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Hydrodynamics of thin liquid films

Effect of the surfactant on the rate of thinning

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With 2 figures

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Introduction

The outflow of the liquid from the thin films plays an essential role for the behaviour of foams and emulsions and on that account it has been a subject of numerous investigations. The references (1) and (2) (and the sources cited there) form a far incomplete list of the investigations dedicated to greater or lesser degree to this problem. The rate of film thinning is usually calculated according to *Reynolds*' eq. [19], an essential condition for the applicability of the latter being zero radial velocity of flow on the film surface. For foam and emulsion films stabilized with soluble surfactants this condition may not be realized for the stretch of the adsorption monolayer (leading to reduction of the flow rate on the surface) is partially compensated by volume and surface diffusion. This effect is discussed in detail in (3) and its importance for the hydrodynamics of free films is pointed out in (2). On the basis of this conception a quantitative theory of the thinning of free films was worked up in (4), where the effect of the surface diffusion was disregarded and the perturbation of the adsorption monolayer due to the outflow was assumed to be small. The theory was developed for the case of low surfactant concentration, i.e. for surface concentration proportional to the volume concentration (*Henrys*' adsorption isotherm).

In the theory presented here these approximations are avoided and as a result some new interesting corollaries are obtained. It turns out that at small film thicknesses and strong surfactants surface diffusion can be more important than the bulk diffusion. This leads to qualitative changes in the film behaviour. Besides, the results demonstrate that though it is possible for the velocity of thinning to be practically constant in certain concentration interval, still, its value would be higher than that corresponding to *Reynolds*' eq. [19]. This means that strictly regarded *Reynolds*' equation is inapplicable for the cases when the film is stabilized with a soluble surfactant.

2. General formulation of the problem

The exact solution of the problem turned out to be possible as a result of a certain simplification of the method of calculation. This requires to carry out in brief again all the derivations. The details about the physical meaning of the employed equations and approximations are given in (4).

We shall calculate the velocity of thinning $V = -dh/dt$ of liquid plane-parallel film[1]) with thickness h (t denotes time) and radius R (fig. 1).

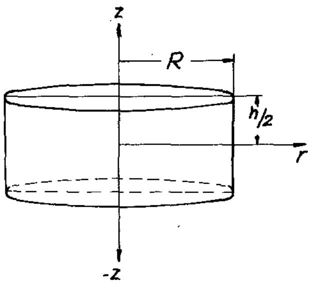

Fig. 1. Definition of the coordinate system. (Not to scale)

For the system considered here the general *Navier-Stokes*' equations describing the liquid motion (5, § 5) can be substantially simplified. Since the natural time scale in the case is h/V [see e.g. (5, § 9)], it is easy to show that the time

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[1]) In fact the film surface is never completely plane but is thicker in the middle (this is the so-called dimpling). At certain conditions this phenomenon can be disregarded. This problem is considered in details in (6).

dependent term is of the order of magnitude of V^2/h. Henceforth, for small values of *Reynolds*' number[2]), it can be neglected together with the inertial terms which are of the same order. This means that the process behaves as a steady one i.e. that its parameters depend on time only through h.

The outflow is assumed to have a radial symmetry. Since the film is thin ($h \ll R$), we shall always neglect the terms of the order of h/R. Thus *Navier-Stokes*' equations are eventually reduced to the well known equations of the lubrication theory [see e.g. (5, § 27)]:

$$\frac{\partial p}{\partial r} = \frac{\partial^2 v_r}{\partial z^2} \qquad [1\,a]$$

$$\frac{\partial p}{\partial z} = 0 \qquad [1\,b]$$

$$\frac{1}{r}\frac{\partial}{\partial r}(r v_r) + \frac{\partial v_z}{\partial z} = 0 \qquad [1\,c]$$

v_r and v_z being respectively the radial and normal components of the velocity, p = pressure, and μ = dynamic viscosity.

The distribution of surfactant in the system is described by the equation of convective diffusion (for a system with a cylindrical symmetry):

$$\frac{\partial c}{\partial t} + v_r\frac{\partial c}{\partial r} + v_z\frac{\partial c}{\partial z} = D\left(\frac{1}{r}\frac{\partial}{\partial r}r\frac{\partial c}{\partial r} + \frac{\partial^2 c}{\partial z^2}\right)$$

where D is coefficient of bulk diffusion and c is bulk surfactant concentration.

