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ACOUSTIC SIGNATURES OF ORGANIC FILMS FLOATING ON THE SEA SURFACE

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A spectrum of low-frequency amplitude fluctuations of the ultrasonic signal specularly scattered from a wind-driven water surface covered with monomolecular crude oil origin film of well-defined oceanographically relevant viscoelastic properties, was examined in open-sea conditions. The depression of the spectral energy density of wind-created waves by surface films is inferred from the spectra ratio of the acoustic signal fluctuations spectra with/without films, and compared to that predicted by the Marangoni damping theory. Theoretical computations showed that the film filling factor determined for natural sea surface films in coastal waters of the Baltic Sea plays a principal role in determination of the film rheological properties recovered from the acoustic surface probing, whereas a variation of the growth rate of wind waves affected by the film presence is of secondary importance. It has been demonstrated that the relative spectra can be analyzed to characterize the viscoelastic properties of surface films, which for a gasoline film-coated surface turned out to be comparable to these of natural slicks or weathered crude oil spills.

1. Introduction

Organic sea surface films of biogenic origin are particulary predominant in coastal zones [1]. They modify the physics and chemistry of the sea surface and influence remotely sensed optical and microwave imagery [2, 3]. In addition to these natural films or slicks, we find pollutant organic slicks from petroleum spills or municipal effluents [4]. The numerous effects of surface films on air-sea interfacial parameters and exchange processes have been reviewed by Garrett [3]. One of the most visible and sensible film-induced effects is the attenuation of capillary and short gravity waves. The wave-damping effect [5, 6] which results in a strong resonance-type surface wave damping in the short gravity-capilary region [7] as shown in Section 2. A complete treatment of this problem also involves the physical and chemical properties of the film itself [8]. The result is a resonance-type behaviour of the relative damping coefficient $Y(f)=\alpha_c/\alpha_O$ as a function of surface wave frequency. Here α_c denotes the viscous damping coefficient in the presence of an elastic film, and α_O denotes that of a clean water surface. [9]. The damping ratio can be also extracted from the wind-driven waves spectra (see Sec. 3) measured in the presence $S_c(f)$ and in the absence $S_O(f)$ of a films as a spectral ratio: $Y(f)=S_O(f)/S_c(f)$, as shown in Ref.

[10, 11]. It has to be pointed out that this relation is valid only in the extreme case of the aerodynamically smooth air flow over the wavy surface [12] and if the surface is uniformmly covered with the film [4]. In general, three mechanisms may contribute to surface wave energy dissipation in the film presence: a direct damping influence (viscous damping), modification of wind-wave coupling [13] and modification of wave-wave interactions [14]. The spectra ratio which describes in a quantitative way the film effect is postulated in a form containing terms responsible for surface waves damping and their growth (see Section 2). Moreover, the spectra ratio of wind waves with/without organic films may be expressed by the corresponding ratio of low-frequency amplitude fluctuations spectra of the ultrasonic signal speculary scattered from a wavy surface, as shown in Section 3. Thus these relative spectra can be analyzed to characterize the viscoelastic properties of the spread film using a recently developed Marangoni damping theory. A variation of the growth rate due to the film presence can be evaluated on the basis of the aerodynamic parameters of the air-sea interaction process (see Section 4). These parameters were determined by numerous scientists [15—17].

Natural surface film studies were performed in shallow coastal waters of the Baltic Sea using a novel sampling device [18] for determination of principal structural film parameters (elasticity modulus, film filling factor) affecting to a great extent (compare Section 4), acoustic returns of signals scattered from film-coated surface. Rheological surface properties of an artificial crude oil product were recovered from acoustic surface scattering measurements (see Section 5) by means of the Marangoni damping theory and the best-fit procedure to the data. The parameters characterizing the model slick and its damping signatures are compared to the wave-damping abilities of several artificial organic films of different physicochemical structure. The present study was mainly motivated by the interest in the acoustic signatures of a wave damping effect caused by organic films. One of the aims is also to present a novel acoustic system for continuous measurement of wave-modulating effect from beneath the surface. The presented results are encouraging, however a great deal of supplementary current, meteorological observations and theoretical evaluations will be required to provide the basis for a more detailed interpretation of the acoustic signals in terms of environmental factors in order to develop remote sensing techniques suitable for studies of oil slick behaviour.

2. Surface film damping effect and wind velocity field above slicks

It has already been postulated in previous publications [19, 20] that at least three mechanisms may contribute to surface wave energy dissipation in the presence of a surface film: a direct damping influence (viscous damping), modification of wind-wave coupling [13], and modulation of wave-wave interactions [14, 21, 22]. For small slicks (of the order of tens of meters) and/or light to moderate winds, the situation is not so complicated [9]. In this case one can consider that the influence of the film on short-wave ripples is determined mainly by the anomalous flattening of free linear surface waves in the presence of SA (surface-active) film [23] which exceeds considerably a conventional viscous attenuation and becomes especially apparent in the centimetr-wavelength range. The first experiments with such slicks verified this assumption [24] at least, for a gentle breeze. The main physical mechanism responsible for losses, in the absence of surface films, is viscous dissipation in the bulk water. For small amplitude water waves, the viscous energy damping coefficient is gives by the familiar expression [23]:

$$\alpha_0 = 4\,\nu k^2, \tag{1}$$

where ν is the water kinematic viscosity and k is the wave number related to the wave frequency by the Kelvin dispersion equation. In the approximation considered it may be written for a spectral energy density of wind waves affected by such losses S_{ds} [25]:

$$S_{ds} = \alpha_0 S, \tag{2}$$

where S is the hypothetic steady state spectrum in the absence of any losses. When the viscoelastic surface films are presented, expression (2) must be multiplied by a corrective factor — the damping ratio $Y(f)$ [5, 26].

$$Y(f) = \frac{1-2\tau+2\tau^2-X+Z(X+\tau)}{1-2\tau+2\tau^2-2X+2X^2}, \tag{3}$$

where

$$t = (w_d - 2\omega)^{1/2}, \quad X = \frac{E_o k^2}{(2\nu\omega^3)^{1/2}}, \quad Z = \frac{E_o k}{4\nu\gamma\omega}, \tag{4}$$

are dimensionless quantities and $f = \omega/2\pi = (Tk^3/\rho + gk)^{1/2}/2\pi$ is the Kelvin dispersion law. In (3) and (4) T, ρ, and g are the surface tension, density of water, and acceleration due to gravity, respectively. The constant characteristic rheological parameters of the film used are: the dilational elasticity modulus $E_o = -dT/d(\ln\Gamma)$, where Γ is the surface concentration of a film, forming material. Gibbs excess [27] and the characteristic frequency w_d, which for spread (insoluble) films depends upon the structural relaxation of SA molecules within the monolayer. The film and its viscoelastic properties are completely characterized by E_0 and w_d parameters which are assumed to be slowly varying functions of frequency. Their evaluation changes according to whether the film is soluble or insoluble [2]. Graphically, for each choice of E_0 and w_d parameters, the relative damping $Y(f)$ plots versus frequency as a cuspidate curve. The frequency where the peak occurs is essentially controlled by the value of E_0, while the peak height Y_{max} (damping intensity) is determined by w_d. The apparatus and method for determining these parameters as well as their physical meaning and the values taken have been already described and discussed in detail elsewhere [28]. In brief, a measurement of the pattern $Y(f)$ may lead to characterizing the nature of the surface film and its wave-damping ability as shown in Ref. [9, 29]. Thus the evaluation of the effect of surfactants upon $S(f)$ requires a comparison of the spectrum in the absence $S_o(f)$ and in the presence of SA substances $S_c(f)$ all other parameters remaining the same. The low amplitude theory mentioned above suggests the adoption of the provisional formula [2, 10, 11, 30]:

