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Hydrodynamics of thin liquid films**Effect of surface diffusion on the rate of thinning of foam films**

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With 4 figures

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Introduction

In the theoretical investigations of the influence of soluble surfactants on the motion of the liquid surfaces of bulk phases the effect of surface diffusion is usually neglected, for the respective diffusion flux is considerably smaller than this of the bulk (volume) diffusion (see e.g. (1)). With thin films, however, the situation could be altered because, during the thinning, the bulk diffusion flux diminishes, while the surface flux does not practically change. Hence below a certain thickness the hydrodynamic behaviour of the system is chiefly determined by the surface diffusion. This effect has been pointed out in reference (2) where the following equation for the rate of thinning of a plane parallel film has been obtained

$$\frac{V}{V_R} = 1 - \left(1 + \frac{2D_s}{Dh} \cdot \frac{\partial \Gamma_0}{\partial c_0} \right) \frac{3D\mu}{\Gamma_0 \partial \sigma_0 / \partial c_0} \quad [1]$$

Here h is film thickness, V is velocity of thinning ($V = -db/dt$, t is time), D and D_s are the coefficients of bulk and surface diffusion respectively, μ is viscosity of the film liquid, σ_0 is the equilibrium surface tension of the solution from which the film is formed, c_0 and Γ_0 are the equilibrium bulk and surface surfactant concentrations and

$$V_R = \frac{2}{3} \cdot \frac{h^3}{\mu R^2} \cdot \Delta p \quad [2]$$

is Reynolds' velocity (see (2, 3)) of thinning of a film formed between two rigid surfaces

pressed together by the same driving pressure Δp as the film under investigation. For foam films formed in a capillary of radius R_c (fig. 1) $\Delta p = P_c - \Pi$, where Π is disjoining pressure and $P_c = 2\sigma_0/R_c$ is capillary pressure of the meniscus (4, 5).

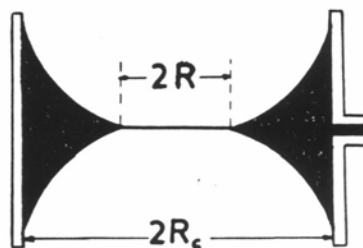


Fig. 1. Thin liquid film of radius R formed in a capillary of radius R_c

Equation [1] is valid under the following conditions: a) the surface viscosity can be neglected¹⁾, b) the adsorption equilibrium is established before the film is formed, c) the rate of adsorption is great enough to provide the equilibrium surface-sublayer. These conditions are fulfilled with aqueous solutions of short chain fatty acids (7). The aqueous solutions of valeric (C_5) and caproic (C_6) acids in particular have one more advantage: in a relatively wide concentration range (up to 10^{-2} M/l for valeric acid and up to $4 \cdot 10^{-3}$ M/l for caproic acid) the lowering of the

¹⁾ The influence of the surface viscosity on the drainage of microscopic films is studied in reference (6), where it is shown that this effect can usually be neglected.

surface tension $\Delta\sigma_0$ is a linear function of concentration

$$\Delta\sigma_0 = b \cdot c_0. \quad [3]$$

At small thicknesses where the effect of surface diffusion prevails the unit in the brackets in equation [1] can be disregarded, so that by means of [3] and Gibbs' adsorption isotherm this equation acquires the form

$$\frac{V}{V_R} = 1 + \frac{k}{b}; \quad k = \frac{6D_s\mu}{bc_0}. \quad [4]$$

The purpose of the present paper is the experimental verification of equation [4].

Experiment

The acids were of high purity (> 99% according to chromatography analysis).

The values of the surface tension necessary for determination of the constant b in [3] were measured by Wilhelmy's method with roughened glass plate. Our data for $\Delta\sigma_0$ differed from those of other authors (as compiled in (8)) with no more than $\pm 0,1$ dyn/cm. The values of b thus obtained were $7 \cdot 10^5$ dyn.cm².M⁻¹ for the solutions of valeric acid and $2.2 \cdot 10^6$ dyn.cm².M⁻¹ for those of caproic acid. The measurements of the dependence of the film thickness on time were carried out by the microinterferometric method (4) with a capillary of radius $R_c = 2.13 \cdot 10^{-1}$ cm and film radius $R = (1 \pm 0.04) \cdot 10^{-2}$ cm. The velocity of thinning V was determined through graphic differentiation of the $h(t)$ curves.