In the manner already used for simplifying *Navier-Stokes*' equation (see above) it can be shown that both the time dependent term and the convective term are of the order of cV/h, and for small values of *Peclet*'s number ($Pe = Vh/D$) they can be neglected. Thus for the case of cylindrical symmetry a simpler equation is obtained:

$$\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial c}{\partial r}\right) + \frac{\partial^2 c}{\partial z^2} = 0. \qquad [2]$$

The solution of the system [1]–[2] must satisfy the condition for surfactant conservation[3]) (3):

$$\frac{\partial \Gamma}{\partial t} + \frac{1}{r}\frac{\partial}{\partial r}(r v_r \Gamma) - D_s\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial \Gamma}{\partial r}\right) = -D\frac{\partial c}{\partial z}; \quad \text{when} \quad z = \frac{h}{2}$$

where Γ is surfactant surface concentration and D_s is coefficient of surface diffusion. Since we have a steady process we can write:

$$\frac{\partial \Gamma}{\partial t} = \frac{\partial \Gamma}{\partial c}\frac{\partial c}{\partial h}\frac{\partial h}{\partial t} = -V\frac{\partial \Gamma}{\partial c}\frac{\partial c}{\partial h}.$$

Comparing this expression for $\partial\Gamma/\partial t$ to the term $D\,\partial c/\partial z$ we can see that $\partial\Gamma/\partial t$ can be neglected if $V(\partial\Gamma/\partial c)/D \ll 1$. The latter ratio has the structure of *Peclet*'s number but the length scale $\partial\Gamma/\partial c$ in the case depends on the surfactant adsorbability. Thus the condition for surfactant conservation takes the form:

$$\frac{1}{r}\frac{\partial}{\partial r}(r v_r \Gamma) - D_s\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial \Gamma}{\partial r}\right) = -D\frac{\partial c}{\partial z}; \quad \text{when} \quad z = \frac{h}{2}. \qquad [3]$$

Further on we have used the following limiting conditions:

$$v_z = -\frac{V}{2}; \qquad \text{when} \quad z = \frac{h}{2} \qquad [4]$$

$$\text{a)}\ \frac{\partial v_r}{\partial z} = 0; \quad \text{b)}\ \frac{\partial c}{\partial z} = 0; \qquad \text{when} \quad z = 0 \qquad [5]$$

$$\mu\left(\frac{\partial v_r}{\partial z}\right) = \frac{\partial \sigma}{\partial r}; \qquad \text{when} \quad z = \frac{h}{2} \qquad [6]$$

$$\text{a)}\ p = 0; \quad \text{b)}\ c = c_0; \qquad \text{when} \quad r = R \qquad [7]$$

where $\sigma = \sigma(r)$ is the local value of the surface tension, and c_0 is the equilibrium bulk concentration of surfactant. The condition [7] allows for the fact that the liquid in the meniscus is immobile. Since the solution must not have any singularity in all cases when expressions of the kind const/r appear we shall put const = 0.

Taking into consideration [1b] and [5a], after integrating [1a] on z we obtain:

$$v_r = \frac{z^2}{2\mu}\frac{\partial p}{\partial r} + B(r) \qquad [8]$$

where $B(r)$ is an integration constant. Substituting [8] in [1c] and then integrating consecutively on z (eq. [4] is used at this step) and on r we obtain:

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[2]) For a thin aniline film [see (4)] *Reynolds*' number is of the order of 10^{-9}.

[3]) Because of the symmetry of the system we shall carry out all the calculations only for the upper surface $z = h/2$.

$$Vr = \frac{h^3}{12\mu}\frac{\partial p}{\partial r} + 2Bh. \qquad [9]$$

Separating in [2] the variables r and z by putting $c(z, r) = \varphi(z)\,\psi(r)$, we have:

$$\frac{1}{r}\frac{d}{dr}\left(r\frac{d\psi}{dr}\right) = -\chi^2\psi$$

and

$$\frac{d^2\varphi}{dz^2} = \chi^2\varphi \qquad [10]$$

where χ is a constant. The function $\varphi(z)$ can be expanded in series on the even powers of z. Since for the thin film $z \leq h/2 \ll R$, we shall confine ourselves to the quadratic term which suffices for accounting the bulk diffusion flux in [3]. Taking also into consideration [7b] we can write down:

$$c = c_0 + \left(1 + \frac{\chi^2 z^2}{2}\right)\psi. \qquad [11]$$

In the cases where c is not differentiated on z, we shall neglect the term $\chi^2 z^2/2$. The concrete form of the function ψ is immaterial for the further solution.

