Horizontal Surface Tension Gradients Induced in Monolayers by Gravity Water Wave Action

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ABSTRACT

Surface tension gradients have been measured for three different monolayers (oleyl alcohol, palmitic acid methyl ester and cetyl trimethyl ammonium bromide) spread on a wavy water surface (waves with 1-Hz frequency; 2-cm wave height). The wave-induced surface tension gradients were determined indirectly using 1) a wave-follower mounted surface-potential ionization probe and 2) a pulsating spreading oil patch. The films can sustain unexpectedly large surface tension variations of the order 12-14 ($\times10^{-3}$) N m^{-1} and were found to experience a relaxation, i.e., a significant change of surface potential and surface tension variation with time (order of 1500 s) and with position on the wave (phase shift). The relaxation and phase shift are attributed to a reordering of the film molecules and the subsequent modification of the mutual interaction between the film molecules and the water molecules of the underlying water layer.

1. Introduction

There is a widespread occurrence of natural surface films on oceanic waters, especially in coastal regions. These films or slicks often appear as surface active monolayers and are of biogenic origin. Monolayers of surface active materials are capable of damping water surface waves. The elastic properties of such an adsorbed or spread film causes a resistance to the periodic surface expansion and compression of the flow due to the wave motion. The flow underneath the film is thus altered and a higher energy dissipation by viscous friction occurs. This in turn, results in increased damping of surface waves (for details see Hühnerfuss *et al.*, 1984a).

Historically seen, most work using wave damping to investigate surface film properties such as surface tension gradients, has been done using capillary waves with frequencies >10 Hz (for a review, see Lucassen-Reynders and Lucassen, 1969; Stone and Rice, 1977; Hühnerfuss *et al.*, 1981; Hühnerfuss *et al.*, 1983). However, the dilation and compression of a film, causing horizontal surface tension gradients, also occurs in the presence of gravity water waves with frequencies <5 Hz. Gravity water waves cause horizontal contraction and extension of the surface at the crests and troughs of the waves respectively. The aim of this article is to investigate the response of surface films to this gravity water-wave action, especially with respect to horizontal surface-tension gradients, which are instrumental in wave damping processes. This article complements initial work by Hühnerfuss *et al.* (1982) and Hühnerfuss *et al.* (1984a) on the damping of gravity water waves by various types of surface films.

The artificial surface films used in this study were oleyl alcohol (OLA) (Z-9-octadecen-1-ol), palmitic acid methyl ester (PME), cetyl trimethyl ammonium bromide (CEM3AB). The choice of the three types of film used was motivated by the results of a number of authors who analyzed natural surface films and found them to contain mostly compounds with C_{16} and C_{18} alkyl chain lengths, e.g., palmitic and stearic acid derivatives and the respective alcohols (for further discussion see Hühnerfuss *et al.*, 1982, and Hühnerfuss *et al.*, 1984a).

2. Method of measurement

The measurements were performed in a laboratory wave channel (Hühnerfuss *et al.*, 1976). The channel is 26 m long, 1 m wide, 0.5 m deep, and is equipped with a hydraulically driven wave flap.

One approach to measuring the surface contraction and extension of a film on a wavy water surface involves a direct measurement of the electrical surface potential of the film. It is assumed that the film's surface potential is proportional to its concentration

(Harkins and Fischer, 1933; Adamson, 1982). Previously reported measurements of surface film potentials were performed under static conditions using either the air ionization electrode or the vibrating electrode method (Adamson, 1982; Gaines, 1966). The former was more suitable for our purposes. Our probe was constructed according to Bewig (1964) and Williams *et al.* (1980) and consists of a gold foil electrode coated with the alpha emitter ^{241}Am (Amersham Buchler, Braunschweig, Fed. Rep. of Germany) which is connected to the input of a FET operational amplifier configured as a voltage follower, Fig. 1. The alpha emitter ionizes the air gap between the probe and the film surface, making it sufficiently conducting so that a potential difference can be measured.

In order to measure the surface potential over a wavy surface, the probe was mounted on a wave follower (Werner, 1981, see also Baldy *et al.,* 1978) so that it remained a fixed distance above the film-covered wavy surface, Fig. 2. Static measurements were performed first to determine the dependence of the surface potential on the height of the probe from the surface using a traversing mechanism. A typical result is shown in Fig. 3 for the films used in this study. On the basis of this result, the wave follower was adjusted so that the probe remained 1 cm above the surface. This placed the probe in a vertical region of the curves shown in Fig. 3, so that the error of the wave follower (±2 mm) had a minimal effect on the measurement.

