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Abstract

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THE EFFECT OF WAVES AND TIME ON THE ABILITY OF A MONOLAYER TO REDUCE THE EVAPORATION OF WATER

(Presented by Academician A. N. Frumkin, 27 III 1964)

Considerable attention has recently been devoted to questions concerning the effect of monolayers on the evaporation of water. There are studies devoted to the ability of monolayers of long-chain aliphatic substances (alcohols, acids, ethers, etc.) to reduce the evaporation of water from a calm surface^(1,2). Studies on the damping of waves by monolayers of surface-active substances are known. However, the ability of monolayers of long-chain substances to reduce the evaporation of water under wave action has not yet been studied. Meanwhile, this question has both theoretical and practical significance. On the one hand, a wave may disturb the state of the monolayer, the degree of packing of molecules in it and, consequently, the permeability of the monolayer. On the other hand, a wave sets in motion the adjacent layers of liquid and air and thereby could affect diffusion processes in the liquid and gas phases. This factor also had to be checked in connection with the existing view that the effect of waves on evaporation from a clean surface is practically negligible.

We studied the effect of waves on the reduction of water evaporation in the presence of a depressor. Evaporation measurements were first carried out from a clean water surface and then from a surface covered with a monolayer. A paraffin-coated bath, $60 \times 20 \times 2$ cm, filled to the brim with distilled water, was used. The wave was produced by a T-shaped glass wave generator connected to a mechanical-oscillation generator powered by an audio generator. At a distance of 10 cm from the wave generator, above the water surface, there was an absorber with LiCl, used according to the Langmuir–La Mer method^(3,4). The distance from the mesh (nickel in our apparatus) to the water surface was usually 0.1 cm; in calibration experiments on the apparatus, however, it was varied from 0.05 to 2.0 cm by means of a stand with a micrometer screw, which, in addition, made it possible to measure the wave amplitude by the method of touching the surface with a rod. At the same distance (10 cm) a plate on a quartz spiral

Fig. 1

Figure 1: Fig. 1

was placed for measuring the two-dimensional pressure of the monolayer $F^{(5)}$. The temperature of the water and air was measured by means of resistance thermometers and thermometers at various depths. The temperature of the water surface was maintained at all stages of the experiment at $20 \pm 0.5^\circ$. The oscillation frequency ν was usually 20 Hz; in individual experiments, 20-60 Hz. At $\nu = 20$ Hz the wave amplitude under the absorber was 0.04-0.05 cm for a clean surface and 0.01-0.02 cm in the presence of a monolayer.

Monolayers of the depressor, for which pure cetyl alcohol from Schuchardt (m.p. $47.5-48^\circ$) was used, were applied from a solution in hexane (and from powder). The amount of substance applied was regulated by the number of drops over the entire surface. With this method of application, the “compression” curve of the monolayer $F-a$ was very close to the compression curve of a monolayer with a barrier. Measurements of the absorption of water vapor M and of the monolayer pressure F were carried out in two series: a) first on a clean surface for 0.5-1.0 hour, and then, after applying a monolayer at a definite surface concentration, for a long time until reaching

slowly decreasing value $F = 17-20$ dyn/cm; the initial area per molecule in the monolayer in these experiments was varied from $a = 19.7 \text{ \AA}^2$ to $a = 15.5 \text{ \AA}^2$ ($a < 19.7 \text{ \AA}^2$ corresponded to an excess of alcohol compared with a saturated monolayer), b) with the same sequence of the experiment, but under continuous action of the wave.

In Fig. 1, I, curves are shown for the dependence of the magnitude of absorption of water vapor by the absorbent M on time τ , at $a = 19.1 \text{ \AA}^2$ for the experiment without a wave (a) and with a wave (b). The moment of application of the monolayer is marked by an arrow. In Fig. 1, II, curves are shown for the dependences $F(\tau)$ and $r(F)$, where the resistance of the monolayer to evaporation

$$r = A(w - w_0) [(t/m)_f - (t/m)_w]$$

was calculated according to (3, 4). Here m is the increase in weight of the absorbent, having base area A , over time t . The index f refers to the surface covered by the monolayer, the index w to the clean surface; w and w_0 are the equilibrium concentrations of water vapor above the surface and above the absorbent, respectively, $M = m/At$.