$$Y(f) = S_O(f)/S_C(f). \tag{5}$$

It has to be pointed out that the ratio of the spectral energy densities (non-slick/slickarea) defined by (5) is assumed to be equal to the relative damping $Y(f)$ only in the limiting case of a smooth air flow arround the sea surface i.e.. Reynold's number $R_e = hu_*/v_a \leqslant 1$ where h is the effective roughness height, u_* is the friction velocity, and v_a is the kinematic viscosity of air [12, 21]. In general, the relative damping should not be directly interpreted as corresponding to the depression in the spectral energy density S_o/S_c of surface waves as follows from Eqs. (3), (4) and (5). It would be so if the film were uniformly distributed over the surface. However, during the period of the experiment, the film may be partially dispersed by an air flow, waves and tidal currents, so that the surface under study is only in part covered with the viscoelastic film. In this case one shall introduce a fractional filling factor [4, 10, 11, 31] i.e. F — the ratio of the area covered with a film with respect to the total area considered and write for the effective damping ratio $Y_{ef}(f)$ the following expression:

$$Y_{ef}(f) = \frac{1}{1 - F + (F/Y(f))}, \tag{6}$$

where $Y(f)$ is given by Eq. (3). FISCELLA *et al.* [11] have shown that when the radar cell is not uniformly covered by the film, the depression of the spectral energy will be significantly smaller than that expressed by (3) even for a surface coverage of 95% (F = 0.95).

Now, let us consider in detail how the wind wave spectrum is affected by the Marangoni damping and the aerodynamical roughness change of the sea surface, both caused by the film presence. Generally, evolution of the wind wave spectrum is governed by energy balance equation [32, 33]:

$$\frac{d}{dt} S(k)/\omega(k) = Q_s - Q_{dis} + Q_{nl}. \tag{7}$$

One should determine how the film in the equation for the energy spectrum $S(k)$ modifies the components Q_s, Q_{dis}, Q_{nl} which describe excitation, dissipation and nonlinear interactions of the spectral excitation, dissipation and nonlinear interactions of the spectral components.

The wind wave spectrum is determined by the combined effect of a number of factors. The first factor is the transformation of the wind velocity field over a slick and, correspondingly, the variation of the regime of wind wave excitation Q_s. Another factor is the anomalous flattening of free linear waves in the presence of a SA film [23] which exceeds considerably a conventional viscous attenuation (Q_{dis}). The resonance excitation by the atmospheric pressure pulsations, PHILIP'S mechanism [34], and MILES instability [35] are assumed to be the mechanisms of ripple excitation, and the viscous damping taking into account the effect of a SA film, and the nonlinear limitation described phenomenologically (e.g. due to the second harmonic generation in waves) are assumed to be the mechanisms of limitation. The corresponding terms in the right-hand side of Eq. (7) have the form [24]:

$$\omega Q = \frac{k^2}{4\rho^2\omega^2} \Pi_a + \beta(V)\, S(k) - \alpha\, S(k) - \delta\, S^2(k), \tag{8}$$

where Π_a is the pulsation spectrum of the atmospheric pressure, V is the wind speed, β is the Mile's increment, α is the wave decrement as a function of a wave number k, δ is the coefficient of nonlinear spectrum limitation. In the case when the interaction between different spectrum components is neglected, it is assumed that there is a balance between the excitation of ripples and their limitation for each wave number.

When the breeze is gentle (wind speed $V \lesssim 2$—5 m/s), the increment $\beta(V)$ is less than α, and the spectrum level $S(k)$ is low, one can neglect the last component in Eq. (8) finding the stationary value $S(k)$ from the balance condition of the other three terms.

The author characterizes quantitatively the degree of the spectra variability due the film presence by a contrast value $S_o(f)/S_c(f)$. Then, supposing the spectrum of the air pressure pulsation above the slick and nonslick region to be unchangeable, we have [24]:

$$S_0(f)/S_c(f) = \frac{\alpha_0 Y(f) - \beta(V_c)}{\alpha_0 - \beta(V_o)}. \tag{9}$$

Subscripts c and 0 denote that the corresponding values belong to the film-covered and clean water areas, respectively. Since in the centimetre-wavelength range, the decrement $\alpha_c = \alpha_0 Y(f)$ exceeds the value α_0 (by an order of magnitude if the film elasticity is rather large), when calculation the contrast one can neglect the wind variation above the slick $(V_c - V_0)/V_0 \simeq 10$—30% [13] and assume at low to moderate winds $\beta(V_c) \simeq \beta(V_0)$. Under these assumptions Eq. (9) reduces to the previous formula Eq. (5). At wind velocities $V < 2$ m/s, the values of β in Eq. (9) can be neglected; the contrast in this case is easily found from the ratio of decrements. When calculating the contrast, the author used the empirical approximation for the increment β given by PLANT [36] which results from several growth rate experiments showing a quadratic relation to the friction velocity of the wind u_*:

$$\beta = \frac{(0.04 \pm 0.02)\, u_*^2 \omega \cos\theta}{c^2}, \tag{10}$$

for wind-induced growth rate over the frequency range $g/2\pi V_{10}$ to 20 Hz, where c is the wave phase speed and θ is the angle between wind and wave directions.

The friction velocity of the air flow was determined from vertical wind profiles measured above the water surface at a height of z as shown in Ref. [17]. The wind profiles over water film-covered surface differ from those of clean water, although both profiles folow a logarithmic distribution. The friction velocity of the wind $u_* = (\tau_s/\rho_a)^{1/2}$ where τ_s is the wind shear stress and ρ_a is the density of air, and the roughness parameter z_0 of the water surface can be derived from the wind profiles near the surface by applying the following dependence:

$$V(z) = (u_*/K)\ln(z/z_o); \tag{11}$$

where K is the Kármán constant = 0.4. The equivalent wind speed at a standard height $z = 10$ m was extrapolated from Eq. (11). The aerodynamic drag coefficient c_d is defined as follows:

$$c_d = \tau_s/\rho_a V_{10}^2 = (u_*/V_{10})^2. \tag{12}$$

The presented principle may be developed into an analytical method by applying an acoustic remote sensor able to deduce spectra ratios (contrast) from acoustic scattering measurements within a polluted and a non-polluted sea area, as postulated in the next section.

3. Characterization of wind-driven surface using specularly scattered sound

The scattering coefficient will be defined here as the ratio of the received intensity, when the acoustic wave is reflected by the surface under study, to the received intensity when the wave is reflected in the specular direction by a plane surface. This definition of the scattering coeffcient is equivalent to the scattering coefficient defined by BECKMANN and SPIZZICHINO [37], for electromagnetic waves. For a detailed discussion about the scattering models applicable to microwave and acoustic scattering at rough surface, the reader is referred to the review articles by OGILVY [38—40].