The analog output signal of the surface potential probe was recorded with a strip-chart recorder and with a spectrum analyser (Hewlett Packard 3582A or Wavetek/Rockland 5820A). Each measurement was performed first for a clean surface. A 75 millimolar solution of the film material in distilled ethanol was then dropped at a distance of 8 m from the probe at a rate of 0.75 ml/min and was transported to the probe by the wave-induced Stokes drift.

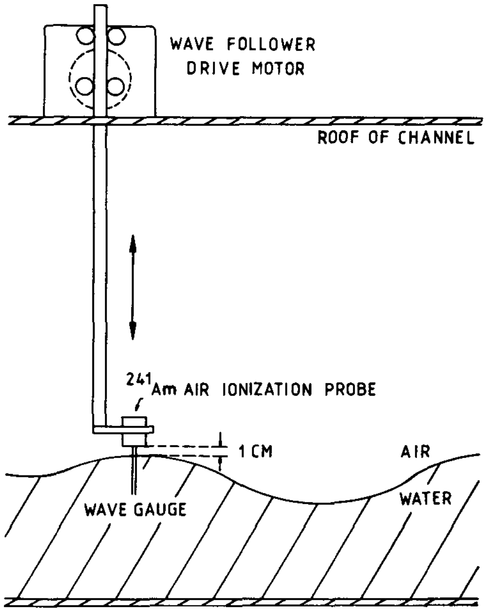

FIG. 2. Wave follower with air-ionization probe mounted.

A second method used to determine the magnitude of the surface tension gradients induced in a film by wave action relies on the classical surface tension measurement with calibrated piston oils according to Adam (1937). The set of piston oils used in this experiment was prepared by mixing known quantities of 1-dodecanol with nonspreading paraffin oil. After calibration in a Langmuir trough by the piston monolayer technique (Zisman, 1941), the accuracy of the surface tension measurements is approximately $\pm 0.5 \times 10^{-3}$ N m^{-1} (Hühnerfuss *et al.,*1977). Under static conditions, drops of piston oils calibrated according to increasing surface tension are dropped consecutively onto the film surface until a thus formed patch of oil spreads spontaneously. This occurs when the patch possesses a slightly higher surface pressure than the surrounding film (surface pressure equals surface ten-

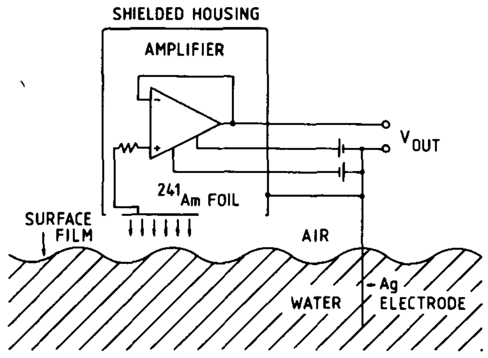

FIG. 1. Schematic diagram of surface potential probe using the air ionization electrode (after Williams *et al.*, 1980).

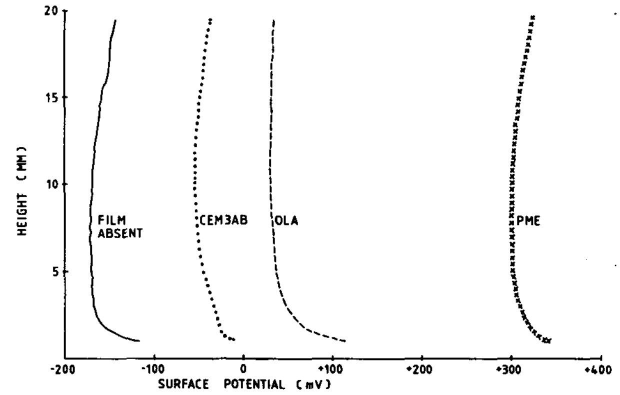

FIG. 3. Typical surface potential profiles measured under static conditions.

sion of pure water minus surface tension of patch or film), i.e., the film has a surface pressure very close to that of the calibrated patch of spreading oil. We applied the method in a similar fashion to our wavy-film-covered surface, noting the patch that first shows a slight pulsation (due to the wave action) and the patch that showed a maximum pulsation without tearing. The difference in the surface pressures of these two patches indicates the magnitude of the wave-induced surface-tension gradients in the film.

