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On the damping of capillary waves by surface films

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The damping of horizontal waves on a deep fluid has been measured and compared with published theoretical predictions for the following systems:

(1) clean water (frequency range: 50 to 920 c/s);

(2) solutions of soluble surface-active agents (frequency range 14 to 800 c/s);

(3) aqueous solutions on which has been spread a monolayer of an insoluble surface-active agent (frequency 150 c/s).

The results for clean water agree closely with the appropriate theoretical equations.

Data on the damping as a function of frequency and concentration for a soluble surfaceactive agent (sodium lauryl sulphate) show a relaxational effect, due to desorption and adsorption of the film during the passage of each wave. Three other surface-active agents of different chain lengths have been studied to determine the effect of the rate of desorption on the damping at different frequencies. The results are consistent with theory.

Soluble and insoluble films possessing different surface compressibilities and shear viscosities have been studied to find how these factors affect the damping at various surface pressures. Results are in excellent accord with the mathematical theory of Dorrestein (1951): the surface compressional modulus is of prime importance in damping capillary waves, and quite low values of this modulus can cause wave damping which considerably exceeds that at a completely immobile surface.

INTRODUCTION

That heat and mass transfer rates increase under conditions where rippling exists at the interface, as a probable result of improved mixing in the bulk, has been repeatedly reported (Grimley 1945; Emmert & Pigford 1954; Davidson, Cullen, Hanson & Roberts 1959; Downing & Truesdale 1955; Vivian & Peacemen 1956). The addition of small quantities of surface-active materials greatly reduces these effects.

In recent years, investigators using soluble surface-active agents in wetted-wall column equipment have repeatedly claimed that there is an optimum damping concentration (Emmert & Pigford 1954; Tailby & Portalski 1961; Kafesjian, Plank & Gerhard 1961). Quite small concentrations (e.g. 10^{-5} to 10^{-3} M) are reported to be sufficient to eliminate almost completely the visible ripples. A stronger solution than the optimum either accomplishes no further damping or, more commonly, causes some restoration of the rippling.

The damping of waves at sea with surface-active agents has been known since antiquity. Pliny in the first century A.D. referred to the use of oil to prevent the breaking of waves over a ship during a storm, and Franklin (1774) relates many instances of the phenomenon. It was Aiken (1883), however, who first studied the subject scientifically, showing that wave damping by a surface film is associated with its resistance to compression.

The present work is concerned with capillary, or surface tension waves, where the wavelength λ is less than 0.5 cm. Brown (1936) studied this aspect, but since

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then only a little work has been done, notably by Vines (1960), Goodrich (1961, 1962) and Davies & Bradley, quoted by Davies & Rideal (1961). Theoretical aspects have been a little better served; Lamb (1932), Levich (1941), Dorrestein (1951) and Goodrich (1961) have contributed to the subject, though their theories have remained inadequately tested by experiment. The subject has recently been reviewed (Davies 1962).

The damping at a *clean surface* results from viscous energy dissipation in the bulk; the surface is completely mobile. In general, the surface tends to contract at a wave crest and expand at a trough, so that *if a monolayer is present*, surface tension stress gradients are produced by the differential surface concentrations. The consequent motion of the surface, and of the attached substrate layer, occurs in the direction of increasing surface tension; and, as a consequence of the alternating drag on the liquid, the rate of energy dissipation is increased.

One may expect the resistance to compression of a monolayer to be a primary factor controlling the additional damping caused by a film (Davies & Rideal 1961). This effect is measured by the surface compressional modulus, written C_s^{-1} and defined by $C_s^{-1} = -A \, d\Pi/dA$, where A is the area available to a molecule in the film, and Π is the surface pressure of the film, equal to the lowering of the surface tension. Also important may be the surface dilational viscosity, η_d ; this, however, has never been measured directly, though the surface shear viscosity, η_s (of questionable identity with η_d) can be readily determined.

It was the object of the present work to investigate both soluble and insoluble films in order to answer the following questions:

(1) Does the Kelvin equation ((1) below) give the equilibrium surface tension of film-covered surfaces (i.e. when the surface tension fluctuates between the crests and troughs)?

(2) Does the damping at clean surfaces agree with theory?

(3) For a particular concentration of a soluble surface-active agent, does the damping show a frequency (relaxational) effect? Is there time for some 'short-circuiting' of the surface stresses by partial adsorption and desorption of the surface film during the passage of a wave? Conversely, does a rather weakly adsorbed film behave as insoluble at sufficiently high frequencies?