If the surface may be considered to be perfectly reflecting, as in an underwater scattering from a water/air interface [41], it is now possible to simplify the definition. In this case the intensity measured on the projector axis, at a distance equal to the total path-length used in the scattering measurements, may be substituted into the definition of the scattering coefficient for the speculary reflected intensity from a plane surface. Since the scattered waves are essentially planar over the aperture of the received, the intensity I_s is determined from acoustic pressure measurements p_s ($I_s \sim p^2_s$). Assuming that the output voltage U of the hydrophone is a linear function of the acoustic pressure ($U \sim p_s$), the average value of the measured scattering coefficient and/or relative intensity $\delta_m(\theta_i, \theta_r)$ is given by WELTON et al. [42].

$$\delta_m(\theta_i, \theta_r) = \sum_{j=1}^{N} [U_j(\theta_i; \theta_r)]^2 / N U^2_{\text{axis}}, \tag{13}$$

where θ_i, θ_r the angles of incidence and reflection, $U_j(\theta_i, \theta_r)$ is a single, independent sample of the voltage amplitude for a given projector and receiver orientation, N is the number of independent samples taken at a given orientation, and U_{axis} is the projector on axis voltage over the same path-length used to measure $U_j(\theta_i, \theta_r)$.

The scattered field registered in a specular direction from an individual surface may be regarded as composed of coherent and diffuse fields [43]. The smooth surface scatters coherently into the specular direction, as expected, with a little scattered energy away from close to specular.

The effect arises because of constructive interference between all the scattered wavelets from all parts of the surface, in the specular direction. An increase in roughness leads to energy being redistributed out of the coherent component into the more widely spread diffuse field. As a consequence, the main lobe of the scattered energy becomes weaker and the presence of diffuse field leads to significant off-specular amplitudes. In the extreme case, for a very rought surface, there is now only slight variation in signal amplitude with angle of incidence, as the scattered field is totally diffuse and closely isotropic [39]. Coherent and incoherent contributions to the total scattered field depend on the "roughness parameter" for the surface [44], which for specular scatter ($\theta_i = \theta_r$) is defined by Beckmann's g parameter as follows:

$$\sqrt{g}=4\pi\,(h/\lambda)\,\cos\theta_i, \tag{14}$$

where h/λ is the root-mean-square wave height/acoustic wavelength ratio.

The signals scattered from a very rough surface (i.e., $g \gg 10$) are incoherent and, as shown in Ref. [40, 43], there is no coherently scattered field.

The limiting, specularly scattered, relative intensity for a very rough surface (so-called "high-frequency" scattering) is given by the formula: [44, 45]

$$\delta_{hf}(\theta_i) = \frac{\pi A}{32\,\langle s^2\rangle R_1^2 \cos\theta_i} \qquad \text{for } g \geqslant 10\,, \tag{15}$$

where R_1 is the distance between the transducer and the surface, A is the insonified surface area, $\pi = 3.14...$, $\langle s^2\rangle$ is the mean- square slope of the surface. The mean square slope of the wind-excited water surface can be derived from the omnidirectional spectral energy density $S(f)$ of the surface waves as follows [21]:

$$\langle s^2\rangle = \int k^2\, S(f)\, \mathrm{d}f\,. \tag{16}$$

As it can be from Eq. (15), the relative specular scatter for a rough surface in indepent of the driving frequency and is a function only of the geometry of the experiment and the root mean-square slope of the ruffled surface [42].

Recent measurements of high-frequency slope spectra using a wave-following laser surface slope meter have been reported by LUBARD *et al.*, [46] and PLANT [36]. Their results show that such spectra follow an $1/f$ law to a good approximation at a wind speed of 7.5 m/s. If we assume it to hold for a variety of oceanic conditions, then we may approximate the upwind/downwind slope spectrum $S_s(f)$ as follows

$$S_s(f) = 0.75\,k^2\, S(f), \qquad 0<f<1.5\,f_m,$$
$$S_s(f) = \alpha'/f\,, \qquad 1.5 f_m<f, \tag{17}$$

and $$\alpha' \leqslant \frac{0.05}{\ln(13.3/f_m)}\,,$$

where $S(f)$ is any standard spectrum applicable near the dominant wave frequency f_m. Having considered Eqs. (13), (15), (16) and (17) one can note that $U^2(f) \sim 1/S_s(f) = 1/k^2S(f)$. Thus it is possible to obtain from acoustic scattering measurements performed for a clean and film-covered wavy water surface, assuming the fixed experiment geometry, the following expressions for the spectral energy depression of water waves by surface films:

$$\delta_c / \delta_0 = [U_c(f) / U_0(f)]^2 = S_0(f) / S_c(f), \tag{18}$$

where a surface waves spectrum component of frequency f is taken into account, $U_0(f)$ and $U_c(f)$ are the spectra of the low-frequency amplitude voltage fluctuactions of the ultrasonic signal scattered from a wind-excited surface of clean water and covered with a viscoelastic film, respectively. δ_c, δ_0 are scattering coefficients of acoustic waves derived from scattering measurements for both kinds of the surface mentioned.

4. Sea surface coverage and aerodynamic parameters of wind-surface interaction

To provide data for the proper interpretation of results recovered from remote surface probing, natural surface film studies have been successfully carried out in shallow coastal areas of the Baltic and Mediterranean Seas in 1990 and 1991 [47].

A novel sampling device was constructed by the author [18], which leads to collection of undisturbed film-coated water together with an adjacent subphase layer of a few centimeters in thickness. The film sampler is a submersible rectangular double-walled vessel which "cuts out" a sea area region measuring 45 cm x 35 cm and 8 cm in thickness. Coupled with a torsion wire balance attached to a filter paper Wilhelmy plate, the sampler represents a modified Langmuir trough apparatus to perform force-area isotherm measurements. Preliminary studies performed in shallow offshore waters of the Baltic and Mediterranean Seas showed a good reproductibility of the force-area isotherms, although the film properties (elasticity modulus, film filling factor, isotherm reversibility) are subjected to a large seasonal and areal variability, as widely discussed elsewhere [47]. The filling factor is derived from pressure-area isotherms as shown in Ref [18].

Figure 1 presents F as a function of wind speed V_{10} for measurements carried out in two significantly different sites of the Baltic Sea: A) off Orłowo (Poland) in June, August 1990 and B) off Oksywie (Poland) in April, May 1991. We were largely concerned with a broad category of condensed films in offshore waters. The elasticity modulus averaged over more than 50 samples collected was equal to $\bar{E}_0 = 24.9 \pm 19.9$ (Orłowo) and 21.0 ± 17.4 mN/M (Oksywie). Even though there was no pronounced biological activity in these water, moderate to strong film patches were present at most times. The areal extent and their homogeneity was determined by the velocity and direction of ambient winds. In a highly contaminated area in Orłowo where a high level of anthropogenic pollution is found, large surface regions are uniformly and completely film-covered ($F = 1$) in the wind speed range 0.5—2.5 m/s. For

