

The Damping of Waves by Surface-Active Substances. II

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In my preceding paper¹ it has been shown that the spreading of a surface-active substance on the surface of a liquid affects the boundary conditions at the surface and eventually alters the very character of the wave motion of the liquid. In particular, the formation of vortices in the surface layer is intensified, which in a viscous liquid leads to increased energy losses on friction, *i. e.*, to an increase in the coefficient of damping of surface waves. The preceding paper was devoted to the case of an insoluble surface-active substance. The present work is concerned with the damping produced by surface-active substances soluble in the substrate.

It will accordingly be assumed in the sequel that the surface-active substance forms a "surface solution" of high concentration on the surface of the liquid, and a weak volume solution in the bulk of the liquid.

A surface solution is always in a state of statistical equilibrium with the adjacent layer of the volume solution, just as a vapour in the layer adjacent to the liquid surface is always saturated and remains in equilibrium with the liquid.

If waves are generated on the surface of a liquid, the concentration of the adsorbed substance is varied and tangential forces proportional to the concentration gradient arise in the surface film.

In the case of an insoluble substance the total number of molecules present on the surface remains constant and the change produced in the concentration is given by formula (18) of the first

¹ V. Levich, *Acta Physicochimica URSS*, **14**, 307 (1941).

communication, whilst the corresponding tangential stress arising in the film is expressed by equation (25) of the first communication.

However, if the surface-active substance deposited is insoluble in the substrate, the above formulae become inapplicable, since the total number of molecules adsorbed on the surface is no longer constant, but varies as a result of transitions of molecules from the surface into the volume and in the reverse direction. Since a surface solution is in equilibrium with that part of the volume solution which is contiguous to the surface, an extension of the surface will evidently involve a transition of molecules from the volume to the surface, whereas a compression will produce an opposite effect.

If the deformations produced by the waves occur with a period T , then, evidently, two limiting cases are possible:

1. The relaxation time for the equilibrium between the surface and volume solutions (or rather the adjacent part of the latter) is great compared to the period of the wave $\frac{2\pi}{\omega}$;
2. The relaxation time is small compared to $\frac{2\pi}{\omega}$.

In the former case the deformation will proceed so rapidly that the equilibrium between the volume and surface solutions will fail to set in, and the molecules will have no time to pass from the volume to the surface solution and backwards.

Then the presence of the volume solution will not affect the course of the process and all the conclusions of the preceding paper¹ will be valid.

In the second case the volume and surface solutions may be considered to be in a state of permanent statistical equilibrium.

It is this latter case that constitutes the object of our further analysis.

Let us, as before, designate by v_0 the surface concentration on the undeformed surface, and let v' denote the total change of concentration due to the deformation.

Similarly, let c_0 and c' denote, respectively, the concentration of the volume solution and its change due to the diffusion of the substance dissolved in the volume to the surface as a result of deformation of the latter.

Then the condition of equilibrium between the volume and surface

solutions may evidently be represented in the form:

$$\mu_s(v_0 + v') = [\mu_s(c_0 + c')]_{z=0}, \quad (1)$$

where μ_s is the chemical potential of the surface solution and μ_v the chemical potential of the volume solution. The value of the latter is taken near the surface, *i. e.*, when $z \cong 0$.

Inasmuch as the deformations of the surface and, consequently, the concentration changes are infinitesimal, the chemical potentials may be expanded in powers of v' and c' neglecting all terms except those of the first order. Then we shall have:

$$v' = \frac{\left(\frac{\partial \mu_s}{\partial c}\right)_{c=c_0}}{\left(\frac{\partial \mu_v}{\partial v}\right)_{v=v_0}} (c')_{z=0}$$

and, since the volume solution may usually be considered weak,

$$\begin{aligned} \mu_v &= RT \lg c + \psi(p, T), \\ v' &= \frac{RT}{c_0} \frac{1}{\left(\frac{\partial \mu_v}{\partial v}\right)_{v=v_0}} (c')_{z=0}, \end{aligned} \quad (2)$$

where the value of c' is taken near the surface, *i. e.*, when $z = 0$.