(4) How does effect (3), if it exists, depend on concentration?

(5) How does the hydrocarbon chain-length of the surface-active agent (and therefore its solubility) alter effect (3)?

(6) Does a soluble surface-active agent exhibit an optimum damping concentration?

(7) Does this optimum concentration vary with frequency?

(8) How does the damping, for soluble and insoluble films, compare with the theoretical treatments of Levich and Dorrestein?

Questions (1), (3), (4), (5), (7) and (8) have not been answered previously. To study these effects satisfactorily, it was necessary to work with higher frequency waves than have been used by previous investigators: by improvement of the technique we were able to measure damping in waves of frequencies up to 920 c/s.

THEORETICAL

Kelvin (1871) and Lamb (1932) derived an equation for the velocity V of propagation of a wave on a deep fluid (depth $\gg \frac{1}{2}\lambda$) of constant surface tension γ

$$V^2 = (f\lambda)^2 = \frac{g}{k} + \frac{\gamma k}{\rho},\tag{1}$$

where f is the frequency of the waves (in cycles per second), g is the gravitational acceleration, ρ is the liquid density and $k = 2\pi/\lambda$. For capillary waves, g/k is negligible compared with $\gamma k/\rho$.

The damping coefficient, Δ , is defined by

$$a = a_0 e^{-\Delta x},\tag{2}$$

where a is the amplitude of a wave at a distance x along the surface from the source. In theoretical treatments, the damping is expressed as a modulus of decay τ , i.e. the amplitude decreases with time (t) according to

$$a = a_0 e^{-l/\tau}.$$
(3)

It can be shown that Δ and τ are related by $\Delta = 1/\tau U$, U being the group velocity of the waves, given by $U = V - \lambda (dV/d\lambda). \tag{4}$

If $\lambda < 0.3$ cm, one can deduce that $U \approx 1.5 V$.

For a clean (fully mobile) surface $C_s^{-1} = 0$, and there are therefore no surfacetension gradients; the wave damping at this surface arises from the velocity gradients in the subjacent bulk liquid. According to Lamb (1932), τ_m given by

$$\tau_m = 1/2\nu k^2 = \lambda^2/8\nu\pi^2 \tag{5}$$

and hence

whence

$$\Delta_m = 8\nu \pi^2 / \lambda^2 U. \tag{6}$$

Here ν is the kinematic viscosity of the bulk liquid, and subscript *m* indicates that the interface is fully mobile.

For a surface which is immobilized by a surface film; i.e. having no horizontal velocity components, Lamb obtained

$$\tau_{\rm imm.} = (8/\nu k^2)^{\frac{1}{2}} \tag{7}$$

$$\Delta_{\rm imm.} = \frac{1}{U} \left(\frac{\nu \sigma k^2}{8} \right)^{\frac{1}{2}}.$$
(8)

Here the subscript indicates that the surface is immobilized, and σ is given by

$$\sigma^2 = gk + \gamma k^3 / \rho.$$

Levich (1941) obtained for an *insoluble* film a general equation for τ in terms of C_s^{-1} , ν , k and γ . His equation has two limits: (i) when $C_s^{-1}/\gamma \to 0$, i.e. the surface is clean, the result is identical with equations (5) and (6); and (ii) when $C_s^{-1}/\gamma \to 1$ the film should become rather rigid, and the result is identical with equations (7) and (8). For *soluble* films Levich allowed for diffusion; his analysis predicts that the order of magnitude of Δ is the same as for an *insoluble immobile* film, though somewhat lowered; but that when $c \to \infty$ the damping is the same as that given by a *pure* liquid of the same (low) surface tension, i.e. $\Delta \to \Delta_m$ (equation (6)).

Dorrestein (1951) extended Lamb's treatment of insoluble films and obtained an expression for the damping as a function of C_s^{-1} and surface viscosity (his analysis uses η_d but he identifies this with η_s). He obtained a modulus ϵ given by

$$\epsilon = \frac{2 \mathrm{i}\theta + \frac{1}{2}\chi}{1 - \chi(1 + \mathrm{i})(2\theta)^{-\frac{1}{2}}},$$

$$\theta = \nu k^2 / \sigma$$
(9)

where and

$$\chi \gamma = C_s^{-1} + 2\pi i \eta_d \rho f.$$

The latter equation is a simplified form applying to capillary waves only.