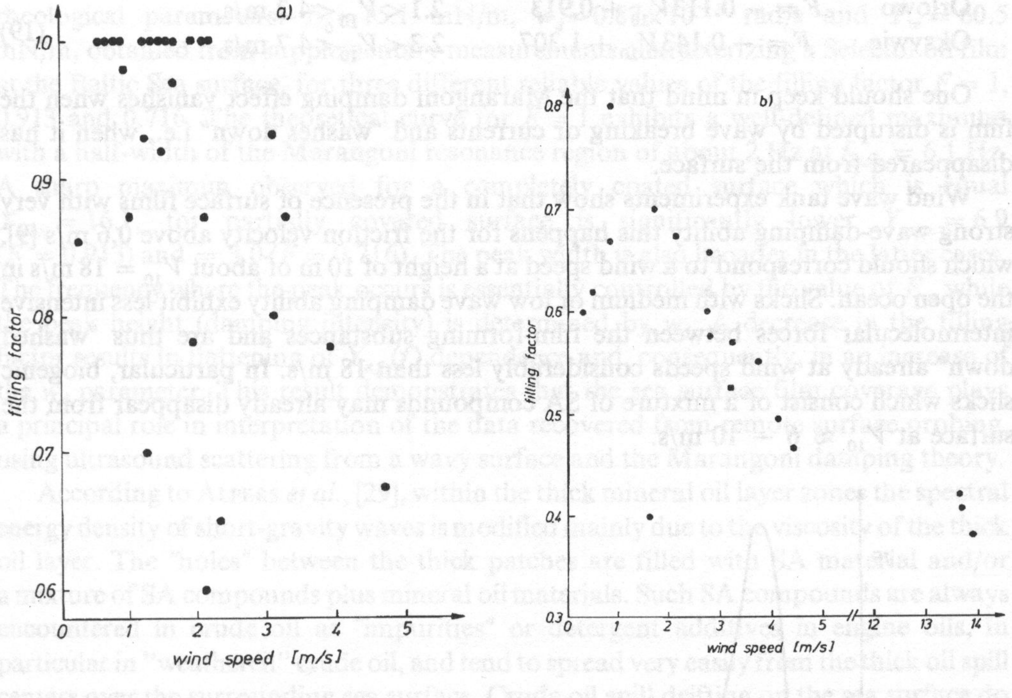

Fig. 1. Film filling factor F as a function of wind speed V_{10} for natural surface film studies performed in shallow coastal waters of the Baltic Sea A) of Orłowo (Poland) in June, August 1990, and B) of Oksywie (Poland) in April, May 1991.

$V_{10}>2.5$ m/s one can observe a rapid decrease of F with increasing wind speed. The mean filling factor registered in the summer time in Orłowo station is equal to 0.913 ± 0.094. The Oksywie site was studied in the spring time after strong wind events. Oksywie is a place distant from human settlements with their municipal effluents, but exhibit the similar $F(V_{10})$ trend, although, the values taken by F in the comparable wind speed range are significantly lower. The latter F values are expected to be found at higher sea states after strong wind events and/or compaction of film patches by surface and tidal currents. The mean filling factor registered in Oksywie and tidal currents. The mean filling factor registered in Oksywie station was equal to 0.716 ± 0.253. All these waters are close to the harbour and are contaminated to a great extent with highly surface-active substances from municipal effluents and oil spills. It is belived that artificial crude oil spills follow the similar $F(V_{10})$ pattern as the naturally-formed slikcs do. Now it is evident that the sea surface can be considered to be uniformly film-covered, as assumed by numerous authors, [6, 29, 52] in lowest wind speed ranges to $V_{10}<2.5$ m/s; for higher winds the filling factor is wind speed-dependent.

It has been found that F appers to be a linear function, as a first approach, of the wind speed (compare Fig. 1. A and B), and can be represented as a least-squares-fit to the data in the following form:

$$\begin{array}{lll} \text{Orłowo} & F = -0.113V_{10} + 0.913 & 2.1 < V_{10} < 4.2 \text{ m/s}, \\ \text{Oksywie} & F = -0.143V_{10} + 1.307 & 2.3 < V_{10} < 4.7 \text{ m/s}, \end{array} \tag{19}$$

One should keep in mind that the Marangoni damping effect vanishes when the film is disrupted by wave breaking or currents and "washes down" i.e., when it has disappeared from the surface.

Wind wave tank experiments show that in the presence of surface films with very strong wave-damping ability this happens for the friction velocity above 0.6 m/s [9], which should correspond to a wind speed at a height of 10 m of about $V_{10} = 18$ m/s in the open ocean. Slicks with medium or low wave damping ability exhibit less intensive intermolecular forces between the film-forming substances and are thus "washed down" already at wind speeds considerably less than 18 m/s. In particular, biogenic slicks which consist of a mixture of SA compounds may already disappear from the surface at $V_{10} \approx 6 - 10$ m/s.

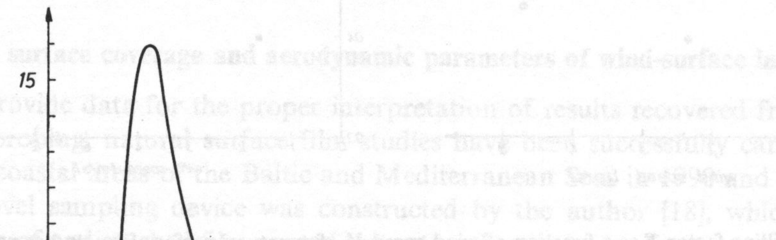

Fig. 2. Effective relative damping Y_{ef} as a function of water wave frequency predicted by the Marangoni damping theory, in which the film parameters ($T_w = 60$ mN/m; $E_o = 15.1$ mN/m and $w_d = 0.87 \times 10^{-3}$ rad/s) originate from supplementary Langmuir through measurements on a Selectol oil film spread over the Baltic Sea surface. The curves correspond to different values of the film filing factor $F = 1$; 0.913, and 0.716, respectively.

Figure 2. illustrates the sea surface coverage effect on the relative damping $Y_{ef}(f)$. Values of Y_{ef} dependence as a function of frequency are calculated by means of the Marangoni damping theory (see Eqs (3), (4) and (6)), by assuming the following film

rheological parameters: $E_0=15.1$ mN/m, $w_d=0.87\times10^{-3}$ rad/s and $T_w = 60.5$ mN/m, obtained from supplementary measurements characterizing a Selectol oil film at the Baltic Sea surface, for three different reliable values of the filling factor $F = 1$, 0.913 and 0.716. The theoretical curve for $F = 1$ exhibits a well-defined maximum with a half-width of the Marangoni resonance region of about 2 Hz at $f_{max} = 6.1$ Hz. A sharp maximun observed for a completely coated surface which is equal $Y_{max} = 16.1$, for partially covered surface is significantly lower $Y_{max} = 6.9$ ($F = 0.913$) and $= 3.0$ ($F = 0.716$). The peak width is also broader in the latter cases. The frequency where the peak occurs is essentially controlled by the value of E_0, while the peak height (damping intensity) is determined by w_d. A decrease in the filling factor results in flattening of $Y_{ef}(f)$ dependence and, consequently, in an increase of the w_d parameter. This result demonstrates that the sea surface film coverage plays a principal role in interpretation of the data recovered from remote surface probing, using ultrasound scattering from a wavy surface and the Marangoni damping theory.

According to ALPERS *et al.*, [29], within the thick mineral oil layer zones the spectral energy density of short-gravity waves is modified mainly due to the viscosity of the thick oil layer. The "holes" between the thick patches are filled with SA material and/or a mixture of SA compounds plus mineral oil materials. Such SA compounds are always encountered in crude oil as "impurities" or detergent additives in engine oils, in particular in "weathered" crude oil, and tend to spread very easily from the thick oil spill centers over the surrounding sea surface. Crude oil spill drifting on the sea surface do not only consist of pure hydrocarbon fractions, but they contain considerable amounts of SA compounds which are being formed by photo-oxidation processes and bacterial decomposition [48]. Within the sea surface area covered with these surface-active compounds, surface tension gradients and thus Marangoni wave damping can be induced on an undulating water surface. As a consequence, two zones exhibiting different mechanisms of wave attenuation can be specified within a mineral oil spill.