From [10] and [11] we have:

$$\left(\frac{\partial c}{\partial z}\right)_{z=h/2} = \frac{\chi^2 h}{2}\psi = -\frac{h}{2}\frac{1}{r}\frac{d}{dr}\left(r\frac{d\psi}{dr}\right). \qquad [12]$$

From this and from [3] after integration on r, we obtain:

$$\Gamma\left(\frac{h^2}{8\mu}\frac{\partial p}{\partial r} + B\right) - \left(D_s\frac{\partial \Gamma}{\partial c} + \frac{Dh}{2}\right)\frac{d\psi}{dr} = 0 \qquad [13]$$

where v_r at $z = h/2$ is expressed through [8]. Deriving [13] we have employed the assumption for local equilibrium with respect to the distribution of the surfactant between the bubble and the surface, i.e. we have assumed that $\Gamma(r) = \Gamma[c(r)]$. This allows us to write:

$$\frac{\partial \Gamma}{\partial r} = \frac{\partial \Gamma}{\partial c}\left(\frac{\partial c}{\partial r}\right)_{z=h/2} = \frac{\partial \Gamma}{\partial c}\frac{d\psi}{dr}. \qquad [14]$$

For the surface tension, by analogy to [14] we have:

$$\frac{\partial \sigma}{\partial r} = \frac{\partial \sigma}{\partial c}\left(\frac{\partial c}{\partial r}\right)_{z=h/2} = \frac{\partial \sigma}{\partial c}\frac{d\psi}{dr}.$$

From [6] and [8] with the aid of the latter equation we can express $d\psi/dr$:

$$\frac{h}{2}\frac{\partial p}{\partial r} = \frac{\partial \sigma}{\partial c}\frac{d\psi}{dr}. \qquad [15]$$

From [9], [13] and [14] we obtain:

$$\frac{\partial p}{\partial r} = -6\frac{\mu V}{h^3}\frac{r}{1+\alpha} \qquad [16]$$

where

$$\alpha = -\left(1 + \frac{2D_s}{Dh}\frac{\partial \Gamma}{\partial c}\right)\frac{3D\mu}{\Gamma(\partial\sigma/\partial c)}. \qquad [17]$$

The force which the liquid asserts upon the film surface is

$$F = 2\pi\int_0^R p r\,dr = -\pi\int_0^R r^2\frac{\partial p}{\partial r}\,dr$$

$$= \frac{6\pi\mu V}{h^3}\int_0^R \frac{r^3}{1+\alpha}\,dr. \qquad [18]$$

(In the second step we have used term-by-term integration and the condition [7a].) This force balances the external force, causing the outflow. The velocity of thinning V_0 of a film with rigid surfaces (i.e. with radial velocity on the film surface equals zero), thinning under the action of the same force, can be calculated from *Reynolds'* equation (2):

$$F = \frac{3\pi\mu R^4 V_0}{2h^3}. \qquad [19]$$

Putting [18] equal to [19] we obtain finally:

$$\frac{V}{V_0} = \frac{R^4}{4}\left[\int_0^R \frac{r^3}{1+\alpha}\,dr\right]^{-1}. \qquad [20]$$

The equation thus obtained is in principle a general solution of the problem, for the function ψ can be found from [10] [ψ is represented through *Bessels'* functions (4)] and with the aid of the adsorption isotherm and [17], the velocity V can be calculated from [20]. However, the result is so intractable, that we prefer to consider two particular cases, which actually cover the whole concentration range.