3. Hydrodynamic theory

As stated by Lamb (1945), ". . . in oscillatory waves the tendency is for any portion of the surface to be alternately contracted and extended, according as it is above or below the mean level." This is not intuitively obvious. If we consider a small-amplitude straight-crested progressive wave of amplitude a, wavenumber k and angular frequency ω propagating in the x-direction in water of depth d, with a profile

$$\zeta(x, t) = a \cos(kx - \omega t), \tag{1}$$

the corresponding velocity component in the x-direction is

$$u = \omega a \frac{\cosh k(z + d)}{\sinh kd} \cos(kx - \omega t), \tag{2}$$

where t is the time and z is positive upward (see Kinsman, 1965; Levich, 1962). Equation (2) applies to water of intermediate depth which is appropriate for the waves used in this study. Equation (2) shows that the horizontal surface velocity has a maximum at the crests and is in the wave direction, and a minimum in the troughs in a direction opposite the wave direction, Fig. 4a. The water particles at the surface experience a horizontal force F which is proportional to their acceleration,

$$F \propto \frac{du}{dt} = \omega^2 a \frac{\cosh k(z + d)}{\sinh kd} \sin(kx - \omega t). \tag{3}$$

As shown in Fig. 4b, contraction occurs at the crests and extension in the troughs. Consequently, in our specific case, surface active films are expected to show a horizontal concentration gradient under the influence of wave action, i.e., a maximum concentration at the crests and a minimum concentration at the troughs. This assumption is supported by studies by Leibovich (1975), Chung (1977) and Kordyban (1982) which have shown that thicker crude oil films are thickest over crests and thinnest over troughs, in agreement with the wave theory.

4. Results and discussion

a. Surface-potential measurements

To gain a qualitative interpretation of the surface potential, it is useful to apply the analogy with a capacitor (Adamson, 1982). Two conducting plates a distance d apart and enclosing a charge density σ, have a potential difference ΔV given by

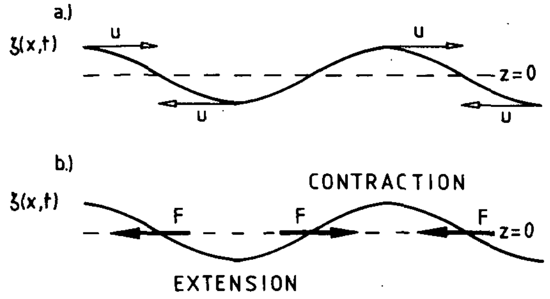

FIG. 4. Horizontal velocity (a) and force (b) components acting on the surface of a gravity water wave propagating from left to right.

$$\Delta V = \frac{\sigma d}{\epsilon_0 \epsilon}, \tag{4}$$

where ϵ = dielectric constant and $\epsilon_0 = 1 \times 10^7/(4\pi c^2) = 8.85 \times 10^{-12}$ (c = speed of light). If one assumes the charge separation to be due to the presence of an effective dipole moment $\bar{\mu}$ for a concentration Γ of polar film molecules/cm^2, then

$$\Delta V = \frac{\Gamma \bar{\mu}}{\epsilon_0 \epsilon} = \frac{\Gamma}{\epsilon_0 \epsilon} \mu \cos\theta, \tag{5}$$

where it is assumed $\bar{\mu} = \mu \cos\theta$, θ being the angle of inclination of the dipoles μ with the normal. Harkins and Fischer (1933) pointed out the empirical nature of this interpretation. Indeed, many recent studies have shown that the water surface is structured and that this structure can be altered by surface films (Drost-Hansen, 1972; Alpers *et al.*, 1982; Hühnerfuss and Alpers, 1983; Hühnerfuss and Walter, 1984). Nevertheless, Eq. (5) indicates that ΔV is proportional to concentration. Since film pressure depends on the concentration, one expects a positive correlation between surface potential and film pressure. Figure 5 confirms this for the three films used in this investigation, namely, surface pressure and surface potential increase with increasing concentration. The curves were measured in the classical fashion using an automated Langmuir trough.

Figure 6 shows a typical measurement using the wave-follower mounted surface-potential probe for a 1 Hz flap-generated wave (wavelength = 156 cm; wave height = 2 cm). The trace shows the expected jump in surface potential with the arrival of the film. The wave-induced surface-potential fluctuations also increase significantly in the presence of the film. The surface contraction and extension due to the wave action cause a horizontal concentration (and surface tension) gradient in the film which in turn is reflected in the fluctuating surface potential, i.e., the wave

