$-groups (oleic acid methyl ester; linolenic acid methyl ester) induced a significant decrease of the wave attenuation effect compared to the saturated compound (stearic acid methyl ester), but no difference was discernible between oleic acid methyl ester and linolenic acid methyl ester. $C\!=\!C$—E-oriented derivatives (elaidic acid methyl ester) and $C\!=\!C$—Z-oriented ones (oleic acid methyl ester) also showed the same wave damping characteristics. Systematic variation of the ester alcohol component supplied the result that surface films of lower alkyl chain derivatives (palmitic acid methyl ester, -ethyl ester) contribute to wave energy dissipation by an E-/Z-isomerization mechanism during wave-induced dilatation and compression of the film, whereas esters with longer alkyl chain are preferably oriented in the E-form. By introducing a branched alcohol component (palmitic acid isopropyl ester) instead of a straight chain one (palmitic acid n-propyl ester) wave damping is decreased.

In this work the second set of wind-wave tunnel experiments is summarized, during

which the hydrophilic head group of the film forming molecules was varied keeping the hydrophobic alkyl chain length constant. Thus, experimental evidence can be presented of the wave attenuation potential of a variety of natural surface active compounds.

Another objective of this investigation is devoted to the mechanism of energy dissipation in water waves due to the presence of slicks and to a possible theoretical description of this mechanism. Several theoretical approaches have been discussed in the literature, the most promising of which are briefly discussed in Part I of this investigation.

Independently obtained results from passive microwave sensors and from Langmuir-trough measurements have in the meantime backed up our postulation that any theoretical description of water wave attenuation by slicks has to include not only the monomolecular surface film itself but the whole system surface film/adjacent water layer; i.e., the "vicinal water layer" (for details see Alpers *et al.,* 1982; Drost-Hansen, 1969; Hühnerfuss and Alpers, 1983; Hühnerfuss, 1983; Hühnerfuss and Walter, 1984).

2. Experimental procedure

An extensive description of the experimental procedure is given in Part I of this work. Herein only the basic concept can be repeated.

The wave damping effect of each substance was investigated in a wind-wave tunnel (for details see Hühnerfuss *et al.,* 1976) such that plunger-generated waves of 1.0, 1.3, 1.8, 2.0, 2.3, and 2.5 Hz were allowed first to propagate over a carefully cleaned water surface and then over a surface covered with a surface film. The amplitudes of the waves were measured by resistance wave gauges of the Danish Hydraulic Institute, Horsholm (Denmark), at distances of 3.5 m, 7.5 m, 11.5 m, and 15.5 m from the point where the film dropped onto the water surface. The obtained amplitude values allowed calculation of the damping coefficient Δ of each surface film/water system, where Δ is the exponent of the exponential function describing the damping to a wave with an amplitude a_0 at a fetch zero and a_x after a distance x:

$$a_x = a_0 e^{-\Delta x}. \tag{1}$$

The various substances applied in this investigation have either been prepared by known procedures or obtained from the Henkel KGaA, Düsseldorf (FRG), or bought from commercial sources (see Table 1). In the latter two cases the substances have either been recrystallized to constant melting point or redistilled. The chemical compounds were spread from a spreading solvent (75 mmol in ethanol, in the case of proteins water with 0.5% or 1% NaCl, in some other cases slight amounts of heptane, in order to promote solvation) by continuously pumping the solution onto the water surface by a precision peristaltic tube pump so that an excess of the surface active

Table 1. The various surface active substances investigated in this work and their sources or methods for preparation.

| Surface active substance	Source/method for preparation
palmitic acid (PS)	EGA, Steinheim (FRG); ca. 99%, recryst.
oleic acid (OLS)	FLUKA, Neu-Ulm (FRG); puriss., redist.
palmitic acid methyl ester (PME)	Autorenkollektiv (1977)
α-bromo-palmitic acid methyl ester (BPME)	Autorenkollektiv (1977)
palmitic acid ethyl ester (PEE)	Autorenkollektiv (1977)
cetyl alcohol (CEA)	FLUKA, Neu-Ulm (FRG); puriss, recryst.
oleyl alcohol (OLA)	Henkel KGaA, Düsseldorf (FRG), redist.
ethylenglycol-mono-cetyl ether (CEEO1)	Henkel KGaA, Düsseldorf (FRG), recryst.
di-(ethylenglycol)-mono-cetyl ether (CEEO2)	Wrigley *et al.* (1960)
tri-(ethylenglycol)-mono-cetyl ether (CEEO3)	Wrigley *et al.* (1960)
cetyl amine (CEAM)	FLUKA, Neu-Ulm (FRG), purum, recryst.
sodium hexadecylsulfonate (CESSNA)	Merk, Darmstadt (FRG), 99%, recryst.
sodium dodecylhydrogensulfate (DDHSNA)	Merk, Darmstadt (FRG), recryst.
1,12-dodecane-di-ol (DDDIA)	EGA, Steinheim (FRG), ca. 99%, recryst.
1,8-octanedioic acid di-butyl ester (ODIBUE)	EGA, Steinheim (FRG), redist.
egg albumin (mol. weight 45 000) ALB)	FLUKA, Neu-Ulm (FRG), 5 × cryst., lyophilisation
γ-globulin (mol. weight 160 000) (GLOB)	Sigma Chemical Co., Taufkirchen (FRG) Bovine Cohn Fraction II, ca. 99%
tri-palmitin (TPG)	FLUKA, Steinheim (FRG), puriss., recryst.
tri-olein (TOLG)	FLUKA, Steinheim (FRG), puriss., redist.
sorbitane-mono-stearate (SPAN 60)	FLUKA, Steinheim (FRG), recryst.
sorbitane-mono-oleate (SPAN 80)	Riedel-de Haen AG, Seelze (FRG)
cholesterol (CHOL)	FLUKA, Steinheim (FRG), puriss.
cholesteryl palmitate (PCHOL)	FLUKA, Steinheim (FRG), purum, recryst.
α-amino-butyric acid cetyl ester hydrochloride (ABSCECL)	Fischer (1905); Autorenkollektiv (1977)
α-amino-butyric acid oleyl ester hydrochloride (ABSOLECL)	Fischer (1905); Autorenkollektiv (1977)
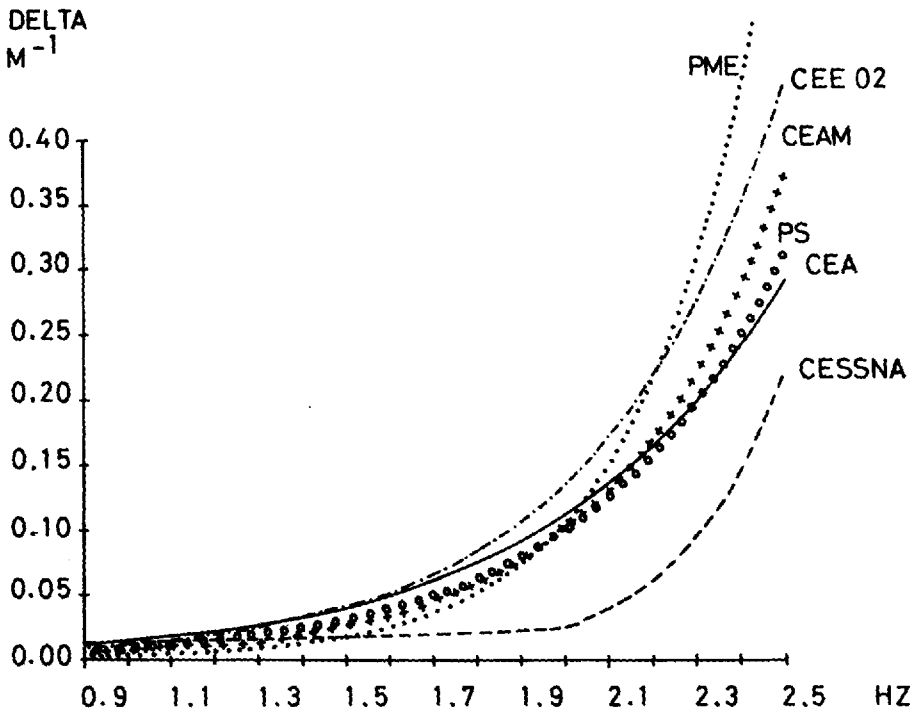
Figure 1. Damping coefficient Δ [m^{-1}] vs. frequency [Hz]. Comparison of palmitic acid methyl ester (..... PME), di-(ethylenglycol)-mono-cetyl ether (·----- CEEO2), cetyl amine (+++++ CEAM), palmitic acid (ooooo PS), cetyl alcohol (_____ CEA), and sodium hexadecylsulfonate (------ CESSNA).