The surface concentration Γ and the bulk concentration c can be represented as sums of the corresponding equilibrium values Γ_0 and c_0, and the perturbations Γ_1 and c_1, caused by the flow ($\Gamma = \Gamma_0 + \Gamma_1$ and $c = c_0 + c_1$). If c_0 is high, the perturbations Γ_1 and c_1 cannot be great ($\Gamma_1 \ll \Gamma_0$ and $c_1 \ll c_0$) because any deviation from the equilibrium distribution leads to diffusion flux which tends to annul the perturbation i.e. the diffusion flux acts as a "damper". At low concentrations, however, the rate of diffusion decreases substantially and the perturbations can become comparable to the equilibrium values Γ_0 and c_0. Therefore it is convenient to consider separately the regions of high concentrations (strong "damping") and of low concentrations (weak "damping").

3. High concentrations

In this case we can use the following expansions in series:

$$\Gamma = \Gamma_0 + \frac{\partial \Gamma_0}{\partial c_0} c_1; \quad \frac{\partial \Gamma}{\partial c} = \frac{\partial \Gamma_0}{\partial c_0} \qquad [21]$$

$$\sigma = \sigma_0 + \frac{\partial \sigma_0}{\partial c_0} c_1; \quad \frac{\partial \sigma}{\partial c} = \frac{\partial \sigma_0}{\partial c_0}. \qquad [22]$$

The quantity α in [17] is then a constant and from [20] we obtain:

$$\frac{V}{V_0} = 1 - \left(1 + \frac{2D_s}{Dh}\frac{\partial \Gamma_0}{\partial c_0}\right)\frac{3D\mu}{\Gamma_0(\partial\sigma_0/\partial c_0)}. \qquad [23]$$

In many cases (7) adsorption of surfactants obeys *Langmuir*s isotherm:

$$\Gamma_0 = \Gamma_\infty \frac{c_0}{a + c_0} \qquad [24]$$

respectively *Szyszkowski*'s equation:

$$\sigma_0 = \sigma_0^0 - \Gamma_\infty kT \ln\left(1 + \frac{c_0}{a}\right) \qquad [25]$$

where Γ_∞ is the maximum surface concentration, a is the adsorption constant, σ_0^0 is the surface tension of the pure solvent, k is *Boltzmann*s constant and T is *Kelvin*s temperature.

Eqs. [23]–[25] yield:

$$\frac{V}{V_0} = 1 + \left[1 + \frac{2D_s\Gamma_\infty a}{Dh(a + c_0)^2}\right]\frac{3D\mu(a + c_0)^2}{\Gamma_\infty^2 kTc_0}. \qquad [26]$$

The latter expression has the advantage to allow the theoretical analysis of the phenomenon. If the adsorption obeys other adsorption isotherms, they (or even experimental data for the dependence $\sigma_0 = \sigma_0(c_0)$ in the general eq. [23]) can be also used.

4. Low concentrations

In this case the expansions in series [21] and [22] cannot be used, but since now $c_0 \ll a$ the eqs. [24] and [25] could be written in a simpler form. Applied for the local quantities Γ and c, they read:

$$\Gamma = \frac{\Gamma_\infty}{a} c = bc \qquad [27]$$

$$\sigma = \sigma_0^0 - \frac{\Gamma_\infty kT}{a} c = \sigma_0^0 - kTbc \qquad [28]$$

so that [17] yields:

$$\alpha = \left(1 + \frac{2D_s b}{Dh}\right)\frac{3D\mu}{kTb^2 c}. \qquad [29]$$

Integrating [15] we obtain (from [7b] and [10] follows $\psi(R) = 0$):

$$ph = -2kTb\psi \qquad [30]$$

from which $c = c_0 + \psi$ can be calculated (cf. [10]).

The case of weak damping corresponds to $c \to 0$ i.e. to $\alpha \ll 1$. Using this approximation from [16], [29] and [30] we obtain:

$$p = \frac{2\Delta\sigma_0}{h}\left\{1 - \exp\left[-q\left(1 - \frac{r^2}{R^2}\right)\right]\right\} \qquad [31]$$

where

$$q = \frac{bR^2V}{2Dh^2}\left(1 + \frac{2D_s b}{Dh}\right)^{-1} \qquad [32]$$

and

$$\Delta\sigma_0 = kTbc_0 = \sigma_0^0 - \sigma_0. \qquad [33]$$

Eqs. [18] and [31] give finally:

$$\frac{Ph}{2\Delta\sigma_0} = 1 - \frac{1}{q}(1 - e^{-q}). \qquad [34]$$

Here we have introduced the notation: $P = F/\pi R^2$.