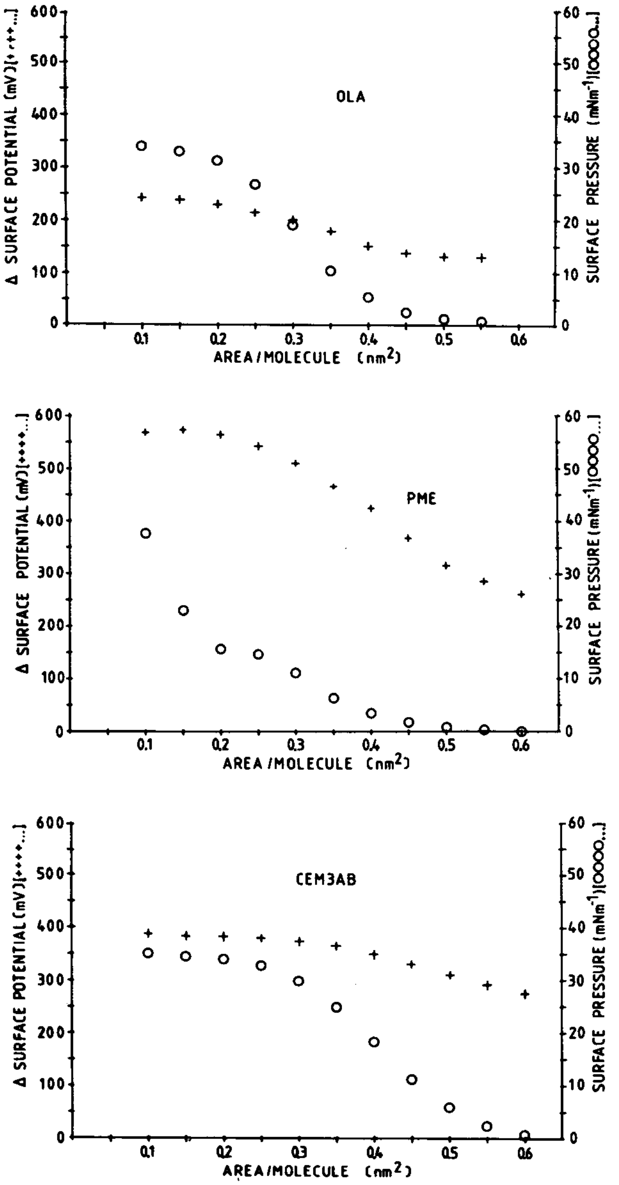

FIG. 5. Langmuir trough compression curves (velocity of compression = 0.016 nm^2 min^{-1}) of surface potential (crosses) and surface pressure (open circles) for oleyl alcohol (OLA), palmitic acid methyl ester (PME), and cetyl trimethyl ammonium bromide (CEM3AB).

action causes a periodic local reorientation of the molecules and their corresponding dipole moments.

Figure 6 also shows that the surface potential fluctuations decrease in time, i.e., the film molecules experience a "relaxation". The physicochemical background of this phenomenon recently has been investigated by means of laboratory relaxation measurements (Hühnerfuss and Walter, 1984) and by surface viscosity measurements (Hühnerfuss, 1984): due to long-range hydrophobic interactions between the film molecules and the adjacent water layer "ice-like" clathrate structures are formed within the upper layer ("vicinal water layer"; for details see Alpers *et al.*, 1982; Hühnerfuss and Alpers, 1983). The intensity of these interactions increases with an increasing ordering of the film-forming molecules and approaches a maximum value when parallel alignment of the alkyl chains (hydrophobic group of the film molecules) is achieved. This configuration gives rise to a large directed dipole moment, causing the increase in the mean surface potential with time in Fig. 6 and a considerable polarization of the adjacent water layer. Thus, as the relaxation progresses, the individual film molecules become less and less randomly oriented and have less freedom to oscillate under the wave-induced forces which results in decreasing surface potential fluctuations. On the other hand, the increasing ordering of the molecules and the subsequent induced structuring of the vicinal water layer causes a mean surface potential increase; e.g., in the presence of a PME surface film (see Fig. 6), after about 30 s a mean surface potential of about 320 mV was measured, whereas after about 500 s a value of about 400 mV was obtained.

In order to assure that the relaxation effect was not due to a gradual fouling of the surface potential probe, the probe was cleaned in the middle of a run. The probe output returned to the precleaned form after a few seconds.

The relaxation effect was substantiated by measuring power spectra of the surface potential output at regular intervals of 160 s with each spectrum being composed of an ensemble average of 8 spectra with bandwidth 0.29 Hz, taking 100 s to record. Figure 7 shows typical spectra for a clean surface and for a film-covered surface shortly after arrival of the film. The time dependent spectral-analysis results are summarized in Fig. 8 for the three different films. In the lower part of Fig. 8, the spectral density difference represents the difference between the film-absent and the film-present spectral peak at 1 Hz (frequency of the water wave) in dB. Concurrent to the spectral peak measurements, the surface potential output was correlated with the output of a fixed wave-height gage placed next to and at the same position, with respect to the length of the channel, of the surface potential probe. The curves in the middle part of Fig. 8 show the phase angle relationship and in the upper part of Fig. 8 the corresponding coherences of the transfer function between the fixed wave-height gage and the surface potential probe. We have arbitrarily plotted only the phase values up to where the coherence dropped to 0.5.