At present there is some evidence testifying thas SA films transform a wind field above the sea surface. In experiments with artifical slicks of large dimensions [13] carried out at wind velocities 7.5 and 4.5 m/s, a decrease in the roughness parameter z_0 by two to seven times, respectively, and an increase in the mean wind velocity V_{10} by 15 and 30%, were registered. Similar effects were observed in the laboratory wind wave tank [17], where the same variations of V_{10} and z_0 and a small decrease by several per cent in the friction velocity in the presence of a SA film were found.

Table 1 collects the exemplary aerodynamic parameters of the wind-surface interaction process derived from the vertical wind profile, reported by numerous scientists and measured in the experiment reported here, for a film-coated (V_c, u_{*c}, z_{0c}, c_{dc} and β_c), and clean water surface (V_0, u_{*0}, z_{00}, c_{d0} and β_0), computed for film-forming substances of differentiated chemical structure according to Eqs. (10—12). For the covered surfaces one can observe an increase in V_{10} by 5—20%, a decrease in u_* by 7—9% and in z_0 by 7 to 34 times, as well as a decrease in c_d by 23 to 70% if compared to the clean water surface reference case. Values of increment β computed from the empirical equation (10) are two times higher than these

Table 1. Aerodynamic parameters of the wind-sea interaction process, for film-covered and film-free surfaces

Film-forming substance	Wind speed V_{10} (m/s)		Friction velocity u_* (cm/s)		Roughness parameter z_o (10^{-5} m)		Drag coefficient c_d (10^{-4})		Growth rate variation $\beta_o - \beta_c/\beta_c$ (%)	Remarks
	V_o	V_c	u_{*o}	u_{*c}	z_{oo}	z_{oc}	c_{do}	c_{dc}		
Oleyl alcohol	4.1	4.9	15.38	14.34	26.63	1.29	14.0	8.7	15.0	Ref. [15]
Methyl oleate	5.5	6.5	18.88	17.33	7.99	0.32	11.6	7.2	18.6	
Oleyl alcohol	5.3	6.3	18.07	16.64	8.58	0.25	11.7	6.9	17.9	
Sodium lauryl sulfate $C_{12}H_{25}SO_4Na$ ($c = 2.6 \times 10^{-2}$ % w.)	10.0	11.8	34.18	31.71	8.27	0.34	11.6	7.2	16.1	Ref. [17]
Vegetable oil	7.5	9.2	23.34	21.47	2.61	0.34	9.7	5.4	18.1	Ref. [16]
Oleic acid	7.5	8.2	25.00	23.03	3.68	0.14	11.1	7.8	17.8	Ref. [24]
Vegetable oil	6.7	7.3	20.17	18.57	1.63	0.16	9.0	6.6	17.9	
Gasoline 94	2.3	2.7	8.05	7.35	1.08	0.33	12.3	7.2	19.9	this experiment

theoretically-predicted by MILES [17]. A variation of the growth rate $(\beta_0 - \beta_c)/\beta_c$ due to the film presence appears to be of the order of 15 – 19.9% seems to support the assumption that the surface film effect on the growth rate of wind waves is of secondary importance in considerations concerning suppression of wind waves. The observed changes of parameters in the aerodynamic intereaction phemomenon seem to be dependent on the chemical nature of the film-composing substance in a complicated way.

Recently, the wind velocity field above slicks has been briefly examined in the paper by ERMAKOV *et al.*, [24]. Their approximate estimates show that the correspon-ding increase of the wind above the slick, referred by numerous authors, can be deduced from the square root of a mean spectral energy depression value in a centimetre wavelength range of surface waves $(\overline{S_o/S_c})_{cm}$ as follows:

$$V \simeq \frac{u_*}{K} \ln (S_o/S_c)^{1/2}{}_{cm}; \tag{20}$$

here they assumed that $u_* = 0.05\, V_{10}$ as in Ref. [21].

5. Preliminary at-sea experiment. Results and discussion

Laboratory surface film scattering measurements showed that the relative damping dependences $Y(f)$ differ significantly from the theoretically predicted ones [49], in which the surface film parameters originated from the supplementary measurements. Several possible reasons for the discrepancy between the theory and experiment performed under small wind wave tank conditions encouraged the author to carry out the acoustic scattering investigation in open-sea conditions with an artificial crude oil origin film.

An experimental evidence of a resonance-like behaviour of the wave damping ratio in the short-gravity-wave region by monomolecular surface slikcs was first given by CINI *et al.* [50], and confirmed in wind wave tank by HÜHNERFUSS *et al.* [7], and in field measurements using a wave staff and an optical spectrum analyzer [24], as well as a radar backscattering system [10, 11, 30, 51]. Recently it has been found by SINGH *et al.* [52] that the depression of the spectral energy density of surface waves by a mineral oil spill cleary exhibits the typical Marangoni-type behaviour. The reader should note that the substance under study in this report is of similar origin. In stands for a commercially available crude oil product. At first glance, their observation of a comparable strong depression both in the presence of a monomolecular slick and in the presence of an oil spill, is surprising because the bulk of a mineral oil consists of exclusively hydrophobic alkyl and aryl compounds that are not able to give rise to wave-induced surface tensionn gradients. The data of SINGH *et aL*, can be explained in the light of the Marangoni theory if SA substances were present is the crude oil spill.

The acoustic system in a form of the free-drifting lightweight buoylike equipment, as shown in Fig. 3., has been already used for remote sensing and monitoring of the sea oil polluted area [53]. It has been found that the system allows for the detection of the oil spill edge passage observed as a rapid in the time record of scattered signals. In addition, all systematic changes of a wavy surface undulation caused by the presence of oil substances express themselves in the corresponding, regular changes of the scattered signal statistics [54]. Simultaneous analyses of all the statistical distribution parameters could be a starting point for determining the fraction weight of the given substance, its layer thickness, and finally the form of the oil pollutant (monolayer, thick layer or individual dispersed spots [53]).