material was available for repairing any hole that might occur. Continuous pumping was necessary because surface films of substances with lower spreading velocities were transported slowly toward the beach end of the wind-wave tunnel by the wave induced Stokes drift.

3. Results

Since wave damping by slicks has been shown to exhibit a maximum when applying film forming substances with an alkyl chain length of C_{16}, a first comparison of the wave attenuation ability between various surface active compounds was performed with a C_{16} alkyl chain length. The hydrophilic head group consisted of a carboxylic acid methyl ester (PME), amine (CEAM), carboxylic acid (PS), or alcohol (CEA) group, respectively; i.e., groups often encountered in natural surface active substances.

In Figure 1 the measured damping coefficients Δ are plotted versus the frequency in the range 1 to 2.5 Hz. The hexadecanol ("cetyl alcohol"; CEA), the hexadecanoic acid ("palmitic acid"; PS), and hexadecylamine ("cetylamine"; CEAM) slicks show

comparable wave damping characteristics. Obviously, the wave attenuation effect in these three cases is dominated by the hydrophobic part of the molecules. This observation is in line with the assumption that the hydrophilic group is in a first approximation only responsible for high energy short range interactions between monolayer and the adjacent water (hydrogen bond formation, ion-dipole and dipole-dipole interactions), whereas hydrophobic interactions between the alkyl chain and the water layer lead to long-range effects in the "vicinal water layer" (for details see Drost-Hansen, 1969; Hühnerfuss and Alpers, 1983; Hühnerfuss, 1983). Recent passive microwave measurements performed in the presence of 9-octadecen-1-ol, Z-isomer ("oleyl alcohol") surface films could only be interpreted by assuming a "penetration depth" of $d \leq 190 \ \mu$m (Alpers *et al.*, 1982). An evaluation of widespread literature data showed that in 12 earlier papers long-range effects of similar penetration depths had been reported (Hühnerfuss and Alpers, 1983). Although the physico-chemical nature of this long-range effect still remains subject to considerable debate, the free enthalpy values, the relaxation time and the O .... O distances measured within this vicinal water layer clearly indicate the formation of "ice-like" clathrate structures. In accordance with Debye-theory this implies an increase of the viscosity of this upper water layer by an order of magnitude.

A deviation from the "normal" wave damping characteristic of C_{16}-compounds can be observed, if additional mechanisms are interfering with the formation of the vicinal water layer. E.g., as already pointed out in Part I of this work, the carboxylic acid methyl ester group (PME) exhibits an extraordinary wave attenuation ability, since an E/Z-isomerization of the alcohol component of the ester group supplies an additional dissipation term to the wave attenuation effect of the surface film.

Another possibility for interfering with the "vicinal water layer," which is induced by the hydrophobic group, can be either "structure breaking" or "structure promoting" effects of the hydrophilic head group: an example for a structure breaking head group is shown in Figure 1 for the wave attenuation curve of an artificial surface active compound sodium hexadecylsulfonate (CESSNA). Obviously, the hydrophilic group and the hydrophobic part of the molecule are in this case counteracting, the result of which is a less intensive hydrogen bond formation and a lower surface viscosity than observed in the presence of alcohols, acids, amines, and ester. This conclusion is in line with previously reported "structure breaking effects" of the SO_4^{2-} group (Frank and Wen, 1957), which appears to interact with the water layer in a similar manner as the sulfonate group.

Another notable characteristic can be concluded from the CESSNA-curve given in Figure 1. Due to the counteracting effects of the hydrophobic and the hydrophilic groups the simple exponential law for the Δ-frequency-curve (see Part I)

$$\Delta = \Delta_0 \, e^{-Bf}, \tag{2}$$

where f is the frequency and Δ_0 and B are regression coefficients, is not longer suitable for describing the wave damping characteristics. At frequencies $f \leq 2$ Hz nearly no

wave attenuation is observed and Δ-values similar to those of pure water are measured. At higher frequencies, however, a very intensive wave attenuation is determined. It can be concluded from these curve characteristics that at least two mechanisms are responsible in this case for the wave energy dissipation and their contribution to wave damping depends in different ways on frequency. A similar wave damping characteristic was observed in the presence of several other substances, the curves of which are not included in Figure 1; e.g., sodium dodecylsulfonate and α-amino-butyric acid hexadecyl ester hydrochloride.

As an example for a slight increase of "structure promotion" by the hydrophilic group the wave attenuation curve of di-(ethylenglycol)-mono-hexadecyl ether (CEEO2) is shown, which can be easily prepared by oxyethylenation of one molecule hexadecanol with two molecules of glycol. In order to investigate, to which extent this prolongation of the hydrophilic group by poly-oxyethylenation of a long-chain alcohol would lead to a "structure promotion," a comparison of several compounds of this series was performed. The wave attenuation curves of hexadecanol (CEA), ethylenglycol-mono-hexadecyl ether (CEEO1), di-(ethylenglycol)-mono-hexadecyl ether (CEEO2), and of tri-(ethylenglycol)-mono-hexadecyl ether (CEEO3), which are given in Figure 2, reveal that the structure promotion can only be observed in the presence of CEEO1 and CEEO2, whereas the tri-oxy-ethylenation (CEEO3) of the long-chain alcohol leads to a very dramatic structure breaking and thus to a much lower wave attenuation effect, which is nearly comparable to wave attenuation at a pure water surface. This effect was verified by repeating the measurements with film forming substances of the homologous series of poly-oxyethylenated octadecanols.

Based on the above developed concept of "structure promotion and structure breaking" several additional surface active compounds, which are known to occur in natural slicks, have been selected and investigated in our wind-wave tunnel, in order to determine their direct wave attenuation effect.

a. Proteins, protein-complexes, and amino acid derivatives. A relatively large fraction of natural surface films may consist of proteins (Baier *et al.,* 1974; Daumas *et al.,* 1976; Lee and Williams, 1974). It is well known that so-called protein complexes (Birdi, 1976; Birdi and Sørensen, 1979), i.e., mixtures of lipids and proteins, exhibit extraordinary surface active characteristics. This fact is taken advantage of in, e.g., the manufacture of hair shampoos: if only $0.1 - 0.3\%$ egg albumin is added to the normally used shampoo, its lather is much softer, more durable, and more beneficial to the skin (A. Heins, Henkel KGaA, Düsseldorf (FRG), private communication). With regard to natural surface films, similar protein-complexes between certain natural lipids and proteins can presumably be formed, since in analogy to the above described hair shampoo characteristics very durable foams are sometimes encountered on the ocean surface during medium and stronger winds.