The imaginary part ϵ' of ϵ determines the degree of damping according to

$$\Delta = 2\pi f \epsilon' / U. \tag{10}$$

The two extreme limits are: (i) when $\chi \to 0$ ($C_s^{-1} = 0 = \eta_d$) the surface is clean, and equation (10) is identical with equation (6); and (ii) when χ is large (C_s^{-1} or η_d or both are very large), the surface becomes immobile and equation (10) becomes identical with equation (8).

The remarkable prediction of equation (10), however, is that for an intermediate value of C_s^{-1} of about 6.4 dyn/cm, Δ should pass through a maximum, at which point it should (if η_d is negligible) be approximately twice as great as for a fully immobile surface, i.e. about $2\Delta_{\text{imm.}}$. This effect is evidently due to an appreciable tendency to reverse flow when the film, compressible and mobile, is disturbed. From Dorrestein's theory one may calculate that the maximum in Δ as a function of C_s^{-1} (i.e. of the surface pressure of a spread, insoluble film, or of the concentration of soluble surface-active substances) should be almost independent of frequency within the range studied in this paper. If η_d is not negligible, the theory predicts that the maximum value of Δ is lowered, till in the limit of the contribution of η_d to the parameter χ greatly exceeding the contribution of C_s^{-1} , Δ should increase from Δ_m to $\Delta_{\text{imm.}}$ without passing through any maximum.

MATERIALS

All water used in the experiments was distilled from tap water containing alkaline potassium permanganate. Sodium lauryl sulphate was supplied by the Atlas Powder Company. The octyl, decyl and tetradecyl derivatives were kindly supplied in very pure form by Dr F. H. Taylor. Sodium octadecyl sulphate was spread from a solution in an *iso*propanol-ethanol mixture. Dodecafluoroheptylphosphate ammonium salt (Du Pont Co.) was spread from a solution in *iso*propanol-ethanol mixture. Crystallized bovine plasma albumin was spread from solution in aqueous *iso*propanol, containing $0.45 \,\mathrm{M}$ sodium acetate.

EXPERIMENTAL

Brown (1936) showed that if F is the focal length of the cylindrical mirror formed by a wave trough, a plot of $\ln F$ against x should be linear with slope Δ . If F is measured at two values of x, then

$$\Delta = \frac{2 \cdot 303 \log_{10} \left(F_1 / F_2 \right)}{(x_1 - x_2)}.$$
(11)

Note that in calculating Δ , x need not be the absolute distance from the wave source; it is sufficient to measure F at known *increments* of x.

The apparatus is a refined version of the systems used by Dorsey (1897), Watson (1901) and Brown (1936).

The liquid and the surface being studied were contained in a long silica tank. Waves were generated on the surface by a glass dipper moving horizontally, attached to an electromagnetic vibrator; the latter was driven by a power audiooscillator monitored for frequency drift on a cathode-ray oscilloscope.

The novel feature of our apparatus was the use of a cathode-ray projection tube, which provided a spot source of light of high intensity, for viewing the waves stroboscopically. The oscillator caused the spot of light to scan vertically at the same frequency as the vibrator (and as the waves). The spot of light scanned past a horizontal slit, and a cylindrical lens was placed so as to give a parallel slit beam of light. With this device, we were able to work at frequencies up to 920 c/s compared with the upper limit of 250 c/s achieved by previous workers.

The optical assembly consisted of a long-focus microscope which could be moved horizontally and vertically and carried Vernier scales for both directions. A piece of glass acting as a 'two-way' mirror was mounted on the microscope carriage immediately beneath the objective lens. The microscope could be moved (independently of the two-way mirror) in the vertical direction, but both travelled together in the horizontal direction.

The beam of light was deflected vertically on to the liquid surface; subsequent reflexion of the light by a trough of a wave produced a slit image at a distance above the liquid surface equal to the focal length (F) of the cylindrical mirror constituted by the trough. Thus a series of stationary images was formed above the surface of the liquid.

The experiments were performed in a draught-free darkroom at room temperature (20 to 25 °C). Before a run, the tank and dipper were cleaned with hot chromic acid followed by washings with syrupy phosphoric acid, hot tap water and distilled water.

