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Abstract

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Corresponding Member of the Academy of Sciences of the USSR B. V. DERYA-GIN, S. P. BAKANOV, and Yu. S. KURGIN

ON THE INFLUENCE OF MONOLAYERS ON THE EVAPORATION OF DROPS

1. Introduction. The phenomenon of the retardation of water evaporation by films of certain surface-active substances, such as stearic and oleic acids and especially cetyl alcohol, has long been known ([1]). A theory of this phenomenon was proposed by Langmuir, who considered that the presence of a monolayer on the surface of water creates a resistance to the evaporation of water ([2]). Two distinct phenomena—the overcoming of the monolayer by water molecules and evaporation from the surface of the monolayer—were described by Langmuir by a single phenomenological parameter, the condensation coefficient α. Similarly, Bradley ([3]) explained the retardation of the evaporation of liquid drops by insoluble monolayers by ascribing to the latter a decrease in the value of α down to 10^{-6}.

The theory set forth below is based on a separate accounting of two effects that determine the influence of films on the rate of evaporation of liquids.

2. Quasi-stationary evaporation of a drop covered by an insoluble film of a foreign substance. Let us define the rate of evaporation, in an infinite medium, of a stationary drop of radius a, covered by an insoluble liquid film of a foreign substance of thickness δ, as the change in the mass of the drop per unit time, $-dM/dt$.

In the film, owing to dissolution in it of the substance of the drop, stationary diffusion of the liquid molecules occurs; it is described by the Laplace equation

$$\Delta C_1 = 0, \qquad a < r < a + \delta. \tag{1}$$

Here C_1 is the number of molecules of the substance of the drop in 1 cm^3 of the film.

From the surface of the film the liquid molecules evaporate into the air. Through the region immediately adjacent to the surface of the film, of thickness λ ([6]), of the order of the mean free path of vapor molecules in air, the vapor is transported by molecular flow, and farther on, beginning at the surface of the sphere of radius $a + \delta + \lambda$, it diffuses in the air.

Stationary diffusion of the vapor in air is described by the equation

$$\Delta C_2 = 0, \qquad r > a + \delta + \lambda, \tag{2}$$

where C_2 is the concentration of the vapor in the air.

Since the problem has spherical symmetry, the solutions of equations (1) and (2) are expressed in the form

$$\begin{aligned} C_1 &= A_1/r + B_1, \qquad && a < r < a + \delta; \\ C_2 &= A_2/r + B_2, \qquad && r > a + \delta + \lambda. \end{aligned} \tag{3}$$

From the condition of equilibrium of the liquid of the drop with the solution of the liquid in the film at the boundary $r = a$, we obtain that at this boundary the concentration of the solution of the liquid in the film C_1 is equal to the concentration of the saturated solution of the liquid in the film C_p,

$$C_1\big|_{r=a} = C_p. \tag{4}$$

At the boundary $r = a + \delta$ the solution of the liquid in the film is in equilibrium with vapor of concentration C_0'.

Starting from Henry' s law, we obtain the boundary condition at the interface $r = a + \delta$:

$$C_1\big|_{r=a+\delta} = \frac{C_p}{C_0} C_0', \tag{5}$$

where C_0 is the concentration of vapor saturated at the temperature of the droplet.

If $C_2\big|_{r=a+\delta+\lambda}$ is the vapor concentration at a distance λ from the surface of the film, then the molecular flux of vapor from the film is equal to $\alpha\frac{\bar{v}}{4}(C_0' - C_2\big|_{r=a+\delta+\lambda})$, where $\bar{v}$ is the mean velocity of the vapor molecules. The "sticking" coefficient α indicates that, of all vapor molecules striking the surface of the film, a fraction α of the molecules passes into the film, while the remaining fraction $(1 - \alpha)$ of the molecules is reflected back into the vapor.

From equality, at the boundary $r = a + \delta$, of the diffusion flux of dissolved liquid in the film and the molecular flux of vapor, we obtain the boundary condition:

$$-D_1 \frac{dC_1}{dr}\bigg|_{r=a+\delta} = \alpha \frac{\bar{v}}{4} \left(C_0' - C_2\big|_{r=a+\delta+\lambda} \right), \tag{6}$$

where D_1 is the diffusion coefficient of the liquid molecules in the film.

From equality, at the boundary $r = a + \delta + \lambda$, of the molecular and diffusion fluxes of vapor in air, we obtain the boundary condition

$$4\pi(a+\delta)^2\alpha\frac{\bar{v}}{4}\left(C_0' - C_2\big|_{r=a+\delta+\lambda}\right) = 4\pi(a+\delta+\lambda)^2\left(-D_2\frac{dC_2}{dr}\bigg|_{r=a+\delta+\lambda}\right), \quad (7)$$

where D_2 is the diffusion coefficient of vapor in air.