In order to investigate whether these extraordinary surface active characteristics of proteins and protein/lipid-complexes also apply to the wave attenuation effect, some
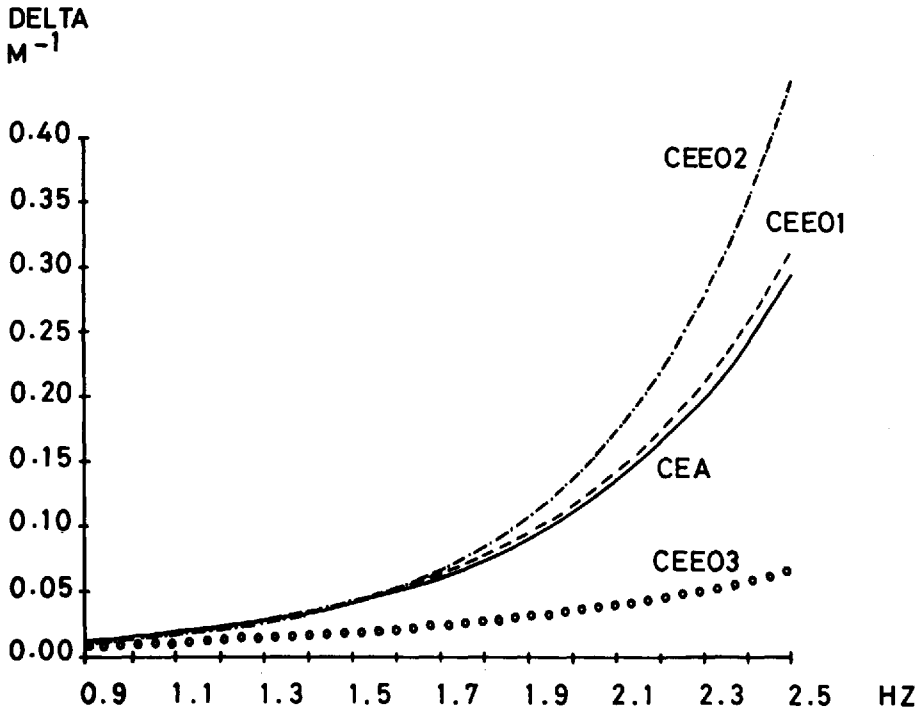
Figure 2. Damping coefficient Δ [m^{-1}] vs. frequency [Hz]. Comparison of cetyl alcohol (_____ CEA), ethylenglycol-mono-cetyl ether (----- CEEO1), di-(ethylenglycol)-mono-cetyl ether (------- CEEO2), and tri-(ethylenglycol)-mono-cetyl ether (ooo CEEO3).

selected substances and mixtures have been included in this investigation. In Figure 3 the wave attentuation curve of an oleyl alcohol/albumin-complex (0.3%; ALBOLA) is compared with the curve of pure oleyl alcohol (OLA). No difference in wave attenuation between the pure surface active compound and its complex with albumin can be observed. The same result was obtained when comparing pure 9-octadecen-1-oic acid, Z-isomer ("oleic acid"; OLS), with its mixture of 0.3% albumin (ALBOLS) (Fig. 4). However, a significant decrease (!) of the wave attenuation ability was observed in the presence of a mixture of hexadecanoic acid ethyl ester and 0.3% albumin (ALBPEE) in comparison with pure hexadecanoic acid ethyl ester (PEE) (Fig. 5). This different behavior of the various protein complexes can be conceivably explained by the assumption that in the case of the unsaturated compounds (OLA; OLS) the albumin molecules can much more easily be integrated between the surface active compounds without significantly expanding the necessary area/molecule of OLA or OLS, respectively. In the presence of palmitic acid ethyl ester/albumin mixtures, however, an optimum interaction between the saturated alkyl chains of the PEE molecules is hindered by the penetrating albumin molecules. As a consequence,
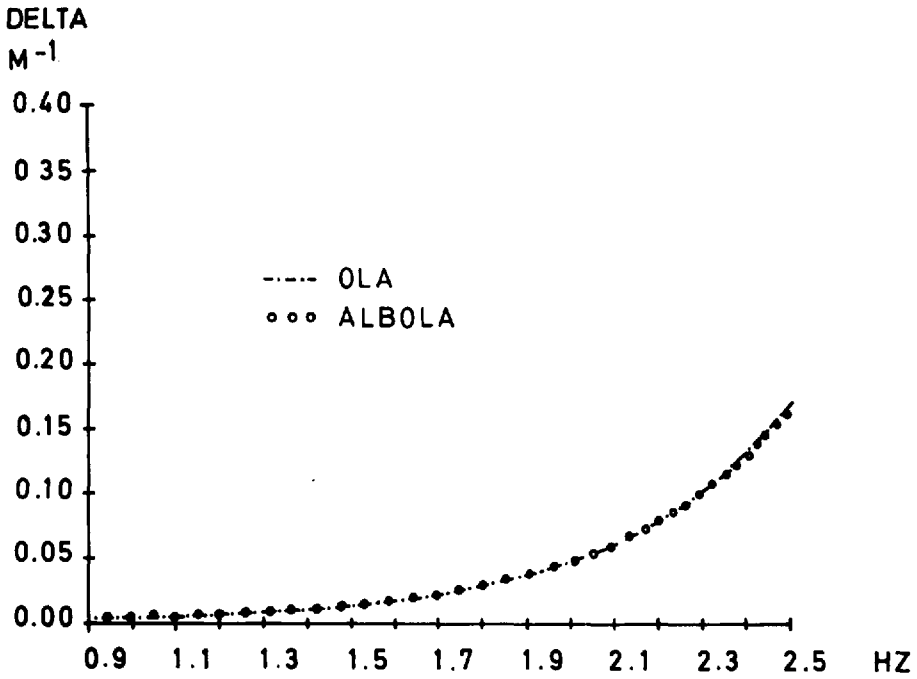
Figure 3. Damping coefficient Δ [m⁻¹] vs. frequency [Hz]. Comparison of pure oleyl alcohol (-·---- OLA), and a mixture of OLA and 0.3% albumin (ooooo ALBOLA).
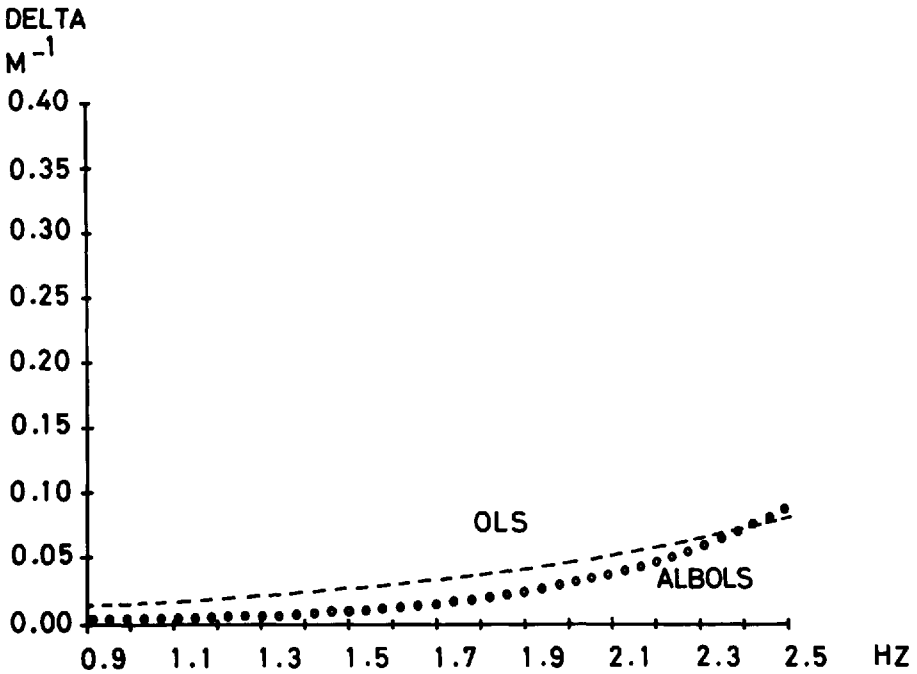