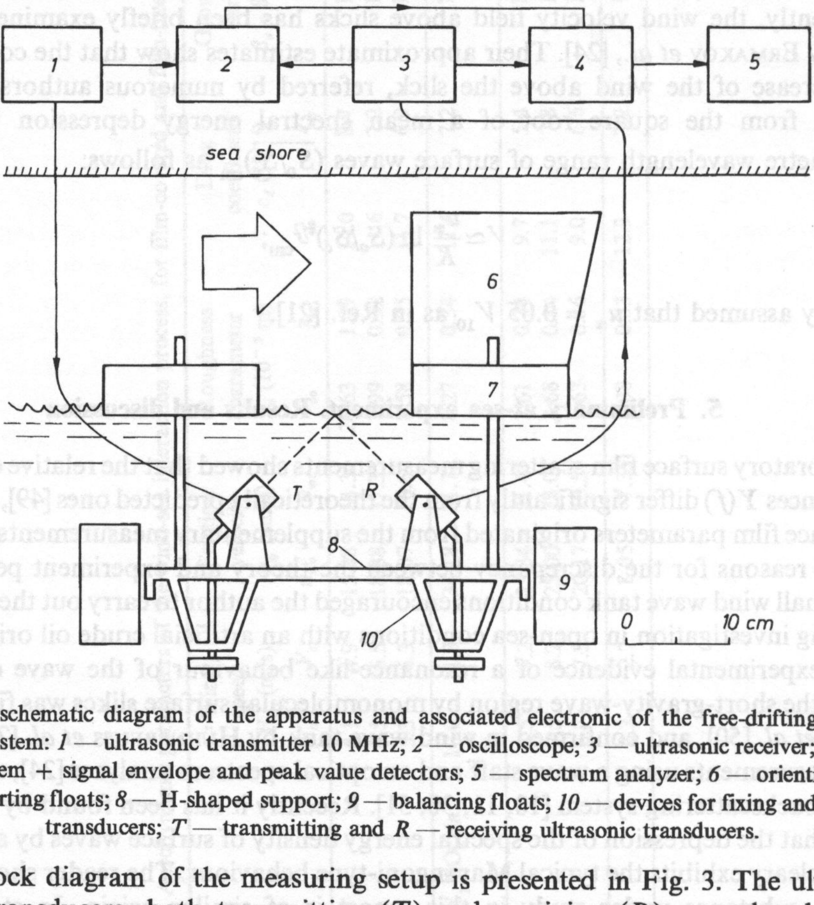

Fig. 3. A schematic diagram of the apparatus and associated electronic of the free-drifting buoylike acoustic system: *1* — ultrasonic transmitter 10 MHz; *2* — oscilloscope; *3* — ultrasonic receiver; *4* — time gating system + signal envelope and peak value detectors; *5* — spectrum analyzer; *6* — orienting wings, *7* — supporting floats; *8* — H-shaped support; *9* — balancing floats; *10* — devices for fixing and orienting transducers; *T* — transmitting and *R* — receiving ultrasonic transducers.

A block diagram of the measuring setup is presented in Fig. 3. The ultrasonic quartz transducers, both transmitting (*T*) and receiving (*R*), are placed on the *H*-shaped support (*8*) of the free-drifting buoy at a depth of 10 cm beneath the water level. Two float wings (*6*) enable self-orientation of the buoy according to the actual wind direction what significantly reduces the influence of surface waves reflected from the supporting floats (*7*) on the measurement. The buoy of a weight of 5 kg is also equipped with balancing floats (*9*) and deviced for fixing and orienting transducers (*10*).

The electronic part of the arrangement is located on the sea shore and connected to the buoy using cables. An ultrasonic transmitter (*1*) operating under pulse regime with a 3 kHz repetition frequency produces series of pulses lasting a few microseconds and filled with a sine wave of 10 MHz frequency. An acoustic projector has a 3° half-power bandwith at a carrier frequency of 10 MHz. The incident anagle of ultrasonic beam is equal to 45°. The scattered signal is registered in the specular direction. After amplification by an ultrasonic receiver (*3*), for visual inspection of the signal an oscilloscope (*2*) is used. A time gate of the electronic circuit (*4*) enables the envelope and peak value detections of the signal part corresponding only to surface scattering. Then the frequency analysis of the signal amplitude fluctuations is performed by means of an analog tunable band-pass filter (*5*) having a width of 23% (Type 1621 Bruel and Kjaer) in the frequency band 2—40 Hz. The signal was registered for about 3 min in one registration. The spectra were measured 7—10 times and an average spectrum was adopted in further considerations. The standard deviation from the mean in the collected set of data was ranging from 8 to 12% of the registered signal value. A period of the signal examination was limited to about 21—30 min in order to perform the measurement under substantially the same weather conditions and slick state which appeared to evolve in time. Four supporting floats are distans from each other by 25 cm, thus the sea under study surrounded by them has a rectangular shape and is 25 cm wide and 50 cm long. In the center of this "channel" the acoustic beam scattering takes place.

It should be pointed out that the occurrence of floats can affect conditions of surface wave generation, result in not uniformly film-covered surfaces, change the wind stress and produce an additional turbulent flow over the surface screened by the floats. It has been demonstrated in preliminary studies, using fine talc powder deposited at the surface within this area, that the film homogeneity is not affected by the float presence. It is believed that the self-orientation of the buoy, according to the actual wind direction, which leaves a 25 cm — wide sea area unaffected by the floats, provides very similar conditions of surface generation for both film-covered and free sea surfaces. In addition, subsequent discussion concerns the relative scattered signal spectrum referred to the clean water case, where the only surface film effect is an important factor.

The study of an artificial oil slick influence on the amplitude fluctuations spectra of the ultrasonic signal scattered at a wavy sea surface was performed in October, 1989 in the Baltic Sea from aboard the platform built on piles about 200 m off-shore Gdynia in a depth of 15 m.

A quantity of oil placed upon the water surface will spread out by surface tension forces if the spreading coefficient $S_{o/w}$ is positive. This is the net surface tension available to drive the spreading [27]:

$$S_{o/w} = T_w - T_o - T_{o/w}, \tag{21}$$

where T_w is the surface tension of water, T_o is the surface tension of oil, $T_{o/w}$ is the oil-water interfacial tension.

Its positive value suggest the ability of oil substance to form on the water surface a coherent bulk film with thicknesses ranging from monomolecular to one resulting from the amount of the liquid and the surface area available. Many oils, including havier hydrocarbons, have negative spreading coefficients and will not spread on water, and appear to form lenses surrounded by monolayers.

Gasoline 94 was used as an artificial slick-forming material in field measurements. In order to characterize the substance to be deployed, the following additional measurements of structural parameters were performed: density, viscosity, surface tension and interfacial tension in contact with sea water collected from the measuring area. Gasoline 94 stands for a light crude oil derivative ($\rho=760$ kg/m^3, $\eta=0.68$ mPa·s) and turned out to have a positive spreading coefficient value against sea water $S_{o/w}=+6$ ($T_o=20.3$ and $T_{o/w}=26.3$ mN/m, $T_w=52.6$ mN/m), and spontaneously formed an uniform slick. An organic substance was deployed from hexan solution at the sea surface, resulting in a slick estimated to be 20 m in radius. A slick dimension, measured from the edge of the spot exposed to the wind up to the measuring point, was of the order of 7–10 m. At the lowest sea states, where the sea surfaces was naturally unruffled, the application of the substance could not be visually determined at all. From a distance the film's presence can only be visually inferred from its surface smoothing effect. Its persistance was quite variable being a function of current, wind, and wave action as well as the accuracy of the initial slick deposition. Slick duration varied between 40 to 100 min., decreasing (as expected) with increasing sea state. The measurements of a mean wind velocity V_5 at a height of 5 m were performed by means of a standard cup anemometer about every 5 minutes. Air and sea water temperatures encountered at the measuring site were 283 and 286 K, respectively. This report deals with the study of small film slicks when the sea is calm at the wind velocity $V_{10}=2\pm0.5$ m/s.

Figure 4 presents the spectral energy depression S_o/S_c, i.e. spectra ratio as a function of water wave frequency in the frequency range 0–40 Hz, for a Gasoline 94 film (circles – experimental points). The dependence was derived from the