In the experiments on clean water, the surface was cleaned prior to the observations by spreading ignited talc on the surface and then sucking off the talc and any contamination through a fine capillary. The cleaning was repeated between observations. In the experiments with adsorbed films, the surface was initially sucked at random points and then allowed to attain equilibrium for 5 to 10 min. When an insoluble film was to be studied, the aqueous substrate was cleaned before the spreading of the film. Spreading was accomplished by means of an Agla micrometer syringe (Davies & Rideal 1961). During these experiments the surface tension was continually monitored with a du Nouy tensiometer employing a roughened mica plate. Surface viscosities were measured on the instrument of Davies & Mayers (1960).

RESULTS

Clean water

The observed values of Δ as a function of frequency are recorded in figure 1. Results refer to runs during which the surface was maintained scrupulously clean by careful cleaning between consecutive measurements of F. Failure to do this, particularly at the lower frequencies, could produce values of Δ very much higher than those for a completely clean surface.



FIGURE 1. Observed damping coefficients for clean water surfaces. Points are experimental; the line represents Δ_m calculated for $\gamma = 73$ dyn/cm.

Adsorbed (soluble) films

The observed variation of Δ with frequency is shown in figures 2 to 5, referring to sodium octyl sulphate, sodium decyl sulphate, sodium lauryl sulphate and sodium tetradecyl sulphate, all in the absence of added salt. The frequencies (f_r) at the inflexions in the curves are summarized in table 1, and compared with theory (see



FIGURE 2. Observed damping coefficients for water containing 10^{-3} M C₈H₁₇SO₄⁻. Points (with broken line drawn through them) are experimental; full lines represent equations (6) and (8).

below) in table 1 and in figure 6. Surface tension measurements were not made during the runs, but on separate occasions, using a sample of each stock solution. An exception to this was provided by 10^{-2} M sodium lauryl sulphate, for which γ



FIGURE 3. As for figure 2, but for $9 \times 10^{-4} \text{ M C}_{10} \text{H}_{21} \text{SO}_{4}^{\sim}$.



FIGURE 4. As for figure 2, but for $5 \times 10^{-5} \text{ M C}_{12} \text{H}_{25} \text{SO}_{4}^{-}$.

was also measured during a run at frequencies between 5 and 1000 c/s; it was found that the surface tension was identical with that for an undisturbed surface. When the solubility (and rate of desorption) of the adsorbed film of lauryl sulphate ions was drastically reduced by added salt, the damping curves (e.g. that of figure 7) showed no evidence of a relaxation effect.



FIGURE 5. As for figure 2, but for $5 \times 10^{-5} \mathrm{M C_{14} H_{29} SO_4^-}$.

TABLE 1

		t_r	calculated	observed
	n_e	calculated	f_{r}	relaxation
solution of	(long-chain	by (A 4)	$(=1/2t_r)$	$frequency, f_r$
long-chain sulphate	$ions/cm^2)$	(ms)	(s ⁻¹)	(c/s)
10 ⁻³ м С ₈	$8.6 imes 10^{12}$	$1 \cdot 2$	420	450
$9 \times 10^{-4} \mathrm{M \ C_{10}}$	$1.6 imes10^{13}$	2.5	200	250 (approx.)
$5 \times 10^{-5} \text{ M C}_{12}$	$4{\cdot}6 imes10^{12}$	13.8	36	80
10^{-4} M C_{12}	$7{\cdot}1 imes10^{12}$	11.5	44	80 (approx.)
$3 \times 10^{-4} \mathrm{m} \mathrm{C_{12}^{-1}}$	$1.5 imes10^{13}$	7.8	64	90
$5 \times 10^{-5} \mathrm{m \ C_{14}}$	$9 \cdot 1 \times 10^{12}$	26.7	19	25

Relaxation effect for films adsorbed from pure water. The energy of adsorption, w, is taken as 600 cal/mole — CH_2 — group throughout, in the calculation of t_r .



FIGURE 6. Comparison of relaxation frequencies f_r (crosses) obtained from the inflexions of curves such as those of figures 2 to 5, with theory (equations (A 3) and (A 4) shown by full line, for alkyl sulphates of different chain lengths (see table 1).



FIGURE 7. Damping curve for $5 \times 10^{-5} \text{ M C}_{12} \text{H}_{25} \text{SO}_{4}^{-}$, dissolved in 0.145 M NaCl. Points (with the broken line drawn through them) are experimental, solid lines represent equations (6) and (8). Note that these results show no evidence of an inflexion due to relaxation, in contrast to figure 4.