It was noted, however, that the shape of the surface-potential time series used to determine the spectra for Fig. 8 often changed during the relaxation of the films (e.g., appearance of secondary maxima and minima), especially where the coherence was very low.

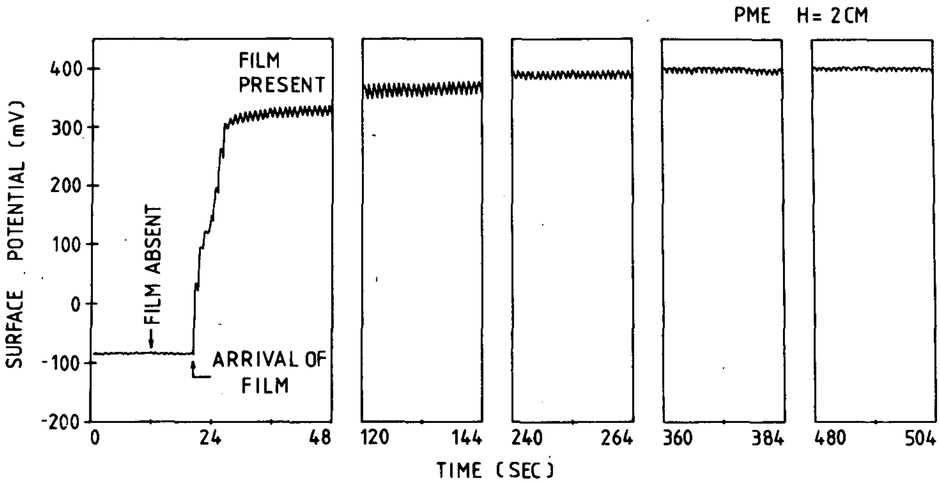

FIG. 6. Typical surface potential trace for palmitic acid methyl ester (PME) showing response to 1 Hz water wave of 2 cm height.

The curves in Fig. 8 of the three film-forming substances investigated in this work, oleyl alcohol (OLA), palmitic acid methyl ester (PME), and cetyl trimethyl ammonium bromide (CEM3AB), exhibit significantly different characteristics which can be interpreted in light of the above mentioned molecular interactions between the surface film and the adjacent water layer:

PME consists of a saturated straight-chain alkyl group and a sterically large ester group, which is oriented in the E-configuration in the case of a freshly spread surface film, i.e., the molecules at first are nearly randomly oriented. In the course of continuous ordering of the molecules, the saturated alkyl chains can achieve a parallel alignment, and their mutual interaction becomes so strong that the alcohol com-

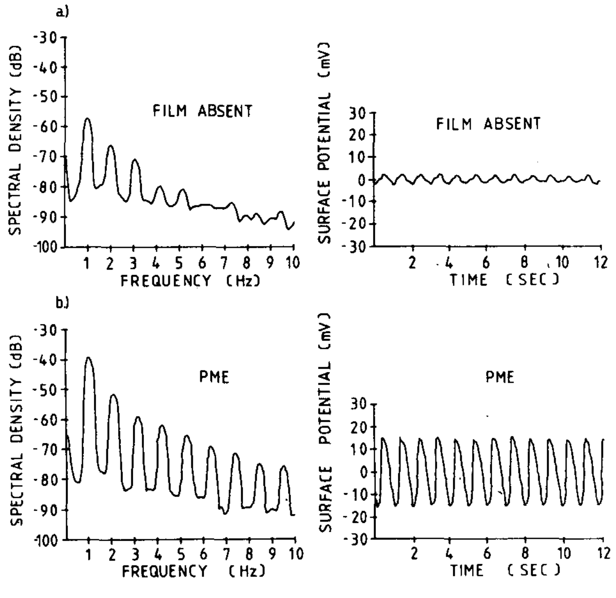

FIG. 7. Typical spectral plot with a time-series sample of surface potential response to 1 Hz water wave of 2 cm height for (a) clean water surface and (b) film of palmitic acid methyl ester (PME) covered water surface.