Figure 4. Damping coefficient Δ [m⁻¹] vs. frequency [Hz]. Comparison of pure oleic acid (----- OLS), and a mixture of OLS and 0.3% albumin (ooooo ALBOLS).
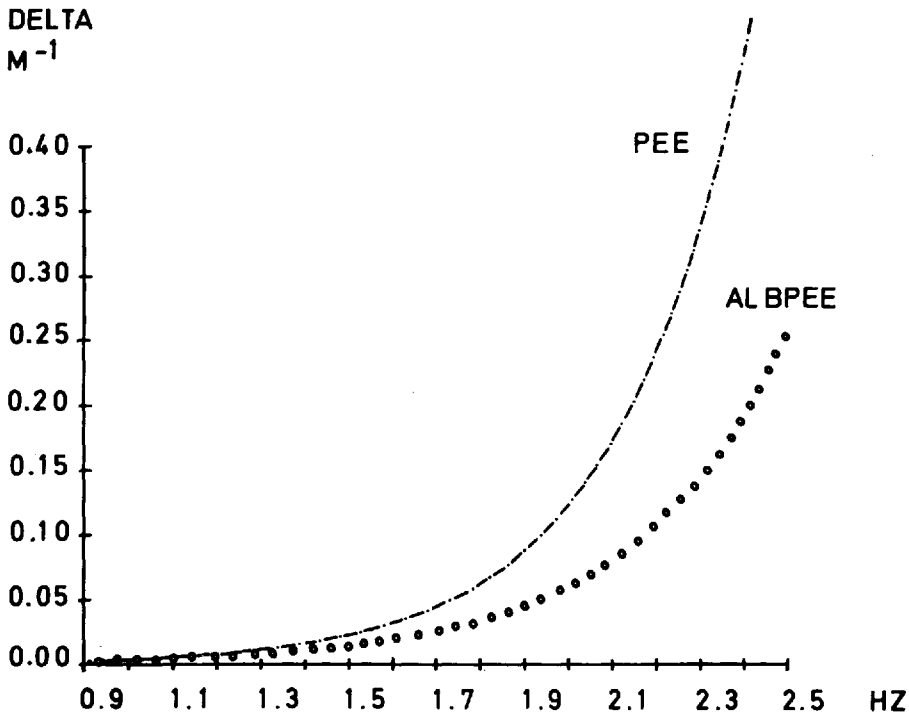
Figure 5. Damping coefficient Δ [m^{-1}] vs. frequency [Hz]. Comparison of pure palmitic acid ethyl ester (------ PEE), and a mixture of PEE and 0.3% albumin (oooo ALBPEE).

this "disturbance effect" appears to reduce the possibility for an optimum hydrophobic interaction between the surface film and the adjacent water layer significantly. This conclusion would be in line with the assumption that the degree of the hydrophobic interactions between the hydrophobic compound and the adjacent water layer is several orders of magnitude greater, if the hydrophobic groups can approach one another so closely that mutual inductive effects lead to relatively large directed dipole moments of the film molecules, which in turn can then polarize the water dipoles as described by Alpers *et al.* (1982) and by Hühnerfuss and Alpers (1983).

In order to verify this "disturbance hypothesis," a comparison of the wave attenuation ability was performed between a pure hexadecanoic acid methyl ester (PME) and a derivative of this compound, which has a well-defined "disturbance" in the molecule itself: α-bromo-hexadecanoic acid methyl ester (BPME) (Fig. 6). Due to the α-bromo group, which itself exhibits no significant polarization effect within the water layer, the long alkyl chains are prevented from coming closely together and, in consequence, the wave attenuation effect of BPME is drastically reduced in comparison to the pure PME. Similar results have been obtained with unsaturated alkyl chains
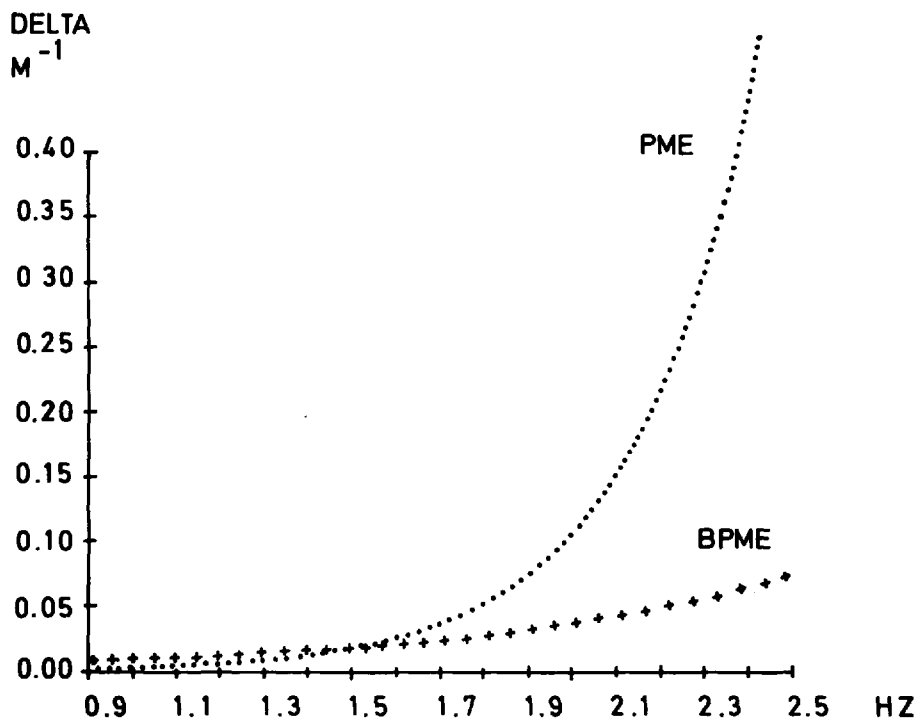
Figure 6. Damping coefficient Δ [m^{-1}] vs. frequency [Hz]. Comparison of palmitic acid methyl ester ($\cdots\cdots$ PME) and α-bromo-palmitic acid methyl ester ($+ + + + +$ BPME).

(see Part I of this work: comparison between octadecanoic acid methyl ester and 9-octadecen-1-oic acid methyl ester, Z-isomer) and branched alkyl chains (Part I: comparison between hexadecanoic acid propyl ester and -isopropylester).

In the light of this "disturbance hypothesis" the E/Z-isomerization mechanism, which was extensively investigated in Part I of this work, gets a new perspective: it can be safely assumed that the driving force for this mechanism is not only the compensation effect of the C=O- and the alkyl-O-dipole bond moments (Fig. 7), which is optimum in the Z-form, but that the better mutual interaction between the long chain alkyl groups encountered in the Z-form, thus leading to the much better hydrophobic interaction with the water layer than in the case of the E-configuration, at least plays a comparable role.