Spread (insoluble) films

Damping by a monolayer of sodium octadecyl sulphate spread on water at constant Π was studied at different frequencies to compare with the results for soluble films. The result is shown in figure 8.



FIGURE 8. Points (and broken line through them) represent damping by an (insoluble) monolayer of $C_{18}H_{37}SO_4^-$, spread on water at $\Pi = 23$ dyn/cm. The full line represents equation (8).

The purpose of the work on insoluble films, however, was to measure Δ as a function of Π . The surface-active agents used possessed different properties, characterized by C_s^{-1} and η_s , and the effect of these parameters at a particular value of Π was studied.

All measurements of Δ at the different film pressures were obtained at 150 c/s. This frequency was chosen because it is sufficiently high for the waves to be considered as purely capillary, while not being so high as to cause very pronounced damping, with the accompanying experimental difficulties. Results are shown in figures 9 to 11. In these experiments, Π was measured during each run.



FIGURE 9. Damping of film of $C_{18}H_{37}SO_4^-$ spread on 0.1 M NaCl. Points and broken line are experimental at 150 c/s, while full lines represent equations (8) and (10), for $\eta_d = 0$ throughout.

Separate measurements were made to determine the force-area variation, from which C_s^{-1} was obtained. The surface viscosity was measured as a function of surface pressure, the latter being measured on the tensiometer during the experiment. The films of octadecyl sulphate and of the fluoro derivative showed no measurable surface viscosity even at maximum surface pressure. The films of protein spread on 0.01 N HCl showed surface shear viscosities increasing steadily from 10^{-4} surface poise at $\Pi = 2 \text{ dyn/cm}$, to 1 surface poise at 7 dyn/cm.

Measurement of wavelength

During each run the wavelength λ was measured as well as Δ . While the experimental error in measuring the horizontal distance between the points of observation of F has a negligible effect on the value of Δ , such errors could affect the third decimal place in the value of λ .



FIGURE 10. As for figure 9, but for dode cafluoroheptyl phosphate spread on 0.1 N NaCl, measured at 150 c/s.



FIGURE 11. As for figure 9, but for plasma albumin spread on 0.01 N HCl, measured at 150 c/s.

DISCUSSION

For clean water the results are in accord with the theoretical equations (1) and (6). The surface tension, calculated from the observed wavelengths over the frequency range 50 to 920 c/s, was $72 \cdot 7 \pm 1$ dyn/cm. The measured damping coefficients were in agreement with Δ_m to within 3% over the same frequency range (see figure 1). However, the effect of extremely slight traces of contamination was very marked, leading to anomalously high damping coefficients. We suspect that the work of Brown (1936) and of Vines (1961) was in error because of trace contamination; Goodrich (1961) obtained good agreement with theory up to 250 c/s, for carefully cleaned surfaces.

When a monolayer of octyl sulphate ions is adsorbed from 10^{-3} M sodium octyl sulphate solution, the damping is much greater than for pure water, as may be seen from figures 1 and 2. At the higher frequencies (e.g. 600 to 800 c/s) the observed damping coefficient is, as predicted from the Dorrestein theory of damping by insoluble films, rather greater than Δ_{imm} . As the frequency is reduced, however, one observes that the measured Δ decreases rather more steeply below 450 c/s. Other films show this effect at other frequencies (table 1), and we deduce that in the lower frequency range appreciable desorption and adsorption is occurring during the passage of each wave, 'short-circuiting' the surface pressure gradients and causing Δ to be less than otherwise. The observed inflexion frequencies are in fair agreement with our calculations (see Appendix), as shown in table 1 and figure 6. At frequencies higher than 450 c/s, the film behaves as if it were quite insoluble.

Decyl sulphate ions, adsorbing from 9×10^{-4} M solution, show similar effects. The inflexion point, as the frequency is decreased, is at about 250 c/s, indicating partial solubility of the film at lower frequencies (figure 3). This lower frequency (compared with that for the octyl compound) is compared with theory in table 1 and figure 6. The surface tension calculated from the measured wavelengths is higher at the low frequencies, values above and below the inflexion point being respectively 58 and 64 dyn/cm. For an equilibrium adsorbed film, the tension measured by the du Nouy tensiometer was $62 \cdot 7 \text{ dyn/cm}$.

