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INFLUENCE OF SURFACE-ACTIVE AGENTS ON THE THINNING OF A VERTICAL LIQUID FILM

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1. PHYSICAL STATEMENT OF THE PROBLEM

The objective of the article is to explain and model the anomalously slow process sometimes observed in experiments where a vertical liquid film thins out in the gravitational field. We consider the case in which it is known for certain that equilibrium of the gravitational and capillary forces is impossible. For example, a film of ordinary water with an average thickness H = 0.01 cm formed on a square frame of side L = 1 cm sometimes has a "lifetime" of the order of a few seconds. However, simple calculations show that a vertical layer of pure water in the earth's gravitational field ($g = 981$ cm/sec^2), starting from the rest state, attains zero thickness in a few hundredths of a second. The same result is confirmed by simple estimates. Assuming that the density, kinematic viscosity, and coefficient of surface tension of water are equal to $\rho = 1$ g/cm^3, $\nu = 0.01$ cm^2/sec, and $\sigma = 72$ g/sec^2, respectively, we see at once that the ratios of the capillary and viscous forces to the force of gravity are extremely small:

$$\frac{\sigma H}{\rho g L^3} \sim 7 \cdot 10^{-4}, \quad \frac{\nu}{g^{1/2} L^{3/2}} \sim 3 \cdot 10^{-4}.$$

Consequently, the characteristic thinning time of a free film is determined primarily by the force of gravity, which gives $(L/g)^{1/2} \sim 0.03$ sec.

Attempts to take into account the short-lived forces of interaction between the interphase surfaces of the film have failed to give any appreciable increase in the life of the film. Moreover, the strongest steric interactions [1] typical of long-molecular polymer liquids have little bearing on water. The sum total of these considerations has motivated us to study the effect of surface-active agents (surfactants), which are always present in a liquid as contaminants of one kind or another. An excess concentration of surfactants lowers the surface tension of the interphase boundary; according to the principle of minimum free energy, therefore, surfactants are capable of readily adsorbing liquid, even from the surrounding air.

We call attention to the following mechanism of the Le Chatelier–Brown type, which is capable of significantly extending the life of a film. In the initial stage of the thinning process gravity draws a liquid containing dissolved surfactants downward on a free boundary. This creates a surface-tension gradient in the upward direction, which induces Marangoni reactive flow. We emphasize that the incompressibility of the liquid keeps the volume concentration of surfactants almost constant, whereas the surface concentration of surfactants depends mainly on the dilatation of the free boundary. If the initial concentration exceeds a certain critical value, the film acquires an oscillatory flow regime, which decays with time. The thinning rate is now determined by the surfactant diffusion process, which eradicates the surface-tension gradient and causes the film to break. In support of this conjecture we add that the rupture of liquid films is usually observed just before the motion of the liquid fades altogether.

We note that the effect of body forces diminishes as the film thins out, whereas the Marangoni surface forces are practically independent of the film thickness. Consequently, even a small concentration of surfactants is capable of preventing instantaneous rupture of the capillary surface. The critical surfactant concentration for the above example is such that the surface tension of water decreases by no more than 2%.

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The actual lifetime of the film is determined by the stability of the motion of the liquid with free boundaries relative to external disturbances, so that the surfactant diffusion rate alone makes the upper limit of existence of the film too high. In fact, even if we assume that the coefficient of surface diffusion δ is improbably large, say of the order of the kinetic viscosity of water ν, the characteristic relaxation time to a constant surfactant concentration is $L^2/\delta \sim 100$ sec.

Investigations of the influence of surfactants on the thinning of a thin liquid film formed between two converging drops have been reported in several papers [1-3], where the Reynolds equations of wetting theory, which do not contain inertial or gravitational forces and are therefore inapplicable to free vertical films, are used as the hydrodynamic equations. Here we propose to model the thinning phenomenon on the basis of approximate equations derived for various applications [4-6].

2. MATHEMATICAL MODEL

We assume that the motion of a liquid in a vertical layer is symmetrical about its centroidal plane F. Let h(x, t), v(x, t), and γ(x, t) be the thickness of the film, the average velocity of the liquid, and the surface concentration of surfactants, all of which are functions of the position x on F and the time t. We assume that the surface tension of the "contaminated" free boundary is $\sigma - \alpha\gamma$ (α is a positive coefficient). In particular, the surface tension of a "clean" free boundary coincides with σ. In the thin-layer approximation the equations of conservation of mass and momentum have the form [4-6]

$$\frac{\partial h}{\partial t} + \nabla \cdot (h\mathrm{v}) = 0 \text{ on } F; \tag{2.1}$$

$$\rho h\left(\frac{\partial \mathrm{v}}{\partial t} + \mathrm{v} \cdot \nabla \mathrm{v}\right) = \rho h g + \nabla \cdot T \text{ on } F, \tag{2.2}$$

where ∇ denotes the planar gradient, and T is the film stress tensor, which has two components T_μ and T_σ.