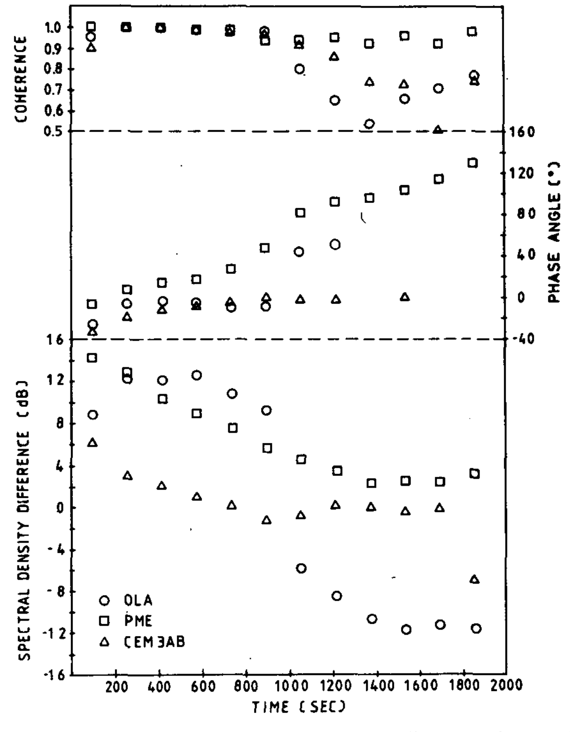

FIG. 8. Relaxation curves based on the difference of the 1 Hz spectral peaks between clean- and film-covered surface potential response (see Fig. 6) for oleyl alcohol (OLA), palmitic acid methyl ester (PME), and cetyl trimethyl ammonium bromide (CEM3AB). 90% confidence interval: +3.0 dB, −2.2 dB. Phase angle and coherence refer to a comparison of the surface potential output to that of a fixed wave height gage.

ponent of the ester group is forced into a Z-configuration, which in turn enables still a more intense mutual interaction between the alkyl groups due to a reduced sterical hindrance. This E,Z-isomerization, which was extensively investigated by Hühnerfuss *et al.* (1982), is strengthened by wave-induced compression effects. In a water wave field a continuous contraction and extension of the surface film leads to a continuous E,Z-isomerization, which implies a continuous variation of polarization within the vicinal water layer. As a consequence, a relatively large value of the spectral density difference between the film-absent and PME film-present case is observed even after the relaxation has reached equilibrium.

In the case of an OLA surface film, the freshly spread molecules also are randomly oriented because of the unsaturated character of the alkyl groups, which implies a large steric hindrance. A continuous ordering of the molecules is possible by a "spoon-type packaging" giving rise to a greater mutual interaction between the film molecules and a greater interaction between the surface film and the adjacent water layer. On the other hand, the elasticity of the surface film is reduced such that significantly smaller concentration gradients and thus smaller surface potential gradients are induced by gravity water waves. As a consequence, a much lower spectral density difference between film-absent and OLA film-present is observed after relaxation has been achieved in comparison to the PME film. The negative values of the OLA relaxation curves in Fig. 8 result from the fact that the film-absent surface potential fluctuations are still quite high (e.g., as seen in the time series in Fig. 7). Though the film-absent surface was very clean as verified by surface tension measurements and the low mean surface potential (−60 to −90 mV), a few foreign molecules remain which interact weakly and thus are very responsive in changing their orientation (causing the relatively high surface potential fluctuation) under the influence of the wave action. Nevertheless, in all the data of Fig. 8, the film-absent cases showed about the same surface potential fluctuations.

The third substance investigated in this work, CEM3AB, contains a positively charged hydrophilic ammonium group, i.e., the single-film molecules cannot approach each other very closely because of the repulsive Coulomb forces both in the freshly spread and in the relaxed surface film. As a consequence only a slight time dependence of the spectral density difference between the film-absent and the CEM3AB-present case can be observed. However, the absolute values remain relatively high compared to OLA, because the positively charged ammonium group and the negatively charged bromide are known to induce counteracting strong polarization effects within the vicinal water layer: the ammonium group basically is a structure-promoting group, whereas the bromide ion is a structure breaker. Thus a relatively large variation of the surface potential has to be expected under the dynamic conditions of a water wave field.

The more or less pronounced modification of the interaction between the respective film molecules and the water layer with time corresponds to a phase shift with time. In the case of the PME film, the above described strong mutual interaction of the Z-configurated relaxed surface-film material leads to significant modifications of several physical parameters of the vicinal water layer: e.g., the surface viscosity is much larger in a closely packed surface film than in a surface film in which the film molecules cannot achieve an optimum arrangement (Hühnerfuss, 1984). It is too early for correlating the observed phase shifts with the experimentally determined surface viscosity increases because additional parameters may also contribute to the phase shift. However, it is noteworthy that strong modifications of the vicinal water-layer parameters with time (PME) coincide with strong phase shifts, whereas slight modifications of the vicinal water-layer parameters with time (CEM3AB) coincide with negligible phase shifts.

b. Spreading oil measurements

A more quantitative determination of the wave-induced surface tension gradients in the film was made using the above mentioned calibrated spreading-oil-patch method. Figure 9 shows the setup used to record the patch contraction/extension and a typical result for such a maximum patch pulsation on a PME film during one period of a 1 Hz water wave. The water level variations in cm can be seen on the scale on the left-hand side of the respective photographs. This particular series of photographs corresponds to a surface tension change of about 12–14 $\times 10^{-3}$ N m^{-1}. The photographs show that the patches indeed are contracted at the wave crests and extended at the wave troughs thus confirming the hydrodynamic theory.