The disjoining pressure was calculated according to Hamaker's equation; $\Pi = -K/b^3$ which according to (9) is obeyed by aqueous films. For K we used the theoretical value $2.7 \cdot 10^{-14}$ erg (10). To suppress the dissociation of the acids and to eliminate the electrostatic disjoining pressure the solutions contained HCl (p.a. distilled) with concentration $7 \cdot 10^{-2}$ M/l. The measurements were carried out in the range $4 \cdot 10^{-6}$ cm $\leq b \leq 1.3 \cdot 10^{-5}$ cm. At greater thicknesses deviations from the plane parallel profile were observed while at smaller thicknesses the use of the theoretical isotherm of the disjoining pressure could lead to substantial errors. The value 10^{-2} g.cm⁻¹.s⁻¹ was used for the viscosity μ . All measurements were carried out at (20 ± 0.2) °C.

Results and discussion

In fig. 2 (for valeric acid) and in fig. 3 (for caproic acid) the experimental dependences of the ratio V/V_R on $1/b$ for two of the measured solutions of each acid are presented. Despite the scattering of the experimental points it is obvious that a linear dependence of V/V_R on $1/b$ exists – with increase of the concentration

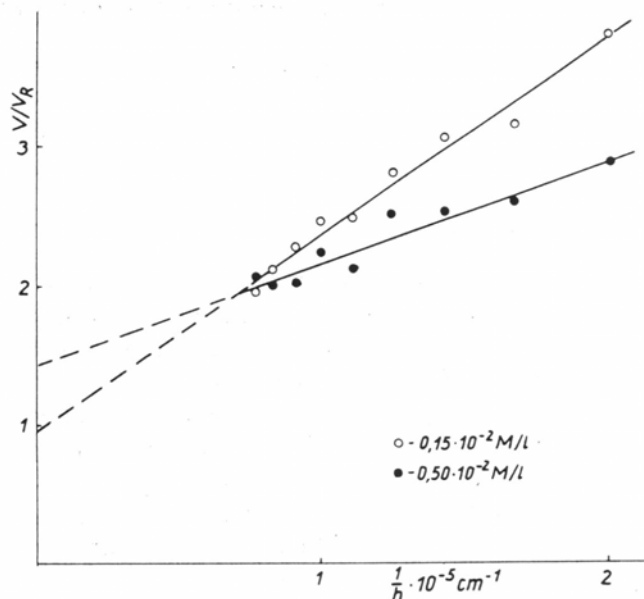


Fig. 2. Dependence of the ratio V/V_R on $1/b$ for aqueous solutions of valeric acid at two of the measured 7 concentrations

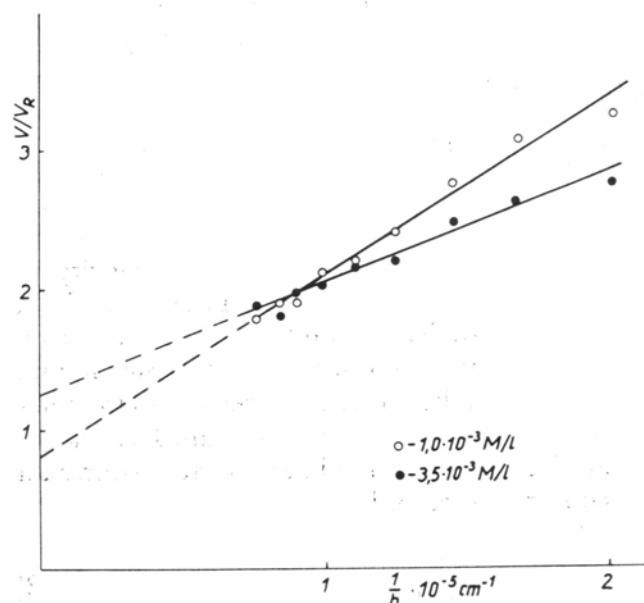


Fig. 3. Dependence of the ratio V/V_R on $1/b$ for aqueous solutions of caproic acid at two of the measured 7 concentrations

c_0 the slopes of the lines decrease. The dependences of the slope k on $1/\Delta\sigma_0 = 1/b \cdot c_0$ for both acids are presented in fig. 4. The latter dependence is also linear.