The vapor concentration in air at an infinite distance from the droplet is

$$C_2\big|_{r=\infty} = C_\infty. \quad (8)$$

From the five boundary conditions (4)–(8), the four constants A_1, A_2, B_1, B_2 and the concentration of equilibrium vapor C_0' are determined.

The evaporation rate of the droplet is equal to the diffusion flux of vapor through the surface of a sphere of radius $r = a + \delta + \lambda$

$$-\frac{dM}{dt} = m\,4\pi(a+\delta+\lambda)^2\left(-D_2\frac{dC_2}{dr}\bigg|_{r=a+\delta+\lambda}\right).$$

Substituting into this expression the value found for $C_2(r)$, we obtain the formula for the rate of quasi-stationary evaporation of a droplet covered by a film of thickness δ:

$$-\frac{dM}{dt} = \frac{4\pi a D_2(C_0 - C_\infty)m}{\dfrac{D_2}{a\bar{v}/4}\dfrac{a}{(a+\delta)^2} + \dfrac{a}{a+\delta+\lambda} + \dfrac{D_2}{D_1}\dfrac{C_0}{C_p}\dfrac{\delta}{a+\delta}}. \quad (9)$$

Without a film, i.e., for $\delta = 0$, expression (9) becomes the well-known Fuchs formula for the evaporation rate of a pure liquid droplet

$$-\frac{dM}{dt} = \frac{4\pi a D_2(C_0 - C_\infty)m}{D_2/\alpha\dfrac{\bar{v}}{4}a + \dfrac{a}{a+\lambda}}.$$

Let us assume that the corresponding formula for the evaporation rate of a droplet through a monolayer can be obtained from (9) in the limiting transition from a macroscopic film of thickness δ to a monolayer ($\delta \ll a$), i.e., we have

$$-\frac{dM}{dt} = \frac{4\pi a^2(C_0 - C_\infty)}{\dfrac{C_0}{C_p}\dfrac{\delta}{D_1} + \dfrac{1}{\alpha\bar{v}/4} + \dfrac{1}{D_2}\dfrac{a^2}{a+\lambda}}. \quad (10)$$

Formula (10) gives an expression for the rate of quasi-stationary evaporation of a liquid droplet covered by a monolayer. The terms of the denominator in (10) may be interpreted as partial resistances to evaporation: $\frac{1}{D_2}\frac{a^2}{a+\lambda}$ is the resistance due to diffusion of vapor

in air, $\frac{1}{\alpha v/4}$ is the resistance of the molecular flux near the surface of the drop; $\frac{C_0}{C_p}\frac{\delta}{D_1}$ is the partial diffusional resistance of the monolayer, which increases as the solubility of the liquid in the film decreases.

Describing the influence of the monolayer on the evaporation rate by two phenomenological parameters α and $\frac{1}{C_p}\frac{\delta}{D_1}$ is equivalent to assigning to the monolayer simultaneously a reflection coefficient and an absorption coefficient for the molecules of the liquid.

The theoretical result obtained shows that, under the condition

$$\frac{C_0}{C_p}\frac{\delta}{D_1} + \frac{1}{\alpha v/4} < \frac{1}{\alpha_{H_2O} v/4}, \tag{11}$$

where $\alpha_{H_2O} = 0.034$ is the condensation coefficient of water, the monolayer should increase the evaporation rate of water.

This paradoxical case is observed experimentally ([4,5]). Analogously, for evaporation from a plane liquid surface we obtain

$$I_0 = \frac{m(C_0 - C_L)}{\frac{L-\lambda}{D_2} + \frac{1}{\alpha v/4} + \frac{C_0}{C_p}\frac{\delta}{D_1}}, \tag{12}$$

where C_L is the vapor concentration in the air at a distance L from the liquid surface.

3. Nonstationary evaporation of a drop covered by an insoluble monolayer of a foreign substance

Consider the nonstationary evaporation of a liquid drop of radius a, covered by an insoluble monolayer of a foreign substance of thickness δ, with $\delta \ll a$.

Nonstationarity arises because of the nonequilibrium initial condition when the drop is introduced into an air medium with a constant vapor concentration in the air C_∞, different from the equilibrium one, the vapor density being much smaller than the liquid density γ, i.e. $mC_\infty \ll \gamma$.

The evaporation rate is equal to

$$I = -\frac{dM}{dt} = m\, 4\pi(a+\lambda)^2 \left(-D_2 \frac{\partial C}{\partial r}\bigg|_{r=a+\lambda} \right). \tag{13}$$

Substituting into (13) the expression for the mass of the drop $M = \frac{4}{3}\pi a^3 \gamma$, we obtain a formula for the velocity of motion of the boundary,

$$\frac{da}{dt} = \frac{mC_\infty}{\gamma} D_2 \left(\frac{a+\lambda}{a}\right)^2 \frac{1}{C_\infty} \frac{\partial C}{\partial r}\bigg|_{r=a+\lambda},$$

from which it is seen that, for $mC_\infty/\gamma \ll 1$, the Péclet number is small and the phase boundary may be regarded as immobile ([7]).