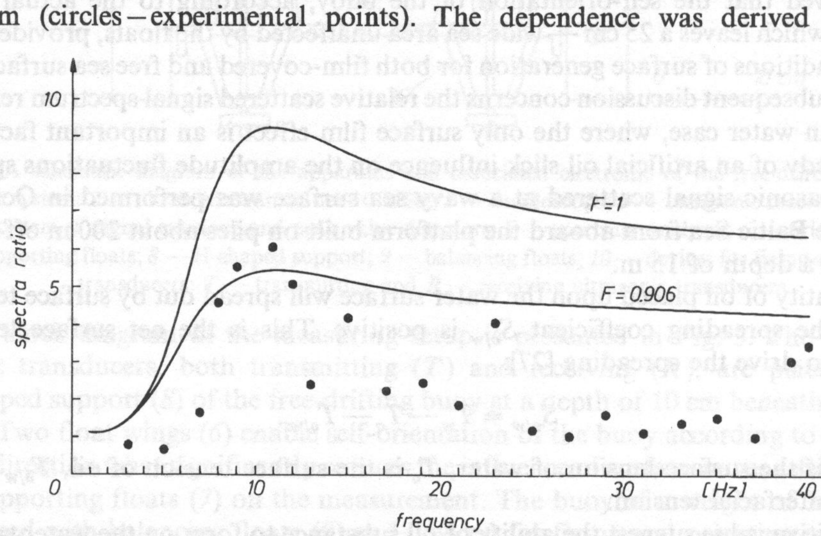

Fig. 4. Spectral energy depression S_o/S_c — spectra ratio of wind-driven waves for the Baltic Sea surface covered with a Gasoline 94 film as a function of water wave frequency as measured by the acoustic scattering system at low wind speeds ($V_{10}=2.3$ m/s). The lower solid line is the best-fit to the data with the film filling factor $F=0.906$. The upper line is plotted using the same best-fit-method film parameters (E_o and w_d) but assuming uniform film covering ($F=1$).

amplitude fluctuations spectra of the ultrasonic scattered signal according to Eq. (18) at a wind velocity of 2.3 m/s. The shape of the spectra ratio clearly exhibits a Marangoni damping phenomenon. However, the experimental points are significantly scattered, especially in the high-frequency region. Thus the intensity and frequency of the spectra ratio peak in Fig. 4 may be interpreted as a maximum of the relative damping Y_{max} and the frequency of the Marangoni damping resonance f_{max}. The coordinates $f_{max}=11$ Hz and $Y_{max}=6.2$, referred to the formulas Eqs. (3), (4) and (5) lead to the rheological film parameters equal to $E_o=5.6$ mN/m and $w_d=3.5$ rad/s. It should be noted that this approximation is based on the assumption that the surface is uniformly film covered ($F=1$). The first solid line in Fig. 4 for $F=0.906$ is the best-fit procedure plot to the experimental points from the frequency range 3–20 Hz surrounding the peak. The viscoelastic film parameters corresponding to this 3-parameter best-fit procedure are equal to $E_o=6.1$ mN/m and $w_d=0.0577$ rad/s. The upper curve is presented for comparison, in which the theoretical equation Y_{ef} describing damping ratio was supplemented with the same parameters but for uniform surface covering $F=1$. The predicted damping intensity is almost two times higher than in the case of the best-fit curve. One can notice that taking into account the film homogeneity correction, leads to obtain apparently different viscoelastic parameters (especially evident for w_d) recovered from the acoustic scattering data. It turned out that the theory-predicted values exceeded those experimentally derived by several per cent in the high-frequency range $f>20$ Hz. This apparent difference could result from the fact that, in this frequency range of surface waves, the registered signal intensity is not simply related to the wind wave spectra (see Eq. (17). The last-mentioned film parameters seem to resemble better the surface properties of crude oil origin films, what has been already shown in laboratory measurements (compare Table 1 in Ref. [28]). The Gasoline 94 film properties were also "in situ" determined using the novel film sampler, for comparison, applied in the same measuring field. The obtained values are in moderate agreement with the data reported above, and are as follows: $E_o=8.3\pm0.3$ mN/m, $w_d=0.0032$ rad/s and $F=0.952$.

Having experimentally measured the relative damping relations, one is now in the position to characterize monomolecular organic films and their smoothing abilities in reference to the results reported by numerous scientists. Table 2 collects the peak frequencies f_{max} and damping intensities Y_{max} of the damping curve derived from laboratory and field experiments carried out with artificial and naturally-formed films of different chemical structure by means of a variety of surface wave field sensors. With regard to monomolecular oleyl alcohol slick OLA, a prononunced wave-damping ability with a maximum at the wave frequency $f_{max}=4.8$ Hz has been observed [55, 56] which implies a relatively large dilational modulus of $E_o=22.5$ mN/m. For comparison, CALLAGHAN *et al.* [57] reported a dilational modulus of 1.65 for North Sea crude oil (NSC) and of 1.76 mN/m for Middle East crude oil (MEC).

Based upon the Marangoni theory, a wave-damping maximum at $f=11.7$ and 11.5 Hz for NSC and MEC crude oil spills can be calculated, what is usually encountered in the presence of weakly damping surface films [48]. Furthermore, the damping intensity

Y_{max} computed by the same theory (for details see Ref. [6]) for NSC $Y_{max}=1.6$ and for MEC $Y_{max}=1.6$ is much lower than the damping intensity of an oleyl alcohol or palmitic acid methyl ester (PME) (see Table 2), which are 27.9 and 40.1, respectively.

According to Hühnerfuss classification [48], the maximum at about 8 Hz are very close to the peak frequency of a natural surface active (NS) compound and triolein (TOLG) "fish oil", which is secreted by plankton and fish. He reported a peak frequency of 6.85 Hz for this natural substance, which implies that it is a material of medium wave-damping ability (see also Murban crude oil, NS and WOS in Table 2).

Table 2. Peak frequencies f_{max} and wave-damping intensities Y_{max} of the spectral energy depression S_o/S_c or relative damping Y dependences, reported from laboratory and open-sea experiments with a variety or organic surface films of different physicochemical structure and origin

Film-forming substance	Film elasticity E_o (mN/m)	Maximum damping frequency f_{max} (Hz)	Damping intensity Y_{max}	Remarks
Hexadecanoic acid methyl ester (PME)	46	3.5	40.1	calculated from the Marangoni theory with E_o and w_d obtained
Oleic acid (OLS)	14	6.1	19.5	in wave tank measurements
Oleyl alcohol (OLA)	22.5	4.8	27.9	Ref. [9, 48]
Hexadecyltrimethylammonium bromide (CEM 3AB)	25.5	4.6	26.3	
Triolein (TOLG) (fish oil)	11.5	6.9	18.3	
Oleic acid methyl ester (OLME)	10.0	8.0	2.3	
North Sea crude oil (NSC)	1.65	11.7	1.6	calculated on the basis of the
Middle East crude oil (MEC)	1.76	11.5	1.6	rheological film properties
"Weathered" crude oil spill (WOS)	10.0	7.8	17.2	Ref. [57]
Olein (technical grade oleic acid)	30.0	4.6	15.8	from the damping of wind waves in open sea experiments
Vegetable oil	10.0	10.0	3.9	Ref. [24]
Natural slick (NS)	6	8.1	3.2	
Murban crude oil	11	8	7.6	Ref. [52]
Natural slick (NS) in polluted waters	25.0	3.8	27.6	from the damping of wind
	18.0	4.2	14.3	waves
	9.0	6.5	5.8	Ref. [4]
Natural slick (NS) in Ligurian Gulf	10.9	7.7	11	from the damping of wind waves
Cetyl alcohol	—	4.0	31.6	Ref. [2]
Methyl alcohol	—	4.3	17.8	
Triton X 100 (concentration 10^{-6} mol)	—	7.1	15.8	

Surface active substances of strong damping ability exhibit maximum wave damping at frequencies between 3.5 and 5 Hz (compare PME, OLA and olein), while weakly damping substances have this maximum at frequencies between 8 and 10 Hz, or sometimes even above 10 Hz (NSC, MEC, vegetable oil and WOS). According to the above discussion, we have got the surface film of weak wave-damping ability comparable to that of natural slicks of biogenic origin and/or weathered crude oil spills. This result also suggests that caution has to be applied when interpreting acoustic scattering data measured at lower wind speeds i.e., under meteorological conditions which are known to be favourable for the formation or natural organic surface films.