Although pure proteins will presumably seldom occur on the sea surface, the wave damping ability of two different protein species have been investigated for completeness: the water soluble pure egg albumin (ALB) and the relatively insoluble γ-globulin (soluble in salt solution) (GLOB-I). As depicted in Figure 8, these two protein compounds exhibit no wave attenuation effect compared to pure water (NO FILM). In
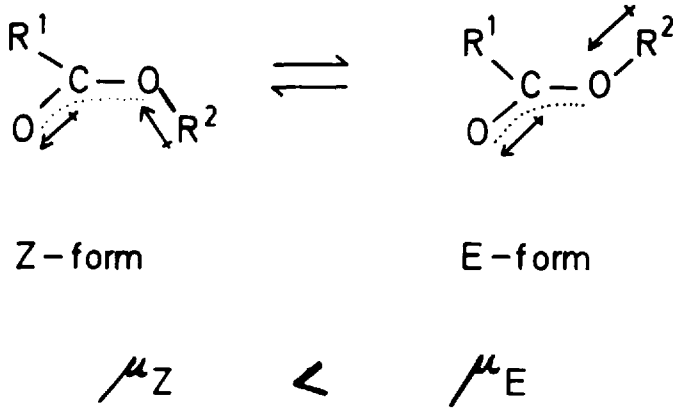
$$\text{Z}-\text{form} \qquad \text{E}-\text{form}$$

$$\mu_Z \quad < \quad \mu_E$$

Figure 7. *Z*- and *E*-configuration of a carboxylic acid ester. Due to partial compensation of the C—O— and the R^2—O— bond moments the *Z*-form exhibits the lower dipole moment than the *E*-form, in which a vectorial addition of these bond moments occurs.
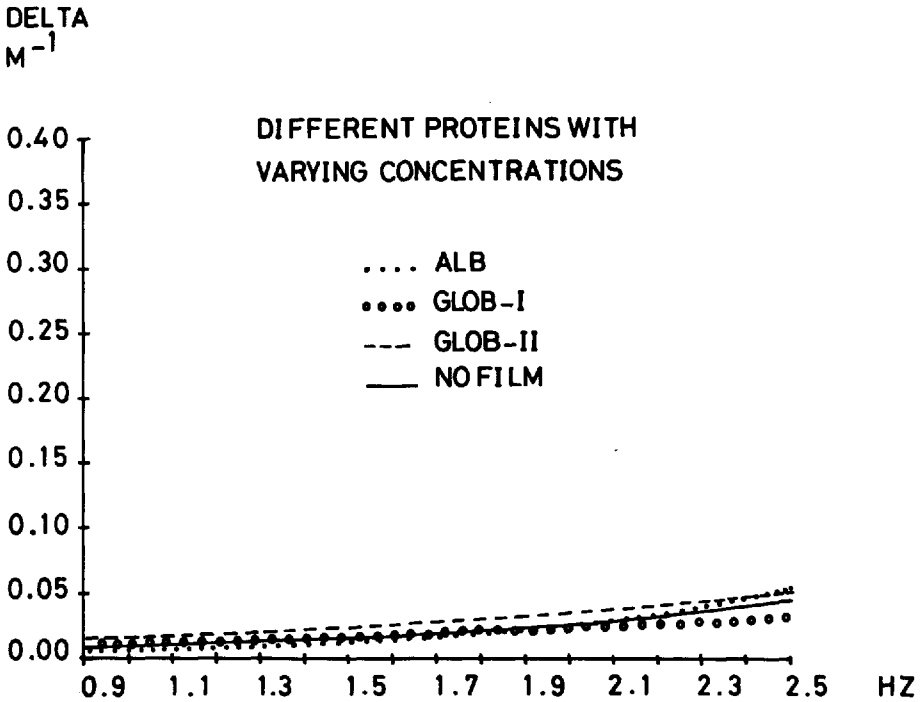
DELTA
M^{-1}

DIFFERENT PROTEINS WITH
VARYING CONCENTRATIONS

.... ALB
•••• GLOB–I
– – – GLOB–II
—— NO FILM

Figure 8. Damping coefficient Δ vs. frequency [Hz]. Comparison of different proteins with varying concentrations, albumin 60 mg/l H_2O ($\cdots\cdots$ ALB), γ-globulin 64 mg/l 0.5% NaCl-Lsg. (ooooo GLOB-I), γ-globulin 64 g/l NaCl-Lsg (------ GLOB-II), and of pure water (—— NO FILM).
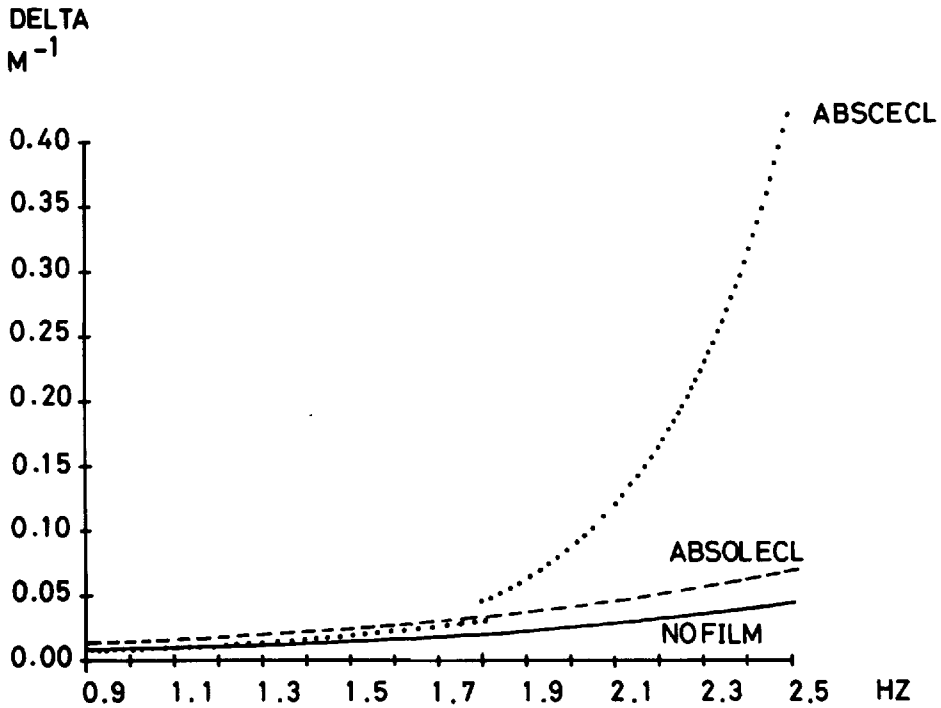
DELTA
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Figure 9. Damping coefficient Δ [m^{-1}] vs. frequency [Hz]. Comparison of α-amino-butyric acid cetyl ester hydrochloride (····· ABSCECL), α-amino-butyric acid oleyl ester hydrochloride (------ ABSOLECL), and of pure water (____ NO FILM).

order to exclude that the concentration of these compounds might have been too low due to the high molecular weight of these compounds, a second set of experiments has been performed with a thousand times higher concentration (GLOB-II). However, within the limits of error no significant deviations from the previously obtained results could be observed (Fig. 8).