Lauryl sulphate, adsorbed from 3×10^{-4} M solution (figure 4), shows an inflexion point just below 90 c/s, again consistent with the desorption hypothesis (table 1 and figure 6). The surface tensions, as calculated from λ above and below the inflexion point, were 41 and 43 dyn/cm respectively. The tensiometer gave 41 dyn/cm. For lauryl sulphate ions adsorbed from 5×10^{-5} M solution in 0.145 M NaCl, γ was calculated to be 42 dyn/cm, equal to the tension measured directly. For the tetradecyl compound, adsorbed from 5×10^{-5} M solution, the inflexion frequency is 25 c/s (cf. figures 5 and 6 and table 1). Mean values of γ calculated from λ above and below this frequency were 56 and 59 dyn/cm respectively, compared with the tensiometer reading of 67 dyn/cm.

Application of the Kelvin equation (1) to the insoluble films of octadecyl sulphate on water gave a value of γ (calculated from λ) of 52.3 dyn/cm, compared with 51.7 from direct measurement. For the same films spread on 0.10 N NaCl at various surface concentrations, the values of γ calculated from equation (1) agreed within $\pm 2 \text{ dyn/cm}$ with those measured directly. For the fluoro derivative spread on 0.1 N NaCl, results agreed within $\pm 5 \text{ dyn/cm}$, the deviations being in both directions. For films of the protein, γ as calculated from λ was generally 2 to 4 dyn/cm less than γ measured directly during the same experiment.

We conclude that the Kelvin equation, accurate to within 1.5% on clean water, is approximately valid for film-covered surfaces even though γ now varies between the troughs and crests. However, because of experimental difficulties, measurement of the wavelength on film-covered surfaces is not a good method of determining γ for these systems. Further, even for insoluble films, the Kelvin equation can give a mean value of γ several dynes per centimetre too low, particularly if the surface viscosity of the film is high.

The relaxation effect depends somewhat on the concentration of sodium lauryl sulphate (table 1). This is predicted by theory: equation (A 4) below shows that t_r must depend on the equilibrium concentration n_e , and since K depends on the interchain cohesion w in the monolayer (equation (A 1)), the greater cohesion at high surface concentrations ($n_e \approx 10^{14}$ molecules cm⁻²) also influences t_r .

The results for lauryl sulphate in table 1 are in the general direction required by theory. The effect of added salt (figure 7) is to reduce the solubility of the film to such an extent that it cannot desorb appreciably during the passage of the wave at the frequencies in the experimental range. The calculated inflexion frequency is of the order of 1 s^{-1} (Davies & Rideal 1961), which is too low to be measured by our apparatus.

Studies by Davies & Wilcockson (1965) show that with adsorbed films of very highly purified lauryl sulphate ions, Δ passes through a maximum at a concentration of 1.5×10^{-4} M (figure 12). The maximum was also found by Davies & Bradley (1960), quoted by Davies & Rideal (1961), and by Tailby & Portalski (1961). The maximum persists at frequencies below the inflexion frequency of 80 c/s. A comparison of the experimental results with classical hydrodynamic theory, in the two limits of fully mobile surfaces (equation (6)) and fully immobile surfaces (equation (8)) is made in figures 1 to 5, 7, 8 and 12. Whereas agreement is excellent for the clean, mobile surfaces, the damping coefficients for soluble films, like those for the insoluble films, are often considerably greater than Δ_{imm} , though the divergence is less at high film pressures. For example, for the lauryl compound at 1.5×10^{-4} M at 50 c/s, Δ/Δ_{imm} . is found from figure 12 to be 1.9. At 150 c/s at this concentration $\Delta/\Delta_{imm} = 1.8$, but at a concentration of 3×10^{-4} M the ratio has fallen to 1.3. The maximum in the measured Δ (see figure 13) occurs when Π ($\approx C_s^{-1}$ for this system) is 5.2 dyn/cm. This figure and the maximum ratios of 1.8 and 1.9, independent of frequency, are in reasonable agreement with Dorrestein's prediction of a ratio of about 2 when $C_s^{-1} = 6.4 \, \text{dyn/cm} \, (\eta_d \text{ being set equal to zero}).$

The theoretical curve (equation (10)) can be brought closer to the experimental line in figure 13 if, when $\Pi > 4$, one substitutes $\eta_d = 10^{-3}$ surface poise, a figure typical of the measured η_s in this system.