The change in the surface concentration is due to two factors: deformation of the surface and diffusion flow from the volume which tends to reduce the effect of the former factor.

The equation of continuity for v' , to within the infinitesimal terms of the first order, may therefore be written as follows:

$$\frac{\partial v'}{\partial t} = -v_0 \frac{\partial v_x}{\partial x} - a^2 \left(\frac{\partial c'}{\partial z}\right)_{z=0}. \quad (3)$$

The second term in eq. (3) is the diffusion flux from the volume; a^2 is the diffusion coefficient. In the first term account is only taken of the concentration change due to but horizontal displacements

$$\left(v_x = \frac{\partial \xi}{\partial t}\right).$$

In the absence of diffusion, eq. (3) is identical with eq. (18) of the first communication¹.

To determine the diffusion flux from the volume solution it is necessary to solve the diffusion equation with respect to c' , taking into account boundary conditions (2) and (3).

However, inasmuch as the boundary conditions contain terms determined by the equations of motion of the liquid, the diffusion equation with boundary conditions (2) and (3), and the equations of motion of the liquid with the corresponding boundary conditions should be solved simultaneously.

The latter are as follows:

$$(p_{xx})_{x=0} = \sigma \frac{\partial^2 \zeta}{\partial x^2},$$

$$(p_{xz})_{x=0} = -\frac{\epsilon_0}{\nu_0} \left(\frac{\partial \psi'}{\partial x} \right).$$

The former equation is identical with eq. (27) of the first communication. The latter, though also identical in form with eq. (28) of the first communication, involves in the present case a different value of $\frac{\partial \psi'}{\partial x}$.

Substituting (2) in eq. (3), we ultimately obtain

$$\frac{\partial c'}{\partial t} = a^2 \left(\frac{\partial^2 c'}{\partial x^2} + \frac{\partial^2 c'}{\partial z^2} \right), \quad (4)$$

$$\frac{RT}{c_0} \frac{1}{\left(\frac{\partial \mu_s}{\partial \nu} \right)_{\nu=\nu_0}} \cdot \left(\frac{\partial c'}{\partial t} \right)_{x=0} = -\nu_0 \frac{\partial v_z}{\partial x} - a^2 \left(\frac{\partial c'}{\partial z} \right)_{x=0}, \quad (5)$$

$$\frac{\partial \vec{v}}{\partial t} = -\frac{1}{\rho} \nabla p + \eta \Delta \vec{v}, \quad (6)$$

$$(p_{xx})_{x=0} = \sigma \frac{\partial^2 \zeta}{\partial x^2}, \quad (7)$$

$$(p_{xz})_{x=0} = -\frac{\epsilon_0}{\nu_0} \left(\frac{\partial \psi'}{\partial x} \right). \quad (8)$$

The solution of eq. (6) has the following form:

$$v_z = \frac{\partial \xi}{\partial x} = -(ikAe^{ks} - lCe^{ls}) e^{ikz + \omega t}, \quad (9)$$

$$v_x = \frac{\partial \xi}{\partial z} = -(kAe^{ks} - ikCe^{ls}) e^{ikz + \omega t}, \quad (9')$$

$$l = \sqrt{k^2 + \frac{\omega}{\eta}}.$$

The solution of eq. (4) satisfying boundary condition (5) is therefore sought in the form:

$$c' = Bf(x) e^{ikz + \omega t}.$$

Substituting this in eq. (4), we obtain

$$c' = B e^{\frac{\sqrt{\alpha + a^2 k^2}}{a} x} e^{ikz + \alpha t}, \quad (10)$$

The amplitude, B , of the diffusion waves may be determined by eq. (5) after substituting c' from eq. (10) and v_x from eq. (9).