Since the above investigated proteins mostly consist of various amino acids, which also can be found in natural surface films as products of hydrolysis processes (Hunter and Liss, 1981), some amino acid derivatives have also been included in our investigations: α-amino-butyric acid hexadecyl ester hydrochloride (ABSCECL) and α-amino-butyric acid oleyl ester hydrochloride (ABSOLECL). As depicted in Figure 9, two very different wave attenuation characteristics of these two amino acids were obtained. While the unsaturated compound ABSOLECL only exhibits a slight wave damping ability at $f \gtrsim 2$ Hz, the compound with the saturated alkyl chain ABSCECL shows very strong wave damping at $f \geq 1.8$ Hz. In spite of the relatively large hydrophilic head group, the saturated compound shows a significantly larger wave damping effect than the unsaturated one, which agrees well with the above developed
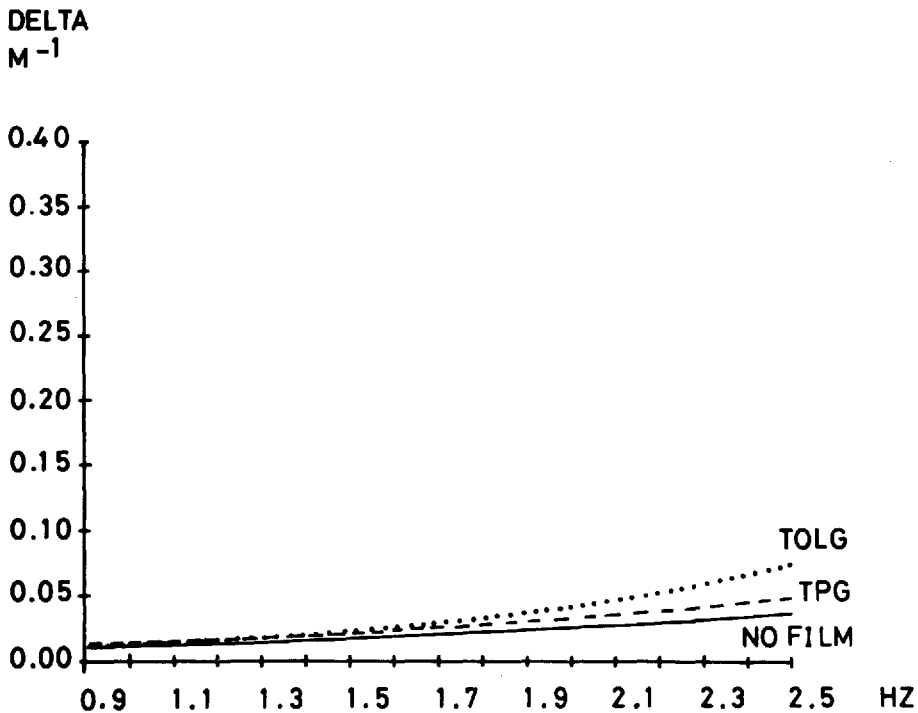
Figure 10. Damping coefficient Δ [m^{-1}] vs. frequency [Hz]. Comparison of various triglycerides, triolein (· · · · · TOLG), tripalmitin (----- TPG), and of pure water (＿＿ NO FILM).

"disturbance hypothesis." The reader should note the similarity of the wave damping characteristics of ABSCECL to that of CESSNA (Fig. 1); i.e., in both cases the simple exponential law cannot describe the wave attenuation curve as already outlined above.

In the light of the result that amino acids possessing a saturated alkyl chain may dampen water waves, it must be concluded that the nearly negligible wave attenuation effect of the proteins, which basically in part consist of amino acids, is due to their well known "folding structure," which turns out to be an "intramolecular disturbance effect" which prevents the molecules from an optimum hydrophobic interaction with the water layer.

b. Triglycerides. Triglycerides very often are found in natural surface films, especially as secretion products of zooplankton and fish (Larsson *et al.,* 1974; Lee and Williams, 1974). However, the wave attenuation experiments performed in the presence of tripalmitate (TPG) and triolein (TOLG) show (Fig. 10) that in the case of derivatives with both saturated (TPG) and unsaturated (TOLG) alkyl chains a wave attenuation not very different from the "NO FILM" case can be measured in the frequency range
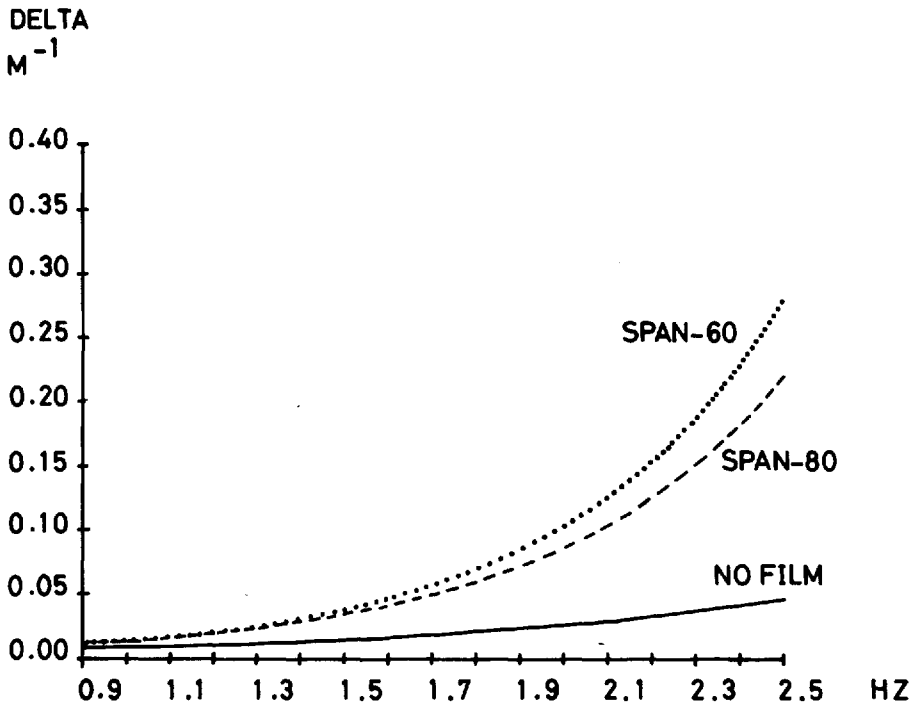
DELTA
M^{-1}

Figure 11. Damping coefficient Δ [m^{-1}] vs. frequency [Hz]. Comparison of various carbohy-drate-derivatives, sorbitane mono-stearate ($\cdots\cdots$ SPAN-60), sorbitane mono-oleate (------ SPAN-80), and of pure water (_____ NO FILM).

investigated in this work. It is assumed that the slight wave attenuation effects observed in the classical pioneering experiments in the last centuries, during which artificial sea slicks have been generated by applying fish oil (see Giles, 1969; Giles and Forrester, 1970), only occur in the short gravity/capillary wave range similar to the wave damping characteristics of oleic acid methyl ester (Hühnerfuss *et al.*, 1981b).