With sodium lauryl sulphate containing a trace of lauryl alcohol, the maximum in the ratio $\Delta/\Delta_{\text{imm.}}$ is only 1.3 at 150 c/s, indicating, according to equation (10) that

the surface dilational viscosity is very important, of the order of 10^{-2} surface poise, as is indeed measured (as η_s) in these systems. Again, the position of the maximum is independent of frequency.

Levich's theoretical prediction that slight solubility of the film will reduce Δ below Δ_{imm} is not borne out by our experiments, nor is his prediction that when c is large, Δ should tend to Δ_m (see figure 12).



FIGURE 12. Results of Davies & Wilcockson (1965) for highly purified sodium lauryl sulphate solutions at 150 c/s (\bigcirc), and at 50 c/s (\times). Broken lines are drawn through the experimental points, and full lines refer to the damping predicted by equations (6) and (8).



FIGURE 13. Results shown in figure 12 for highly purified sodium lauryl sulphate are compared with the predictions from the Dorrestein theory (equation (10)), taking $\eta_d = 0$.

For spread, insoluble films on water, the observed damping coefficients are compared with Dorrestein's theory (equations (9) and (10)) in figures 9 to 11. The surface shear viscosity has been used in these calculations, and the results are plotted against Π rather than C_s^{-1} . The latter quantities are interrelated by the force-area curves. The variation of the measured Δ with Π (figure 9) for octadecyl sulphate also shows remarkable agreement with the Dorrestein equation assuming that $\eta_d = 0$; the maximum in Δ occurs at $\Pi = 3 \text{ dyn/cm}$ (when $C_s^{-1} \approx 7.5 \text{ dyn/cm}$) and is almost double $\Delta_{\text{imm.}}$. The results for the fluoro salt (figure 10) show even closer agreement with the theory, presumably because the assumption that $\eta_d = 0$ is most closely justified for fluoro derivatives. However, the measured values are somewhat below the theoretical at $\Pi > 13 \text{ dyn/cm}$. The maximum, which occurs at $\Pi = 3.5 \text{ dyn/cm}$ ($C_s^{-1} = 5.8 \text{ dyn/cm}$), is slightly greater than $2\Delta_{\text{imm.}}$.

The damping coefficients for the protein film are compared in figure 11 with those predicted by equations (9) and (10) of the Dorrestein theory, substituting in turn $\eta_d = 0$ and $\eta_d = \eta_s$ (as measured). In view of the evident over-correction by including the surface shear viscosity at higher pressures (figure 11), we believe that η_d for a protein film may well be less than η_s : shear may involve untangling the large molecules, thus causing more resistance to shearing motion than to dilation. Indeed, assuming that $\eta_d = 6 \times 10^{-3}$ surface poise when $\Pi > 6 \text{ dyn/cm}$, one may calculate from equation (10) that $\Delta = 0.600 \text{ cm}^{-1}$ at $\Pi = 7$, and that $\Delta = 0.567 \text{ cm}^{-1}$ at $\Pi = 13$; these theoretical figures then agree with the experimental results. If further work substantiates our explanation, we have here a method of obtaining η_d from measurements of Δ and C_s^{-1} .

Appendix. Calculation of 'relaxation frequency' for soluble surface-active agents

For long-chain ions, Davies & Rideal (1961, p. 183) obtain the following equation for the net rate of adsorption at 20 °C:

$$\left(\frac{\mathrm{d}n}{\mathrm{d}t}\right)_{\mathrm{net}} = \frac{134^2 \times 4B_2}{10^{32}c} (n_e^3 - n^3) \exp\left\{\frac{-wm}{RT}\right\} = K(n_e^3 - n^3) \tag{A 1}$$

where

 $n_e = \text{equilibrium surface concentration (in molecules/cm²)},$

n =surface concentration at any time t,

c =bulk concentration of uni-univalent ions (in moles/l.),

 $B_2 = \text{constant}$ depending on the hydrodynamics of the diffusion process,

 $w = \text{desorption energy of each } ---CH_2$ in calories per mole group,

 $m = \text{number of } ---CH_2$ groups involved in adsorption,

R = gas constant,

T = absolute temperature,

and K (a function of m) is an abbreviation defined by the equation.

Equation (A1) is derived for a steady state condition when a thin stagnant layer separates the surface film (of surface potential > 100 mV) from the stirred bulk.