Fig. 1. I –dependence $M(\tau)$; II –dependence $F(\tau)$ and $r(F)$; a –with a calm surface, b –under the action of a wave. Area a in both cases 19.1 \AA^2 .

Fig. 2

Figure 2: Fig. 2

It was established by special experiments that the influence of the wave on absorption M from a clean surface at $\nu = 20$ increases by approximately 5%, and at $\nu = 30-40$ by up to 10%. From the curves in Fig. 1 it is evident that after application of the monolayer (saturated), M decreases sharply, and at first the influence of the wave is almost not manifested; however, with time, absorption under the action of the wave increases strongly. Both for a calm and for a wavy surface, M tends toward the initial value corresponding to the clean surface of water. The duration of the initial period, corresponding to low and identical values of M for the calm and wavy surfaces, depends on the magnitude of the excess of depressor. The greater the excess, the longer this period. The increase of M with time both without a wave and with a wave is explained by the gradual disappearance of the depressor from the surface and a decrease in its surface concentration Γ (mainly as a result of evaporation and, to a lesser extent, dissolution of the alcohol).

As is seen from curves Ia, b of Fig. 1, I, the increase of M with time under the action of the wave proceeds much faster than with a calm surface. It is especially interesting that the wave affects not only the dependence $M(\tau)$, which could be connected with an increased rate of disappearance of the monolayer, but also the dependence $r(F)$, which is seen from comparison of curves a and b in Fig. 1, II, in which r is compared at identical F . The curves $F(\tau)$ in Fig. 1, II show that F is only slightly lower in the case of wave action than with a calm surface. Consequently, the wave exerts a specific influence on the resist-

...of the monolayer at the same macroscopic value of F . Obviously, the wave weakens the protective properties of the monolayer, increasing its permeability as a result of a decrease in the interaction of depressor molecules in the monolayer and an increase in fluctuations of the monolayer density during its deformations on the wave. The possibility of diffusional penetration of water molecules through the monolayer is facilitated by the continuous mutual displacement of alcohol molecules in the monolayer, as a result of which jumps of water molecules along the hydrocarbon chains inside the monolayer are facilitated. This assumption about the enhancement of monolayer-density fluctuations under the influence of the wave is also confirmed by the fact that, as F increases, the influence of the wave on r decreases. From Fig. 1, II, it is seen that at high F the curves $r(F)$ tend toward the same value of r . The same follows from other experiments relating to $F = 43-45$ dyn/cm (at $\nu = 20$). The wave affects the magnitude r most strongly at $F \leq 25-30$ dyn/cm, i.e., at a less dense packing of the monolayer, at which r rapidly decreases to small values, as also for a quiescent surface.

Fig. 2. Dependences $F(\tau)$ (I); $M(\tau)$ (II); 1, 2, 3, 4, 5 correspond respectively to $(\Gamma - \Gamma_\infty)/\Gamma_\infty$ 0.01; 0.031; 0.042; 0.091; 0.212

The influence of the wave on the evaporation of water cannot be explained by an acceleration of diffusion processes in the adjacent phases, as is evident from the weak change of M under the influence of the wave for a clean surface. Comparison of the values of r at identical F shows that the decrease in the protective properties of the monolayer is determined not by a decrease in the total concentration of the monolayer (unsaturated), occurring as a result of an increase in the surface of the monolayer under the influence of the wave, in comparison with the quiescent surface, which was considered in (6).