5. Discussion

Let us begin with the case of strong damping and assume that the film is thick enough so that the term allowing for surface diffusion is vanishing. Thus with low concentrations[4]) ($c_0 \ll a$) eq. [26] takes the form:

$$\frac{V}{V_0} = 1 + \frac{3D\mu a^2}{\Gamma_\infty kTc_0} \simeq \frac{3D\mu a^2}{\Gamma_\infty kTc_0}. \qquad [35]$$

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[4]) Further on it is shown that even in the region in which *Henry*'s isotherm is valid damping can be strong.

The expression thus obtained coincides with eq. [26] from (4).

With high concentration ($c_0 \gg a$) we obtain:

$$\frac{V}{V_0} = 1 + \frac{3D\mu}{\Gamma_\infty^2 kT} c_0. \qquad [36]$$

Thus the function V/V_0 vs. c_0 has a minimum at $c_0 = a$ whose value is $V/V_0 = 1 + 12 D\mu a/\Gamma_\infty^2 kT$. Therefore when the film is stabilized with soluble surfactant, V is always greater than V_0, i.e. the radial velocity is never zero on the surface and *Reynolds'* equation is not applicable. The abscissa of the minimum of the function V/V_0 coincides with the abscissa of the maximum of the damping coefficient of the capillary waves calculated according to *Szyszkowski's* equation (8). Only when the surfactant is strongly adsorbable ($a \to 0$) so that it is in practice insoluble *Reynolds'* equation remains valid. The increase of the velocity V for $c_0 > a$, obviously is due to the fact that in this region $\Gamma \simeq \Gamma_\infty$ and further increase of c_0 does not lead to any significant change of the surface concentration, and only increases diffusion flux.

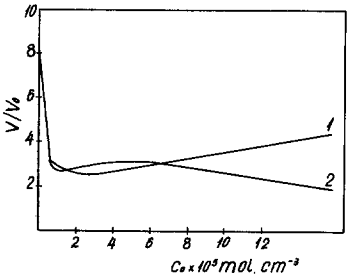

Fig. 2. Dependence of V/V_0 vs. c_0 for aniline films stabilized with lauric alcohol in the absence of surface diffusion ($D_s = 0$ or/and $h \to \infty$). Curve 1 is calculated according to eq. [26] with $a = 2.26 \cdot 10^{-5}$ mol · cm^{-3} and $\Gamma_\infty = 6.42 \cdot 10^{-11}$ mol · cm^{-2}. Curve 2 is calculated according to eq. [23] by means of graphical differentiation of the experimental curve $\Delta\sigma_0$ vs. c_0 from (4). Values of the other parameters: $D = 1.3 \cdot 10^{-5}$ cm^2 sec^{-1}; $\mu = 4.4 \cdot 10^{-2}$ g cm^{-1} sec^{-1}; $T = 292$ °K

In fig. 2 curve 1 shows the dependence V/V_0 vs. c_0 calculated according to eq. [26] (without the term allowing for surface diffusion) for aniline films stabilized with lauric alcohol ($D = 1.3 \cdot 10^{-5}$ cm^2 sec^{-1}; $\mu = 4.4 \cdot 10^{-2}$ g cm^{-1} sec^{-1}; $T = 292$ °*K*; $a = 2.26 \cdot 10^{-5}$ mol cm^{-3}; $\Gamma_\infty = 6.42 \cdot 10^{-11}$ mol cm^{-2}) [5]. Curve 2 in the same figure differs from curve 1 only by that, that it is built according to eq. [23] where the values of $(\partial\sigma_0/\partial c_0)$ are calculated by graphical differentiation of the experimental curve (c_0) [fig. 3 in (4)] and Γ_0 is determined from *Gibbs'* isotherm:

$$\Gamma_0 = -\left(\frac{c_0}{kT}\right)\frac{\partial\sigma_0}{\partial c_0}.$$

As it is seen from the figure, curve 2 yields not a distinct minimum but sooner a rather large plateau. With high concentration the velocity V does not increase but decrease. This shape of the curve is resulted by the inapplicability of *Szyszkowskis* equation. Although in a quite wide concentration range the velocity V remains practically constant, *Reynolds'* equation is not valid because there $V \simeq 2\,V_0$.