Table 1 summarizes the results of evaluating a number of patches as a function of time, where the surface tension variation has been determined from the difference in surface pressure between a slightly pulsating and a fully pulsating patch. Surprisingly high values of up to 14.8×10^{-3} N m^{-1} were measured. This represents about 30% of the total surface tension lowering caused by the film and verifies the extremely elastic nature and strong damping property of such films. This result confirms that the surface potential gradients discussed in Section 4a indeed decrease during relaxation as a result of molecular ordering effects and not as result of decreasing surface tension gradients, i.e., the pulsating patches show that the surface tension gradients increase as the relaxation progresses (Table 1). This latter effect is caused by the closer packing of the

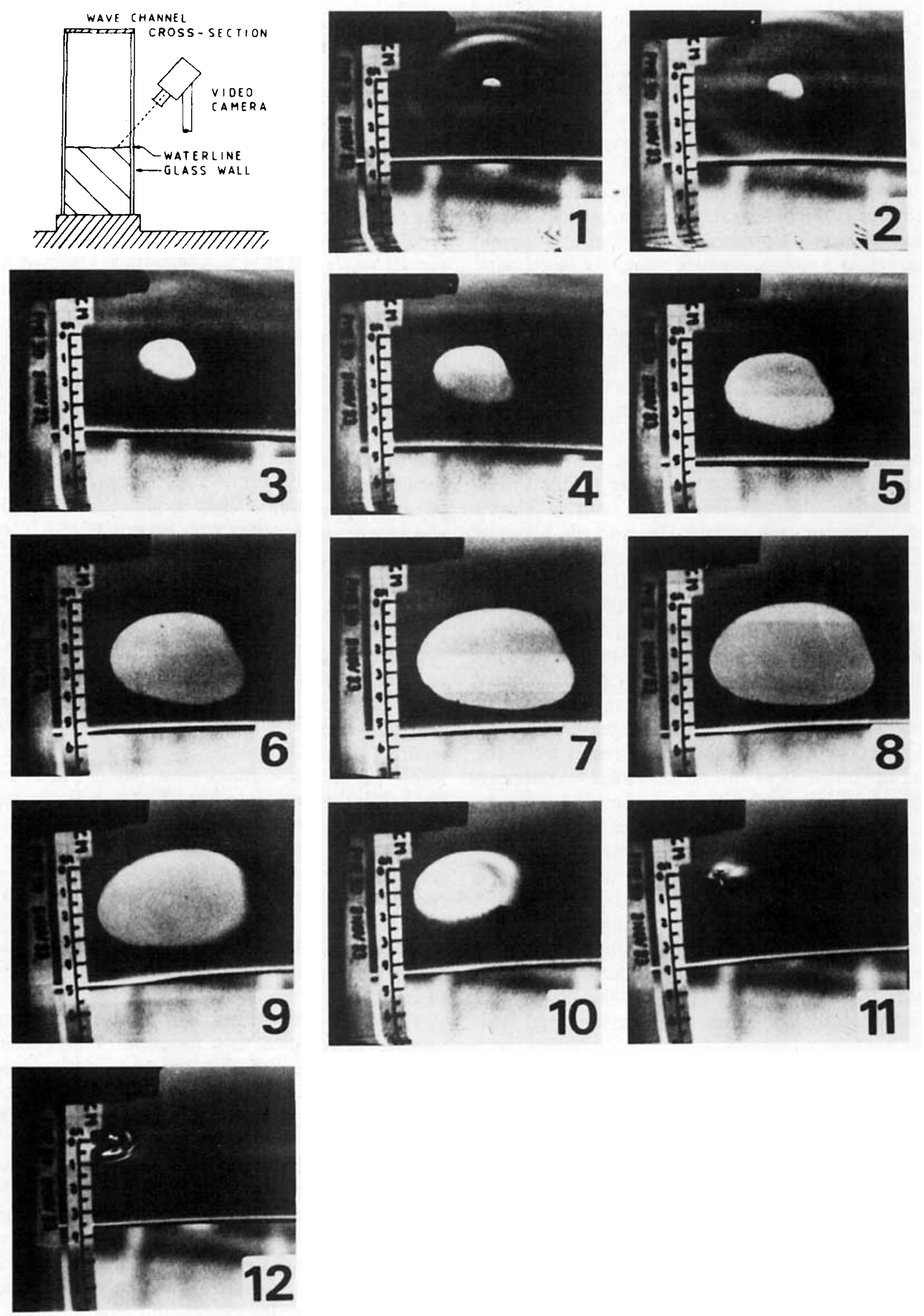

FIG. 9. Setup for pulsating calibrated-patch experiment with an example showing maximum patch contraction/extension on a palmitic acid–methyl ester (PME) film for a 1 Hz water wave with height = 2 cm. Photographs are 0.08 s apart.

TABLE 1. Dependence of the wave induced surface tension variation on time for oleyl alcohol (OLA) and palmitic acid methyl ester (PME) monolayers. Wave height = 2 cm, temperature = 289 K. The data values are estimated to be accurate to $\pm1.0 \times 10^{-3}$ N m^{-1}.

Time (min)	Surface tension variation (10^{-3} N m^{-1}) OLA	PME
1.5–2.0	10.7	—
3.0–3.5	12.3	—
5.0	12.9*	9.2
9.5–10.0	—	10.2
18.5	—	13.8*

* Relaxation approached limiting value.

molecules, which leads to "more solid" phase characteristics of the surface film. It is basic knowledge of surface film chemistry (e.g., see Gaines, 1966) that a more solid phase coincides with "steeper" Langmuir-curves. Consequently, for the same wave-induced surface concentration gradient, larger surface tension gradients must necessarily occur in more condensed films than in less condensed films.

It is also interesting to note that the patch expands uniformly as a function of time or wave amplitude on the back face of the wave, but contracts very suddenly on the front face of the oncoming wave. This sudden contraction only is understandable if larger surface tension gradients are induced on the front face than on the back face of the wave. However, the reason for this anisotropic effect hardly can be concluded from the above presented hydrodynamic theory. However, though the sinusoidally generated waves appear very uniform, wall and bottom friction may contribute to nonlinear effects which also may influence the surface tension gradients on a film-covered water wave.