Then we have

$$B = \frac{v_0 ik (ikA + iC)}{\frac{RT\alpha}{c_0 \left(\frac{\partial \mu_s}{\partial v} \right)_{v=v_0}} + a \sqrt{\alpha + a^2 k^2}}$$

so that

$$c' = \frac{v_0 ik (ikA + iC)}{\frac{RT\alpha}{c_0 \left(\frac{\partial \mu_s}{\partial v} \right)_{v=v_0}} + a \sqrt{\alpha + a^2 k^2}} e^{\frac{\sqrt{\alpha + a^2 k^2}}{a} x} e^{ikz + \alpha t} \quad (10')$$

whence

$$\begin{aligned} \chi &= \frac{RT}{c_0 \left(\frac{\partial \mu_s}{\partial v} \right)_{v=v_0}} (c')_{x=0} = \frac{v_0 ik (ikA + iC) \alpha^{-1}}{1 + \frac{ac_0}{\alpha RT} \left(\frac{\partial \mu_s}{\partial v} \right)_{v=v_0} \sqrt{\alpha + a^2 k^2}} \times \\ &\times e^{ikz + \alpha t} = - \frac{v_0}{1 + \frac{ac_0}{\alpha RT} \left(\frac{\partial \mu_s}{\partial v} \right)_{v=v_0} \sqrt{\alpha + a^2 k^2}} \times \frac{\partial^2 \xi}{\partial x^2}, \end{aligned} \quad (11)$$

where ξ is the horizontal displacement on the surface.

Boundary condition (8) may therefore be written in the form:

$$(p_{xx})_{x=0} = \frac{\epsilon_0}{1 + \frac{ac_0}{\alpha RT} \left(\frac{\partial \mu_s}{\partial v} \right)_{v=v_0} \sqrt{\alpha + a^2 k^2}} \frac{\partial^2 \xi}{\partial x^2}. \quad (12)$$

From eq. (12) it may be seen that in the case of a soluble substance the rôle of the elasticity constant is played by a quantity which depends not only on the elastic properties of the film, but also on the diffusion coefficient, volume concentration and frequency.

It will be readily seen that with a decrease in the volume concentration, *i. e.*, with $c_0 \rightarrow \infty$, this effective elasticity constant tends to ϵ_0 . On the contrary, with increase of c_0 , the effective elasticity constant decreases.

In the limit, as c_0 tends to infinity, the elasticity constant becomes zero. It stands to reason that eq. (12), which has been obtained

in terms of the chemical potential of a weak solution, is only valid at concentrations sufficiently remote from high ones. And yet this expression conveys the general trend of the elasticity constant.

Putting $\alpha = i\omega + \beta$ and substituting (9) and (9') in boundary conditions (7) and (12), we obtain equations from which β can be determined. We shall confine ourselves to the most interesting case — that of capillary waves — and put $\frac{\gamma k^2}{\omega} \ll 1$ as before.

Further, it may always be considered that $\frac{a^2 k^2}{\omega} \ll 1$.

We shall limit ourselves to the case where

$$\frac{ac_0}{RT\sqrt{\omega}} \left(\frac{\partial \mu_s}{\partial v} \right)_{v=v_0} \gg 1.$$

It may indeed be readily seen that when

$$\frac{ac_0}{RT\sqrt{\omega}} \left(\frac{\partial \mu_s}{\partial v} \right)_{v=v_0} \ll 1$$

this term may be dropped and we return to the case of an insoluble substance.

If

$$\frac{ac_0}{RT\sqrt{\omega}} \left(\frac{\partial \mu_s}{\partial v} \right)_{v=v_0} \sim 1$$

simple computations show that this also leads to the former expression for the damping coefficient [eq. (37) of the first communication¹]. If

$$\frac{ac_0}{RT\sqrt{\omega}} \left(\frac{\partial \mu_s}{\partial v} \right)_{v=v_0} \gg 1,$$

then, after neglecting the corresponding terms, we find from (7) and (12):

$$\left[i \frac{2\eta k^2}{\omega} + \frac{\epsilon k^2}{\omega^2} \times \frac{RT}{c_0 \left(\frac{\partial \mu_s}{\partial v} \right)_{v=v_0}} \frac{\sqrt{i\omega}}{a} \right] A -$$

$$- i \left[-1 + \frac{\epsilon k^3}{\omega^3} \times \sqrt{\frac{i\omega}{\gamma k^2}} \times \frac{RT}{c_0 \left(\frac{\partial \mu_s}{\partial v} \right)_{v=v_0}} \times \frac{\sqrt{i\omega}}{a} \right] C = 0, \quad (13)$$

$$\left[2 \frac{\beta}{\omega} + \frac{2\eta k^2}{\omega} \right] A - C = 0. \quad (14)$$