One can calculate n_e to a good approximation (Davies & Rideal 1961, p. 190) at 20 °C by

$$n_e = 5.51 \times 10^{13} c^{\frac{2}{3}} \exp\left\{\frac{wm}{3RT}\right\},$$
 (A 2)

which is valid in the absence of added salt, provided that the surface potential exceeds $100 \,\mathrm{mV}$ and that $n_e/n < 0.3$.

The time required for the equilibrium surface concentration to be partially restored, following a small change in the surface concentration away from n_e , can be calculated from these equations. If this time, t_r , is comparable with the time taken for the wave motion to change the surface concentration from its maximum value (at a crest) to its minimum (at a trough), there will be 'short-circuiting' of the surface compressional stresses of the film, twice in the passage of each wave. The wave frequency f_r , below which this relaxation effect will occur is therefore given by

$$t_r = 0.5/f_r.\tag{A 3}$$

One calculates t_r by integrating equation (A 1) between the appropriate limits: for a 10 % change from n_e , $n = 0.9n_e$, and when this initial change has been 60 % restored, $n = 0.96n_e$. The time taken for this degree of restoration is given by

$$t_r = 0.335/Kn_e^2,\tag{A 4}$$

where K is the exponential function of chainlength defined in equation (A1). Results are summarized in table 1.

For a smaller initial change than 10%, the time for recovery changes only slightly. Thus for a 0.001 % change, the integration limits are $n = 0.999996n_e$ and $n = 0.99999n_e$; the 60% recovery time is then $0.305/Kn_e^2$.

All results have been calculated for a temperature of 20 °C; but a change of 10 degC has only a small effect on t_r . That a 60 % recovery has been chosen as being significant in the 'short-circuiting' relaxation effect is reasonable but arbitrary. The time for 70 % recovery, for a very small change in n, is calculated to be $0.40/Kn_e^2$.

References

Aiken, J. 1883 Proc. Roy. Soc. Edinb. 12, 56.

Brown, R. C. 1936 Proc. Phys. Soc., Lond. 48, 312, 323.

- Davidson, J. F., Cullen, E. J., Hanson, D. & Roberts, D. 1959 Trans. Instn. Chem. Engrs, 37, 121.
- Davies, J. T. 1962 Chem. Ind. (Rev.), p. 906.

Davies, J. T. & Bradley, P. J. 1960 Quoted by Davies & Rideal (1961) and by Davies (1962)

Davies, J. T. & Mayers, G. R. A. 1960 Trans. Faraday Soc. 56, 690.

Davies, J. T. & Rideal, E. K. 1961; 2nd ed. 1963 Interfacial phenomena. London. Academic Press.

Davies, J. T. & Wilcockson, R. B. 1965 Birmingham Univ. Chem. Engr., 16, 29.

Dorrestein, R. 1951 Proc. Acad. Sci. Amst. B, 54, 260, 350.

Dorsey, N. E. 1897 Phys. Rev. 5, 170, 213.

Downing, A. L. & Truesdale, G. A. 1955 J. Appl. Chem. 5, 570.

Emmert, E. E. & Pigford, R. L. 1954 Chem. Engng Progr. 50, 87.

Franklin, B. 1774 Phil. Trans. 64, 445.

Goodrich, F. C. 1961 Proc. Roy. Soc. A, 260, 481, 490, 503.

Goodrich, F. C. 1962 J. Phys. Chem. 66, 1858.

Grimley, S. S. 1945 Trans. Instn Chem. Engrs, 37, 228.

Kafesjian, R., Plank, A. & Gerhard, E. R. 1961 A.I.Ch.E.J. 7, 463.

- Kelvin, Lord 1871 Phil. Mag. (4), 42, 368.
- Lamb, H. 1932 Hydrodynamics (6th ed.). Cambridge University Press.
- Levich, V. G. 1941 Acta Physicochim. U.S.S.R. 14, 307, 321; Physicochimical hydrodynamics. New Jersey: Prentice-Hall Inc. (1962).
- Tailby, S. R. & Portalski, S. 1961 Trans. Instn Chem. Engrs, 39, 328.
- Vines, R. G. 1960 Aust. J. Phys. 13, 43.
- Vivian, J. E. & Peaceman, D. W. 1956 A.I.Ch.E.J. 2, 437.
- Watson, P. R. 1901 Phys. Rev. 12, 257