The point where the sudden contraction occurs provided a convenient reference for checking whether a phase shift also could be observed with the pulsating patches. A careful evaluation of the video still pictures (50 half-pictures per second or per patch pulsation) revealed that a phase shift (lag) of about 70 deg occurred for PME between the times 5.0 min (300 s) and 18.5 min (1110 s) of the relaxation (same times as used in Table 1). This is in good agreement with the surface-potential fluctuation phase shift shown in Fig. 8, i.e., the molecule reordering effects (Section 4a) change the properties of the underlying water layer so that the surface tension gradients must also show a phase shift during the relaxation.

A similar phase lag could be determined qualitatively for OLA during the early part of the relaxation. The evaluation, however, was more difficult since the pulsating patches on the OLA film showed a less sharply defined point of sudden contraction.

5. Concluding remarks

This study has confirmed that gravity water waves induce surface concentration and surface tension gradients in monomolecular films. This was done using the novel, and independent, surface potential and pulsating spreading-oil-patch techniques.

Of particular interest is that the monolayers can experience a relaxation where their molecules undergo a reordering in response to the wave action. This film-molecule reordering induces a restructuring of the water molecules in the underlying water layer, which in turn causes the properties (such as viscosity) of the film/water layer system to change. The position relative to the wave profile of the zones of contraction and extension are then shifted. The magnitudes of the wave-induced surface tension gradients, phase angle shifts and surface potential variations depend on the chemical structure of the film-forming substances.

This study was performed at a single wave frequency and amplitude to minimize nonlinear effects inherent in wave channels (Komen, 1980). Nevertheless, the occurrence of the phase angle shift even at a single frequency is very encouraging since a phase angle shift is necessary when experimentally determined wave damping coefficients are to be explained using visco-elastic theory (Lucassen-Reynders and Lucassen, 1969). This will be further pursued in a future paper.

It is eventually hoped that surface films can be accurately remotely sensed so that corrections for wind field determinations (from sea surface roughness) or gas exchange processes can be applied. It is noteworthy that airborne L-band radar data recently obtained over clean and film-covered sea surfaces could only be interpreted by assuming a phase angle shift of the Bragg-scattering capillary waves in the presence of the oleyl alcohol surface film. This assumption, which is discussed separately by Hühnerfuss *et al.* (1984b), is substantiated by the results presented herein.

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