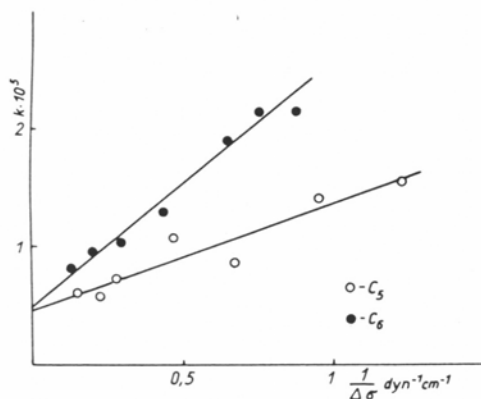


Fig. 4. Dependence of the slope k on $1/\Delta\sigma_0 = 1/b \cdot c_0$ for aqueous solutions of valeric (C_5) and caproic (C_6) acids

These results agree well with equation [4]. We believe that this is a proof that in the systems under investigation the surface diffusion plays a determining role. Indeed, if we assume that the surface diffusion is negligible, from equations [1] (with $D_s = 0$) and [3] and Gibbs' adsorption isotherm we obtain

$$\frac{V}{V_R} = 1 + \frac{3D\mu RT}{c_0 b^2} \quad [5]$$

i.e. in this case the ratio V/V_R should not depend on the thickness b . This is in contradiction with the experimental data reported above. Therefore the observed deviations from Reynolds' equation are not due to the bulk diffusion. The quantitative estimate of the effect related to the bulk diffusion leads to the same conclusion. The coefficients of bulk diffusion D for valeric and caproic acids in water are not known but the data about D of normal alcohols (11) and lauric acid (12) in water suggest that a value of the order of $10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$ can be assumed. Thus for the second term on the right-hand side of [5] we obtain $1.4 \cdot 10^{-2}$ while the experimental results show that at small thicknesses the ratio V/V_R goes up to 3.

At the same time it must be pointed out that the quantitative agreement between theory and experiment is in some respects unsatisfactory. For example the intersections in figs. 2–4 differ

from the theoretical values (unit for V/V_R vs. $1/b$ and zero for k vs. $1/\Delta\sigma_0$). Most probably this is due to the deviations from the plane parallel profile of the film at great thicknesses and low surfactant concentrations. Other possible causes can be: the absence of complete adsorption equilibrium before formation of the film at low concentrations, inaccuracies in the calculation of the disjoining pressure, film radius instability etc.

The values of the coefficients of surface diffusion D_s calculated from fig. 4 are $1.5 \cdot 10^{-4} \text{ cm}^2 \cdot \text{s}^{-1}$ for valeric acid and $3.3 \cdot 10^{-4} \text{ cm}^2 \cdot \text{s}^{-1}$ for caproic acid. Because of the above stated limitations of the method, we do not think that it can give exact values of the coefficients of surface diffusion. Therefore we confine ourselves to affirm that both coefficients are of the order of $10^{-4} \text{ cm}^2 \cdot \text{s}^{-1}$.

In conclusion we must emphasize that such considerable deviations from Reynolds' equation must not necessarily be expected in all systems of this type. Therefore the conclusions made in this work should not be generalized for all other cases. However, they demonstrate the necessity of careful and cautious analysis of the experimental data for the hydrodynamic behaviour of the thin liquid films.

Summary

The rate of thinning of foam films of aqueous solutions of valeric and caproic acids is studied. Substantial deviations from Reynolds' equation have been obtained which correspond to the previous theoretical prediction. The higher rate of thinning of the films is considered to be due to the effect of surface diffusion. From the experimental data and the theory the order of magnitude of the surface diffusion coefficient for these systems has been estimated.

Zusammenfassung

Die Verdünnungsgeschwindigkeit von Schaumfilmen aus wäßrigen Lösungen der Valerian- und Capronsäure wurde erforscht. Bedeutende Abweichungen von der Reynolds' Gleichung, die der theoretischen Vorhersagung entsprechen, wurden festgestellt. Die erhöhte Verdünnungsgeschwindigkeit wurde als Folge der Oberflächendiffusion betrachtet. Die Größenordnung der Koeffizienten der Oberflächendiffusion dieser Systeme wurde aus den experimentellen Werten und der Theorie berechnet.

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