The nonequilibrium component T_μ is related to the dynamic viscosity $\mu = \rho\nu$ according to the equation [4-6]

$$T_\mu = 2\mu h[(\nabla \cdot \mathrm{v})G + (\nabla \mathrm{v})_{\mathrm{sym}}] \tag{2.3}$$

(G is the metric tensor of the plane F). If the phenomenological approach is taken [4, 5], the equilibrium component T_σ must be an isotropic tensor τG, where τ is the effective tension of the film. When the interphase surfaces do not interact, we can set $\tau = 2(\sigma - \alpha\gamma)$. Although this approach leads to a correct formulation of the problem suitable for describing, for example, the dynamics of a closed shell, in the case of a film with fixed edges on a frame it is more sensible to include the dependence of T_σ on the capillary pressure in the second approximation. The order of the system of differential equations is increased in this case, so that boundary conditions for the film thickness can be stated without the construction of boundary layers. In the approximation $\alpha\gamma/\sigma << 1$ we have the relation [6]

$$T_\sigma = 2(\sigma - \alpha\gamma)G + \frac{\sigma}{2}\left[\left(h\Delta h + \frac{1}{2}|\nabla h|^2\right)G - \nabla h \otimes \nabla h\right] \tag{2.4}$$

(the symbol $\otimes$ denotes the tensor product). It is obvious that

$$\nabla \cdot T_\sigma = \frac{\sigma}{2} h\nabla(\Delta h) - 2\alpha\nabla\gamma.$$

The equation of surfactant diffusion along the interphase boundary is written as follows in the thin-layer approximation:

$$\frac{\partial \gamma}{\partial t} + \nabla \cdot (\gamma \mathrm{v}) = \delta\Delta\gamma \text{ on } F. \tag{2.5}$$

We assume for simplicity that the exchange of surfactants between the interior volume and the capillary surface is insignificant (the surfactants are insoluble).

For the system of equations (2.1)-(2.5) we specify the boundary and initial conditions (**n** is the direction of the normal to the boundary ∂F in the plane of the film):

$$\frac{\partial h}{\partial n} = 0,\ \mathrm{v} = 0,\ \frac{\partial \gamma}{\partial n} = 0 \text{ on } \partial F; \tag{2.6}$$

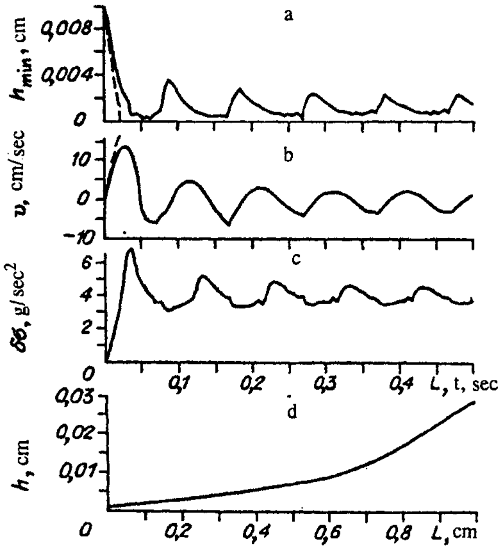

Fig. 1

$$h = H,\ v = 0,\ \gamma = \Gamma \ \text{at}\ t = 0. \tag{2.7}$$

Equations (2.6) imply that the contact angle, the liquid velocity, and the mass flow of surfactants vanish at the frame. We assume for definiteness that H and Γ are constant.

3. NUMERICAL SOLUTION OF THE ONE-DIMENSIONAL PROBLEM

We consider the one-dimensional solution h(x, t), v(x, t), γ(x, t) of problem (2.1)–(2.7). We transform to dimensionless variables by the substitutions x → Lx, t → $(L/g)^{1/2}t$, h → Hh, v → $(gL)^{1/2}v$, and γ → Γγ (L is the length of the film in the direction of gravity *g*). As a result, we obtain the problem

$$\frac{\partial h}{\partial t} + \frac{\partial (h v)}{\partial x} = 0; \tag{3.1}$$

$$\frac{\partial v}{\partial t} + v\frac{\partial v}{\partial x} = 1 + A\frac{\partial^3 h}{\partial x^3} - \frac{B}{h}\frac{\partial \gamma}{\partial x} + C\left(\frac{\partial^2 v}{\partial x^2} + \frac{1}{h}\frac{\partial h}{\partial x}\frac{\partial v}{\partial x}\right); \tag{3.2}$$