c. *Carbohydrates.* A relatively large fraction of the natural surface film composition consists of carbohydrates (Baier *et al.*, 1974; Daumas *et al.*, 1976; Sieburth *et al.*, 1976). Since lower molecular carbohydrates are water soluble, an artificial "hydropho-bization" has to be performed, in order to allow surface film investigations with lower molecular carbohydrate compounds. Such substances are commercially available under the trade name SPAN. In Figure 11 the wave attenuation curves of two derivatives of this kind, sorbitane monostearate (SPAN 60) and sorbitane mono-oleate (SPAN 80) are shown. These two carbohydrate derivatives show a considerable wave attenuation effect independent of the saturated (SPAN 60) or unsaturated (SPAN 80) character of the alkyl chain, although the saturated compound exhibits a slightly
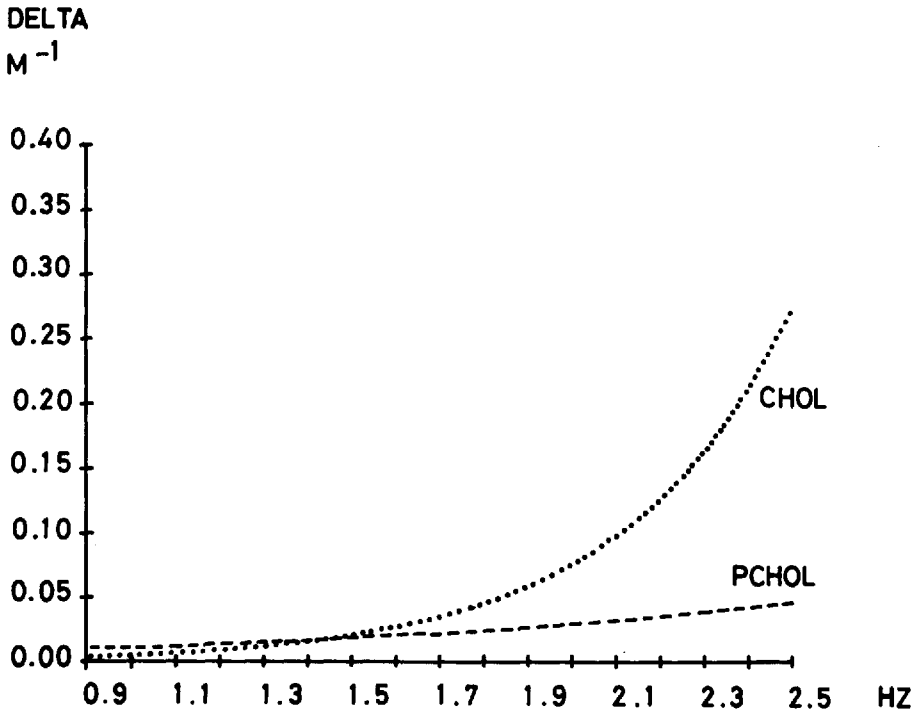
DELTA

M $^{-1}$

Figure 12. Damping coefficient Δ [m^{-1}] vs. frequency [Hz]. Comparison of various sterol-derivatives, cholesterol ($\cdots\cdots$ CHOL), and cholesteryl palmitate (--- PCHOL).

higher wave damping effect. In a first approximation, the wave attenuation character-istics of these carbohydrate derivatives are very similar to the curves of the respective saturated and unsaturated alcohols.

d. Sterols. As an example for this class of chemical compounds, which have also been found in marine waters (Hunter and Liss, 1981; Larsson *et al.,* 1974; Lee and Williams, 1974), cholesterol (CHOL) and the palmitic acid ester of cholesterol (PCHOL) have been investigated in this work (Fig. 12). CHOL exhibits a significant wave damping ability, which is very similar to the wave damping characteristics of alcohols and carbohydrates. The decrease of the wave damping ability of the palmitic acid ester, i.e., a compound with saturated alkyl chain (PCHOL), appears to be surprising at first glance. However, this result is well consistent with previously described observations in the presence of ester compounds with sterically large alcohol components; e.g., palmitic acid isopropyl ester (see Part I), which also showed significant decreases of their wave damping ability in comparison to the respective substances with straight chain alcohol groups.
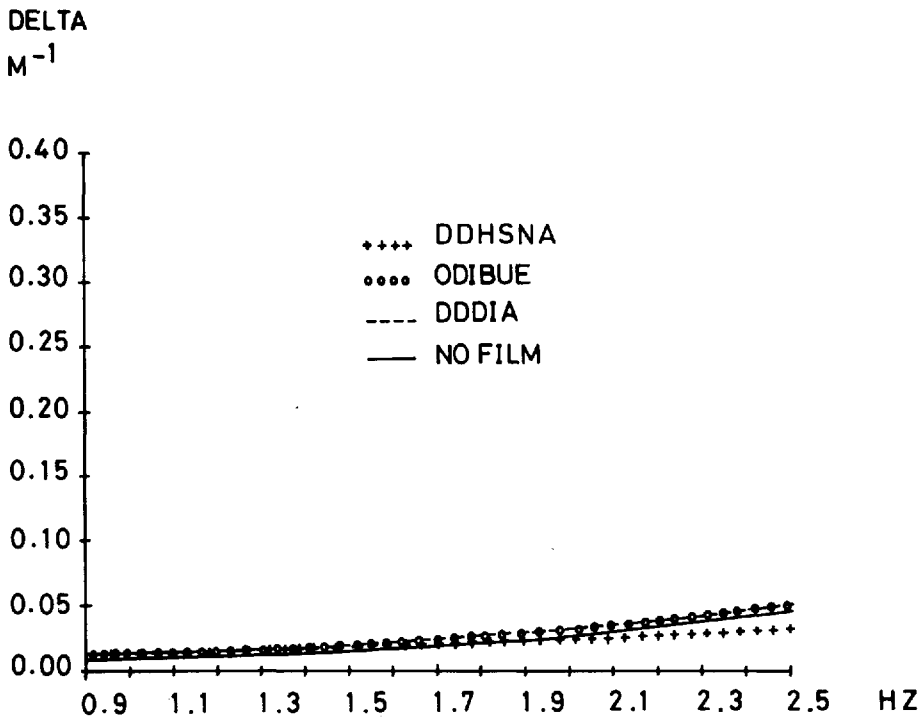
DELTA
M^{-1}

Figure 13. Damping coefficient Δ [m^{-1}] vs. frequency [Hz]. Comparison of various soluble surface active substances, sodium dodecyl-hydrogensulfate ($+++++$ DDHSNA), 1,12-dodecane-di-ol (---- DDDIA), 1,8-octanedioic acid di-butyl ester (ooo ODIBUE), and of pure water (____ NO FILM).

e. Soluble surface active substances. In this work, some selected soluble surface active compounds have been included, which have a considerable tendency to accumulate at the air-water interface, but which can desorb from the surface into the upper water layer as a result of wave induced compression of the surface film. In contrast to these substances, insoluble surface active compounds can only achieve thermodynamic equilibrium at the water surface and are thus forced to endure either considerable elastic compression or collapse. These basically different thermodynamic characteristics of soluble and insoluble molecules result in different wave attenuation mechanisms, which have been extensively discussed by Cini *et al.* (1983). However, the experimental verification with regard to the different contribution of these two mechanisms to wave damping was still lacking. For this reason, three film forming slightly soluble substances have been investigated in this work: sodium dodecylhydrogensulfate (DDHSNA), 1,12-dodecane-di-ol (DDDIA), and 1,8-octanedioic acid di-butyl ester (ODIBUE). As depicted in Figure 13, all three soluble substances

exhibit no wave damping ability in the frequency range investigated in this work, independent of the chemical character of the hydrophilic group and of the steric arrangements of the molecules at the interface, which is very different in the three cases. This result implies that the wave damping term due to desorption and adsorption processes by wave induced compression and dilatation effects plays a minor role compared to the second wave energy dissipation term described by Cini *et al.* (1983); i.e., compression and dilatation of insoluble surface active compounds.

In the light of this result, the observed decrease of the wave damping ability of CEEO3 in comparison to CEEO1 and CEEO2 (see Fig. 2), which was discussed above in the framework of "structure breaking effects" of the tri-ethylen-glycol group, may also be explained by a second effect: due to the increase of the hydrophilic character CEEO3 already partly can desorb from the interface. As described above, this implies a change of the wave damping mechanism; i.e., the wave damping term due to desorption processes becomes dominant which in turn has shown to be less effective than the compression and dilatation term of insoluble compounds.