From eqs. (13) and (14) it may be seen that there exist two regions: I

$$\frac{RT}{c_0 \left(\frac{\partial \mu_s}{\partial v} \right)_{v=v_0}} \times \frac{\sqrt{\omega}}{a} \sim \sqrt{\frac{\eta k^2}{\omega}}$$

or

$$k^{1/2} \sim \frac{\eta^{1/2} a c_0 \left(\frac{\partial \mu_s}{\partial v} \right)_{v=v_0}}{\sigma^{1/2} RT} \quad (15)$$

and II

$$\frac{RT}{c_0 \left(\frac{\partial \mu_s}{\partial v} \right)_{v=v_0}} \times \frac{\sqrt{\omega}}{a} \sim \frac{\eta k^2}{\omega}$$

or

$$k^{1/4} \sim \frac{\eta a c_0 \left(\frac{\partial \mu_s}{\partial v} \right)_{v=v_0}}{\sigma^{1/4} RT} \quad (16)$$

Neglecting the corresponding terms in eqs. (13) and (14) we obtain the following expressions for the damping coefficient:

For the first region,

$$\beta_1 = -\frac{1}{2\sqrt{2}} \frac{\epsilon RT}{a \sigma^{1/2} c_0 \left(\frac{\partial \mu_s}{\partial v} \right)_{v=v_0}} \times \frac{1 + \frac{\epsilon RT k^{1/2}}{a \sigma^{1/2} \eta^{1/2}}}{1 + \frac{\epsilon^2 (RT)^2 k}{a^2 \sigma \eta}} \quad (17)$$

From eqs. (15) and (17) it follows that in region I

$$\beta_1 \sim \eta^{1/2} \sigma^{1/2} k^{7/4}$$

We thus may say that in this region the damping coefficient somewhat reduced as it is owing to the access of molecules from the volume, is nevertheless of the same order of magnitude as in the case of an insoluble film.

In the region intermediate between I and II, *i. e.*, when

$$\sqrt{\frac{\eta k^2}{\omega}} \gg \frac{RT \sqrt{\omega}}{a c_0 \left(\frac{\partial \mu_s}{\partial v} \right)_{v=v_0}} \gg \frac{\eta k^2}{\omega}$$

We have

$$\beta_{1, II} = -\frac{1}{2\sqrt{2}} \frac{\epsilon RT k^{1/4}}{a c_0 \sigma^{1/4} \left(\frac{\partial \mu_s}{\partial v} \right)_{v=v_0}} \quad .$$

Finally, in region II the damping coefficient

$$\beta_{II} = -2\eta k^2,$$

i. e., in the region (II) corresponding to either large wave-lengths or very high volume concentrations, the damping coefficient is the same as in the pure liquid.

The latter result is but natural, since at sufficiently high volume concentrations the solution becomes homogeneous and differs from the pure liquid only in the value of the surface tension.

The results obtained in communication I as well as in the present paper may be directly applied to the case of the electric double layer on the surface of mercury. Bruns, Frumkin and others² have observed the disappearance of the maximum on the current-voltage curve for the mercury electrode due to the damping of capillary waves on the mercury surface. This damping effect is produced by the ions possessing a charge opposite to that of the surface, which are adsorbed from the volume solution on extended surface elements and are desorbed from compressed elements. As is known from the theory of electrocapillary phenomena, the change of the surface tension involved is equivalent to that produced by varying the concentration of a surface-active substance.

The effect just mentioned is therefore identical with the damping effect of a soluble surface-active substance considered in the present paper.

A similar phenomenon of disappearance of the current maximum on the mercury electrode has been observed with insoluble surface active substances deposited on the electrode³.

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² B. Bruns, A. Frumkin *et al.*, *J. Phys. Chem.*, (russ.), **13**, 786 (1939).

³ Rasch, *Bull. Acad. Sci. Bohème*, (1929); Rayman Collection, **3**, 314 (1931); Homanoto Collection, **5**, 427 (1933).