$$\frac{\partial \gamma}{\partial t} + \frac{\partial (\gamma v)}{\partial x} = D\frac{\partial^2 \gamma}{\partial x^2}; \tag{3.3}$$

$$\begin{gathered} \frac{\partial h}{\partial x}(0,t) = \frac{\partial h}{\partial x}(1,t) = 0, \\ v(0,t) = v(1,t) = 0, \\ \frac{\partial \gamma}{\partial x}(0,t) = \frac{\partial \gamma}{\partial x}(1,t) = 0; \end{gathered} \tag{3.4}$$

$$\begin{gathered} h(x, 0) = 1, \\ v(x, 0) = 0, \\ \gamma(x, 0) = 1. \end{gathered} \tag{3.5}$$

Here we have introduced the dimensionless groups

$$A = \frac{\sigma H}{2\rho g L^3};\ B = \frac{2\alpha\Gamma}{\rho g H L};$$

$$C = \frac{4\nu}{g^{1/2}L^{3/2}};\ D = \frac{\delta}{g^{1/2}L^{3/2}}.$$

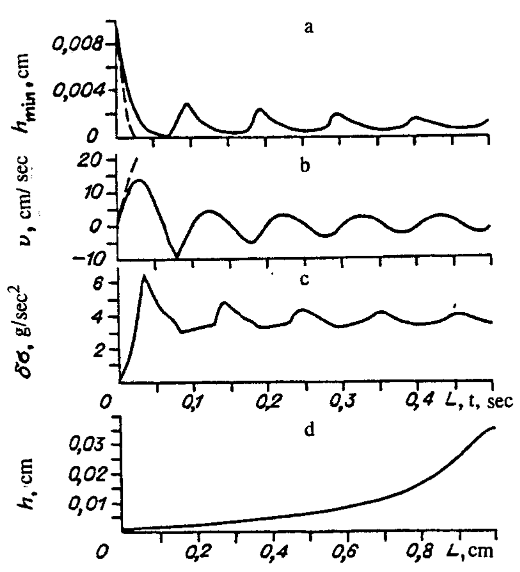

Fig. 2

Invoking the specific characteristics of the boundary conditions (3.4), we approximate the solution by finite trigonometric series:

$$h(x,t) = 1 + \sum_{k=1}^{K} h_k(t)\cos(\pi k x),\quad h_k(0) = 0,$$

$$v(x,t) = \sum_{k=1}^{K} v_k(t)\sin(\pi k x),\quad v_k(0) = 0,$$

$$\gamma(x,t) = 1 + \sum_{k=1}^{K} \gamma_k(t)\cos(\pi k x),\quad \gamma_k(0) = 0.$$

Substituting these functions into Eqs. (3.1)-(3.3), we obtain the system of ordinary differential equations

$$\frac{dh_k(t)}{dt} = -\pi k v_k(t) + H_k(t),$$

$$\frac{dv_k(t)}{dt} = 2\frac{1-(-1)^k}{\pi k} + A(\pi k)^3 h_k(t) + B\pi k \gamma_k(t) - C(\pi k)^2 v_k(t) + V_k(t),$$

$$\frac{d\gamma_k(t)}{dt} = -\pi k v_k(t) - D(\pi k)^2 \gamma_k(t) + \Gamma_k(t),$$

where $H_k(t)$, $V_k(t)$, and $\Gamma_k(t)$ are integral terms that depend nonlinearly on $\{h_1, v_1, \gamma_1; \ldots; h_K, v_K, \gamma_K\}$.

The system of equations with K = 40 has been integrated numerically by the Runge–Kutta method. The calculations are carried out for films of water (Fig. 1) and silicone oil (Fig. 2, $\rho = 0.9$ g/cm^3, $\nu = 0.05$ cm^2, $\sigma = 20$ g/sec^2) having a length L = 1 cm and an initial thickness H = 0.01 cm. Plotted in the cgs system, the figures show the time rates of change of the minimum film thickness (a), the average velocity of the liquid (b), and the surface-tension increment (c), along with the thickness profile at $t = 0.5$ sec (d) for $\alpha\Gamma/\sigma = 0.02$ (Fig. 1) and $\alpha\Gamma/\sigma = 0.06$ (Fig. 2). The dashed curves correspond to thinning of the pure film ($\Gamma = 0$). The Schmidt number is assumed to be identical everywhere: $\nu/\delta = 10$. As mentioned above, the coefficient of surface tension δ does not significantly influence the initial stage of thinning of the film if $\delta >> \nu$. The smallest oscillations of the solution (Fig. 1) appear to be associated with an increase in the error of its approximation by a finite trigonometric series in the case min(h)/H → 0.

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