4. Conclusions from the experimental results and theoretical considerations

Insoluble surface active substances with straight chain saturated alkyl groups possess the most intensive wave damping potential. It is assumed that parallel alignments of the alkyl chains can be achieved and that thus an optimum intermolecular interaction between the hydrophobic parts of the molecules is possible. This gives rise to a large directed dipole moment, and as a consequence a considerable polarization of the adjacent water layer takes effect, as described by Alpers *et al.* (1982) and Hühnerfuss and Alpers (1983). Double bonds, branched alkyl groups, any substitution in the alkyl chain apart from ω-substitution and cyclization of the alkyl group lead to a significant decrease of the wave attenuation ability.

With regard to the hydrophilic part, long chain alcohols, acids, and amines exhibit a considerable wave damping effect. An additional wave energy dissipation term is active in carboxylic acid esters, which have shown to exhibit an E/Z-isomerization due to wave induced compression and dilatation (Hühnerfuss *et al.*, 1982). Hydrophilic groups, which are able to break the "ice-like clathrate structures" having been induced by the above mentioned hydrophobic interactions, lead to a decrease of wave damping. This holds, e.g., for sodium sulfonate groups and other ionic groups, and for very hydrophilic groups like poly-oxy-ethylenated alcohols. It should, however, be stressed that in the case of ionic head groups both structure breaking and structure promoting effects may occur (Frank and Wen, 1957). The specific effect of the respective ion has to be considered in each single case and needs further investigation.

Proteins and triglycerides have no significant wave damping effect, while sterols and hydrophobized amino acids and carbohydrates may exhibit a considerable wave attenuation ability. The wave damping characteristics of the sterols and carbohydrates investigated in this work were very similar to those of long chain alcohols.

In three cases, sodium hexadecylsulfonate (CESSNA), α-amino-butyric acid cetyl ester hydrochloride (ABSCECL), and sodium dodecylsulfonate (DDSSNA), the wave attenuation curve could not be described by the simple exponential law (Eq. 2) indicating that at least two mechanisms are in these cases responsible for the wave energy dissipation, the contribution of which to wave damping is in different manner dependent on frequency.

The investigation of the wave damping ability of three soluble or slightly soluble surface active compounds, sodium dodecylhydrogensulfate (DDHSNA), 1,12-dode-cane-di-ol (DDDIA), and 1,8-octanedioic acid di-butyl ester (ODIBUE), revealed that the two wave attenuation mechanisms discussed by Cini *et al.* (1983) are very different in importance.

Cini *et al.* (1983) introduced a damping ratio function $y(f)$ as a corrective factor, which contains the surface dilatation modulus E

$$E\,e^{j\psi} = -\frac{d\gamma}{d\ln A},\tag{3}$$

where A is the area/molecule and γ the surface tension of water. Parameters E and ψ are assumed to be slowly varying functions of frequency, the evaluation of which depends on the solubility of the surface film.

In the case of a soluble surface film, thermodynamic equilibrium is assumed to exist within the subsurface, the process being essentially diffusional. So the above equation can be modified to

$$E\,e^{j\psi} = E_0\left(\frac{\ln\Gamma}{\ln A}\right),\tag{4}$$

where Γ is the surface film concentration, and E_0 the elasticity modulus. The second term on the right-hand side of this equation accounts for adsorption or desorption processes during compression and dilatation of the surface film due to wave action.

A process similar to diffusion, called "directional packaging," has been assumed for insoluble surface films by Cini *et al.* (1983), taking place above the interface, where a packaging density distribution, which is a function of the vertical coordinate, is assumed. This concept involves a structural parameter, D_p, having the dimensions of a diffusion coefficient, and a derived parameter, n_p, such that the extent of the packaging process is measured by n_p^{-1}. In typical cases n_p is about three orders of magnitude larger than typical n_D -values describing in an analogous manner the diffusion process.

Our wave attenuation results, obtained in the presence of three different soluble surface active substances (DDHSNA, DDDIA, ODIBUE), indicate that only the latter mechanism developed for insoluble surface active substances plays a significant role.

An analysis of the above equations suggests the importance of the wave induced surface tension gradient $d\gamma/d(\ln\Gamma)$ for the wave damping effect. Although the surface

tension term as restoring force in the Kelvin equation only plays a minor role in the frequency range 1–2.5 Hz investigated in this work (see Davies and Rideal, 1963), Lange and Hühnerfuss (1984) could show by both wind-wave tunnel and Langmuir-trough measurements that considerable surface tension gradients are already induced by a 1 Hz water wave as a result of compression and dilatation of the monomolecular surface film. Surface films with saturated alkyl chains, which exhibit a considerable wave attenuation ability, are known to show a higher surface tension gradient, whereas the Langmuir-curves of compounds with unsaturated or branched alkyl chain suggest a much lower surface tension gradient, which is compatible with their low wave damping ability.

It should, however, be stressed that the theory described by Cini *et al.* (1983) indeed allows a reliable prediction of the frequency range of the wave damping maxima of surface films, but the absolute intensities of these peaks and thus the wave dissipation energies cannot yet be calculated. E.g., the homologous series of the long-chain *n*-alkyl alcohols nearly show the same surface tension gradient, as can be demonstrated by Langmuir-trough investigations. Surface viscosity measurements indicate, however, that the influence of these alcohols on the "vicinal water layer" increases with increasing chain length; i.e., the experimentally determined surface viscosity values steadily increase with alkyl chain length (Boyd and Harkins, 1939; Nutting and Harkins, 1940; Hühnerfuss, 1984). On the other hand, this steady increase of surface viscosity is not consistent with the observed maximum in wave attenuation at C_{16} alkyl chain length and, therefore, at least one additional physico-chemical effect has to be taken into account, when interpreting the wave attenuation characteristics of various substances.

A very promising approach for this additional mechanism has already been suggested by Marangoni in the year 1870, and recently this phenomenon has been reinvestigated by Lucassen-Reynders and Lucassen (1969) and by Lombardini *et al.* (1982). Marangoni (1870) showed that surface tension gradients may destabilize an interface by inducing longitudinal "Marangoni waves" (Lucassen-Reynders and Lucassen, 1969). The existence of such longitudinal waves at the surface, when a capillary ripple is also being propagated there, gives rise to resonance-like phenomena, which enhance the dissipation of energy. Resonance between transversal- and longitudinal-type of wave motion will occur, when the wavelength of the transverse capillary wave at a given frequency is equal to that of the longitudinal wave. The only surface dilatational modulus value E, for which the wavelengths of the two types of waves are equal, at a given frequency, is the E-value at the maximum in capillary wave damping (Lucassen-Reynders and Lucassen, 1969). The liquid motion accompanying the longitudinal surface waves exhibits a highly dissipative character, vorticity flow is predominant, and the longitudinal wave usually is damped out much more rapidly than the capillary ripple. This effect is assumed to be the key for explaining the relatively high energy dissipation within a film-covered water wave field. It is noteworthy that

Lombardini *et al.* (1982) concluded from their calculations that no Marangoni wave is expected to be observed with soluble films. This result is well consistent with our experimental results, which also showed a negligible wave damping effect of soluble surface active substances.

It can be assumed that the Marangoni-effect is very suitable for explaining the observed wave attenuation effect. But considerable theoretical investigation is still needed before it will be possible to combine the equations describing the Marangoni-effect with the source functions of wind-wave generation, which is a precondition for quantitatively describing the wave attenuation of wind-generated waves by monomolecular surface films.

It should, however, be noted that in the case of wind-generated waves additional parameters, e.g., the spreading velocity, have to be taken into account, which could be neglected in this work dealing with mechanically generated water waves. Especially for applied purposes (Hühnerfuss and Garrett, 1981), it may be advisable to use substances forming more elastic films with lower surface tension gradient and lower wave attenuation ability, because such films mostly have a higher spreading velocity and can, therefore, more easily repair any "holes" broken into the slick by squally winds.

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