The disappearance of the monolayer with time from the quiescent surface of water, expressed in a decrease of F and an increase of M , is seen from curves I and II of Fig. 2, which refer to different excesses of the depressor $(\Gamma - \Gamma_\infty)/\Gamma_\infty$, where the value taken for Γ_∞ is $8.38 \cdot 10^{-10}$ mole/cm², which corresponds to $a = 19.7 \text{ \AA}^2$. With increasing excess, the state of saturation of the monolayer, characterized by $F \geq 37$ dyn/cm, is maintained longer. Correspondingly, the protective capacity of the monolayer also remains longer at a high level. The dependence of the time τ_{init} , corresponding to the beginning of the fall of F (to values $\leq 37\text{--}38$ dyn/cm), on the excess of depressor is shown in Fig. 3, I . It may be assumed that, at an excess greater than some value, the time τ_{init} will be proportional to the excess in accordance with a constant rate of disappearance of the monolayer at the greatest $F = F_e$, corresponding to equilibrium with crystallites. From the linear portion of the curve $\tau_{\text{init}} [(\Gamma - \Gamma_\infty)/\Gamma_\infty]$ it follows that the rate of disappearance of the monolayer, calculated per unit surface of water in the vessel, is expressed as

$$\Delta \left(\frac{\Gamma - \Gamma_\infty}{\Gamma_\infty} \right) / \Delta \tau_{\text{init}} = 6.5 \cdot 10^{-15} \text{ mole/cm}^2 \cdot \text{sec},$$

or $8 \cdot 10^{-6} \Gamma_\infty / \text{sec}$,

which, in order of magnitude, is close to that found in (7) by another method. From the curves $F(\tau)$ one can determine the specific rate of decrease of F , corresponding to the rate of disappearance of the monolayer,

$$v_f = -(\partial F / \partial \tau) / F$$

as a function of F and of τ . The curves $v_f = f(F)$ pass through a maximum at $F \approx 30$ dyn/cm (Fig. 3, II). In Fig. 3, III the curves $v_f = f(\tau)$ are shown; on these, with an increase in Γ , the maximum shifts toward larger τ . The absolute values of v_f decrease with increasing $(\Gamma_0 - \Gamma_\infty)/\Gamma_\infty$ at all τ . This is evidently associated with the action of a larger number of small crystallites formed during deposition and, possibly, persisting to some extent also when F is lowered to values smaller than F_e , and therefore continuing to feed the monolayer. The possibility is not excluded of an influence of aging of the monolayer as well, which proceeds for a longer time at a large excess and leads to a stronger increase in viscosity and, correspondingly, to a more intense interaction of molecules in the

Fig. 3

Figure 3: Fig. 3

monolayer (8). The gradually falling F is the result of the superposition of two processes

$$F = F_0 - (\partial F / \partial \tau)_{\text{dis}} \tau + (\partial F / \partial \tau)_{\text{spr}} \tau,$$

Fig. 3. *I*-curves $\tau_0 = f(\Gamma - \Gamma_\infty) / \Gamma_\infty$; *II*-curves v_f ; *III*-curves $v_f(\tau)$; 1, 2, 3, 4, 5 correspond to the values $(\Gamma - \Gamma_\infty) / \Gamma_\infty$ in Fig. 2

where $(\partial F / \partial \tau)_{\text{dis}}$ is the rate of disappearance of the monolayer, which is a function of F , temperature T , and external conditions, for example, wave motion of the surface. Here F_0 denotes the initial two-dimensional pressure arising after the completion of the comparatively rapid process of spreading of the monolayer. It depends to some extent on the magnitude of the excess and may be somewhat smaller than F_e , which corresponds to a large excess of crystals (powder). $(\partial F / \partial \tau)_{\text{spr}}$ depends on the state of the crystallites, i.e., on their chemical potential, the magnitude of their total perimeter, on F , and on certain external conditions. The data obtained show that an excess of substance on the surface, which under practical conditions often reaches 20-30 times that of a saturated monolayer, together with compensation for losses of various kinds, is also necessary for maintaining a high F , which reduces the negative action of waves on the protective properties of the monolayer and the losses of the depressant itself to evaporation.

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