Taking into account surface diffusion leads to some interesting consequences. As it is seen from the obtained results (see for instance eq. [23]) surface diffusion will play more important role in thinner films and with stronger detergent (greater $\partial\Gamma_0/\partial c_0$) [6]. Unfortunately, reliable data about D_s are not available so that the region where this effect would be significant cannot be indicated. A rough estimation shows that with aniline films stabilized with lauric alcohol at $h \leqslant 600$ Å surface diffusion becomes predominant over bulk diffusion. As it must be expected surface diffusion increases the velocity V for it hinders formation of a surface tension gradient during the film thinning.

In macroscopic phases (e.g. for case of capillary waves on the surface of a semi-infinite phase), surface diffusion can be neglected [see for instance (3)]. In thin liquid films however this effect is important for when the film thickness decreases the concentration gradient $\partial c/\partial z$ at $z = h/2$ also decreases (see eq. [12]). This results in a decrease of the bulk diffusion flux while the surface diffusion flux remains practically unaltered.

Unfortunately it is not easy to proof this effect experimentally for at small thicknesses disjoining pressure, which also depends on h and is not usually known with sufficient accuracy, appears. Certain possibilities for experimental verification still exist. At $h \to 0$ eq. [26], for example takes the form for all concentrations:

$$\frac{V}{V_0} = \frac{6 D_s \mu a}{\Gamma_\infty kTh c_0}. \qquad [37]$$

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[5] The values of a and Γ_∞ quoted here are different from those quoted in (4). They have been recalculated on the basis of the same experimental curve [see fig. 3 in (4)] in order to fit better *Szyszkowskis* equation with the experimental results.

[6] It must be born in mind, however, that when $\partial\Gamma_0/\partial c_0$ increases $\partial\sigma_0/\partial c_0$ also increases which leads to smaller deviation from *Reynolds'* law.

This function differs substantially from the equation which follows from [26] at great h not only by the presence of h in the expression, but also by the dependence of V/V_0 vs. c_0 – it monotonely decreases when increasing c_0 and does not pass through a minimum. This effect can be used as a criterion for the prevailing influence of the surface diffusion. At higher thicknesses when the term $2D_s\Gamma_\infty a/Dh(a + c_0)^2$ in [26] is of the order of unity such a criterion can be the abscissa of the minimum of the curve V/V_0 which in this case has the value $a(1 + 2D_s\Gamma_\infty/Dh\,a)^{\frac{1}{2}}$.

Let us consider finally the region of a low damping. The general eq. [34] possesses two interesting limiting cases. For high value of q it takes the form:

$$\frac{Ph}{2\Delta\sigma_0} = 1 - \frac{1}{q} \qquad [38]$$

and for $q \to \infty$ (i.e. for $V \to \infty$):

$$Ph = 2\Delta\sigma_0 . \qquad [39]$$

Since at $V \to \infty$ a film does not form at all, eq. [39] must be considered as a condition for the dynamic stability of the film (i.e. as a condition for its existence). Analogical result to an accuracy of a factor two has been obtained in (4) on the basis of semi-quantitative considerations, where it has been shown that at $V \to \infty$ a free of surfactant spot forms in the film centre – as a result the film must rupture.

In the other limiting case (small V) e^{-q} in [34] can be expanded in series to give:

$$Ph/\Delta\sigma_0 = q . \qquad [40]$$

Expressing here P through *Reynolds'* eq. [19] and using [27], [32], and [33] we obtained again eq. [35] which has been derived for the case of low concentrations (*Henry*'s adsorption isotherm) with strong damping. This means that even in the region of validity of *Henry*'s isotherm it is possible to have strong damping. It also shows that the expressions obtained for weak and strong damping overlap i.e. that they describe the whole concentration range.

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Summary

A theory of the effect of the surfactant on the rate of thinning of foam films is presented. The formulae obtained for the separately treated cases of low and high concentrations cover the whole concentration range. The effect of both bulk and surface diffusion is taken into consideration and it is demonstrated that the relative importance of the latter increases with the decrease of the film thickness. The role of the surface diffusion for the stability of foam films is discussed. It is shown that films stabilized with soluble surfactants never strictly obey *Reynolds'* eq. [19] so that the actual velocity of thinning can be substantially higher than that calculated by the quoted equation.

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