Since equilibrium in the monolayer is established rapidly, in a time $T \sim \delta^2/D_1 \sim 10^{-11}$ sec., one may assume that equilibrium is absent only in the gas, and reduce the influence of the monolayer to a change of the equilibrium vapor concentration C_0' at the boundary $r = a$ in comparison with the saturated vapor concentration C_0 in the case of evaporation of a pure liquid. C_0' is found from the solution of the existing quasi-stationary problem, i.e. from the system of equations (4)–(8):

$$C_0' = \frac{\dfrac{C_\infty}{C_p}\dfrac{\delta}{D_1} + \dfrac{1}{\alpha v/4} + \dfrac{1}{D_2}\dfrac{a^2}{a+\lambda}}{\dfrac{C_0}{C_p}\dfrac{\delta}{D_1} + \dfrac{1}{\alpha v/4} + \dfrac{1}{D_2}\dfrac{a^2}{a+\lambda}}\, C_0. \tag{14}$$

Nonstationary diffusion of vapor in air is described by the equation

$$D_2 \Delta C = \frac{\partial C}{\partial t}, \qquad r > a+\lambda, \qquad t > 0, \tag{15}$$

where C is the concentration of vapor in air.

From the equality at the boundary $r = a$ of the molecular flux of vapor to the diffusion flux of vapor in air, we obtain the boundary condition

$$4\pi a^2 \alpha \frac{\bar{v}}{4} \left(C_0' - C\big|_{r=a+\lambda} \right) = 4\pi(a+\lambda)^2 \left(-D_2 \frac{\partial C}{\partial r}\bigg|_{r=a+\lambda} \right). \tag{16}$$

We write the initial condition in the form

$$C(r,0) = C_\infty, \qquad r > a+\lambda. \tag{17}$$

From (13)–(17) we obtain the expression for the rate of nonstationary evaporation of a droplet covered by a monolayer

$$J = J_0 f(t),$$

$$\begin{aligned} f(t) = (1+\nu)\sqrt{\frac{D_2 t}{\pi}}\,\frac{a+\lambda}{(a+\lambda)^2+(1+\nu)D_2 t}e^{-(a+\lambda)^2/4D_2 t} \\ + \frac{1+\nu}{2}\,\frac{(a+\lambda)^4+(\nu+2)(a+\lambda)^2 D_2 t + 2(1+\nu)D_2^2 t^2}{\left[(a+\lambda)^2+(1+\nu)D_2 t\right]^2}\left[1-\operatorname{erf}\left(-\frac{a+\lambda}{2\sqrt{D_2 t}}\right)\right] \\ - \frac{D_2 t}{2}(1+\nu)\,\frac{(a+\lambda)^2+2(1+\nu)D_2 t}{\left[(a+\lambda)^2+(1+\nu)D_2 t\right]^2}e^{1+\nu+\left(\frac{1+\nu}{a+\lambda}\right)^2 D_2 t} \\ \times\left[1-\operatorname{erf}\left(\frac{a+\lambda+2\frac{1+\nu}{a+\lambda}D_2 t}{2\sqrt{D_2 t}}\right)\right], \end{aligned} \tag{18}$$

where

$$\nu = \frac{\alpha\bar{v}/4}{D_2}\frac{a^2}{a+\lambda}; \qquad J_0 = \frac{4\pi a^2 (C_0 - C_\infty) m}{\frac{C_0}{C_p}\frac{\delta}{D_1} + \frac{1}{\alpha\bar{v}/4} + \frac{1}{D_2}\frac{a^2}{a+\lambda}}$$

is the rate of quasistationary evaporation of the droplet.

For $t \gg (a+\lambda)^2/D_2$, $f(t) \to 1$, $J = J_0$, i.e., the initial nonequilibrium is dissipated and a quasistationary evaporation regime is established over a time $T \sim (a+\lambda)^2/D_2$.

The evaporation rate of the droplet at the initial instant is equal to

$$J\big|_{t=0} = J_0\left(1 + \frac{\alpha\bar{v}/4}{D_2}\frac{a^2}{a+\lambda}\right).$$

If the presence of a monolayer on the surface of water leads to values of α greater than $\alpha_{H_2O} = 0.034$, then the rate of evaporation of water through the monolayer at the initial moment of time is higher than the evaporation rate of pure water, which is in qualitative agreement with the results of ([4]).

From the experimentally determined rate of stationary evaporation from 1 cm^2 of a flat liquid surface and the corresponding rate of nonstationary evaporation in the initial period of nonstationarity, one can determine the parameters α and $\frac{1}{C}\frac{\delta}{D_1}$ for each given monolayer.

Institute of Physical Chemistry
Academy of Sciences of the USSR

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Note: Figure translations are in progress. See original paper for figures.