Let us compare the presented results with the values of surface rheological parameters, reported by several authors in laboratory and open-sea experiments with slicks of both artificial and natural origin, derived from the spectral energy depression of wind waves using different surface wave field sensors. The rheological parameters pertaining to an oleic alcohol film, empirically found by FISCELLA *et al.* [10] in wave tank measurements, are $E_o = 9.7$ mN/m and $w_d = 9.65$ rad/s. The work by SINGH *et al.* [52] has presented, for the first time, data which straightforwardly indicate the Marangoni damping behaviour of a crude oil spill. The observed viscoelastic characteristics of the oil employed in the COAATF off Halifax on September 16–17, 1983 are $E_o = 8.0 \pm 0.2$ mN/m and $w_d = 12.0 \pm 0.3$ rad/s, as evaluated by FISCELLA *et al.* [31] by means of the recently developed Marangoni damping theory. Natural sea surface films have been detected and characterized by measurements of short-gravity spectra of wind waves during three experimental periods, one in the Sicilian Channel, and two in the Gulf of Maine [4]. Wind wave spectra with/without organic films were measured "in situ" with a microwave probe. For each of the data set presented in Fig. 5 of LOMBARDINI *et al.* work [4], a theoretical curve is drawn according to Eqs. (3), (4), (5) and (6) with a proper choice of the parameters E_o, w_d and F. For the three cases, the parameters obtained by this best fit method are $E_o = 25.0$; 18.0; 9.0 mN/m, $w_d = 11.0$; 13.0; 6.0 rad/s and $F = 0.996$; 0.880; 0.982. Finally, for coastal waters in the Ligurian Sea, the spectral energy depression curve obtained by photographic techniques by CINI *et al.* [2] allows one to evaluate the rheological parameters to be $E_o = 10.9$ mN/m and $w_d = 0.18$ rad/s. For more experimental data the reader is referred to the paper [2], where the damping ratio $Y(f)$ dependences, registered in the presence of four insoluble films of SA compounds, are depicted in Fig. 4.

The data collected above clearly show that the time of the relaxation process $t_r = 1/2\ w_d$ involved in the surface wave damping effect by monomolecularviscoelastic films is of the order of 0.04 to 2.7 seconds. One should remember that the relaxation time, depending on the type of relaxation process, for soluble films upon diffusional relaxation, and for insoluble ones upon the structural relaxation between inter-molecular forces [5], can vary from 10^{-3} s to several minutes [58]. The characteristic time of the relaxation process in the model slick t_r is 8.67 s. For comparison, water waves with a wavelength of 1 cm are damped within the characteristic time (α_0^{-1} (Eq. (1)) equal to 0.4 s.

In the last decade monomolecular surface films, mostly 9-octadecen-1-ol, cis isomer (oley alcohol, an 18 carbon, monounsaturated fatty alcohol) have been applied as an oceanographic tool for studying the air-sea interaction process at the ocean surface [6, 19]. This material is chosen because it resembles natural slicks in the physico-chemical behaviour [9, 48]. It has been found that long-time scale relaxation times of several minutes measured by the author for crude oil derivatives films [28] were also encountered for an oleyl alcohol film [59].

One can conclude that the Gasoline 94 film spread over the Baltic Sea surface stands for a slick of oceanographically relevant viscoelastic properties. In addition, the experimental spectral energy depression data points could be fitted into the theoretical relation (3) and, after combining Eqs. (3), (5) and (6), the unknown filling factor F can be evaluated, what is of great importance, since it is very difficult to measure this quantity directly which can significantly influence the surface scatter returns [4, 10, 11, 30].

It has been found that the spectra ratio was observed first to increase as the slick drifts over the insonsified area, and then decrease, returning to its preslicked values. It seems that the data collected by this system can be further interpreted to deduce the film weathering and concentration.

Recently, the wind velocity field above slicks has been briefly examined in the paper by ERMAKOV *et al.* [24] (see Sec. 3). Their appproximate estimates show that a corresponding increase of the wind above the slick can be given by the root of a mean spectral energy depression value in a centimetre-wavelength range of surface waves $(S_o/S_c)_{cm}$, what follows from Eq. (20).

Assuming the acoustically determined S_o/S_c values of the order of $2-3$, one can obtain $\Delta V = 0.17$ to 0.30 m/s which corresponds to the wind velocity variation above the studied slick $\Delta V/V \sim 10.4-13.1\%$. This result agrees well with the direct anemometer data of the same order of magnitude (see Table 1). Thus the remote estimating the wind field near the surface covered with a slick, which is of meteorolgical relevance, may be derived from acoustic scattering measurements.

It may be helpful to add that the applied acoustic system consisting of two transducers based on a forward specular scattering geometry has got two features which are of significant interest in future at-sea experiments. The wave staffs measure the surface waves spectra omnidirectionally i.e., integrating over 360° and so-called "spectra of encounter" are derived [19] whereas an acoustic scatterometer senses unidirectionally in reference, to the pointing direction of the acoustic beam. Therefore, a directional pattern of the scattered signal fluctuations spectra with respect to the actual wind direction can be evaluated. The proposed corrections of the "spectra of encounter" in order to get "real spectra" take into account deviations due to the orbital velocity of gravity waves, wave-induced Stokes drift and tidal currents [21]. The spectra of specularly scattered acoustic signals do not have to be corrected [41, 43] and can be directly compared to those obtained at different wind speeds and environmental conditions or theoretically predicted.

These results are encouranging, however a great deal of additional experimental and theoretical evaluation will be required to determine the full capability of the acoustic system for remote sensing of marine surface films under open-sea conditions. A critical element in determining the usefulness of such a system is the quality and thoroughness of the environmental measurements taken simultaneously with the acoustic data.

6. Concluding remarks

Natural surface film studies performed in coastal waters of the Baltic Sea using a novel device for "in situ" sampling and force-area isoterm measurements showed that the film filling factor, affecting the acoustic scattering returns to a great extent, reaches the mean values 0.913 and 0.716 for two different sampling sites studied. In addition, F is a wind dependent quantity. For low wind speeds $V_{10}<2-3$ m/s the sea surface can be assumed to be uniformly and completely film-covered, $F=1$.

Data reported by numerous authors on the vertical wind profile above wavy sea water allowed one to determine the aerodynamic parameters of the air-sea interaction process. For the film-covered surfaces one can notice an increase in V_{10} by 5–20%, a decrease in u_* by 7–9% and in z_0 by 7 to 34 times, as well as a decrease in the drag coefficient c_d by 23 to 70% if compared to the clean surface case. A variation of the growth rate of wind-driven waves $(\beta_0-\beta_c)/\beta_c$ due to the film presence appears to be of the order of 15.0–19.9%, and is of secondary importance in suppression of wind waves. An increase of the wind above the model slick (0.17–0.30 m/s) deduced from the spectra ratio in the centimeters wave range is in agreement with the direct anemometer observation. The measured coordinates $f_{max}=11$ Hz and $Y_{max}=6.2$ referred to the theoretical formulas lead to the rheological Gasoline 94 film surface properties equal to $E_0=6.01$ mN/m and $w_d=0.0577$ rad/s with the filling factor $F=0.906$. The film filling factor plays a principal role in a proper determination of the film properties recovered from the acoustic surface probing. According to the discussion by Hühnerfuss, we have the surface film of weak wave-damping ability comparable to that of natural slicks of biogenic origin and/or weathered crude oil spills.

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