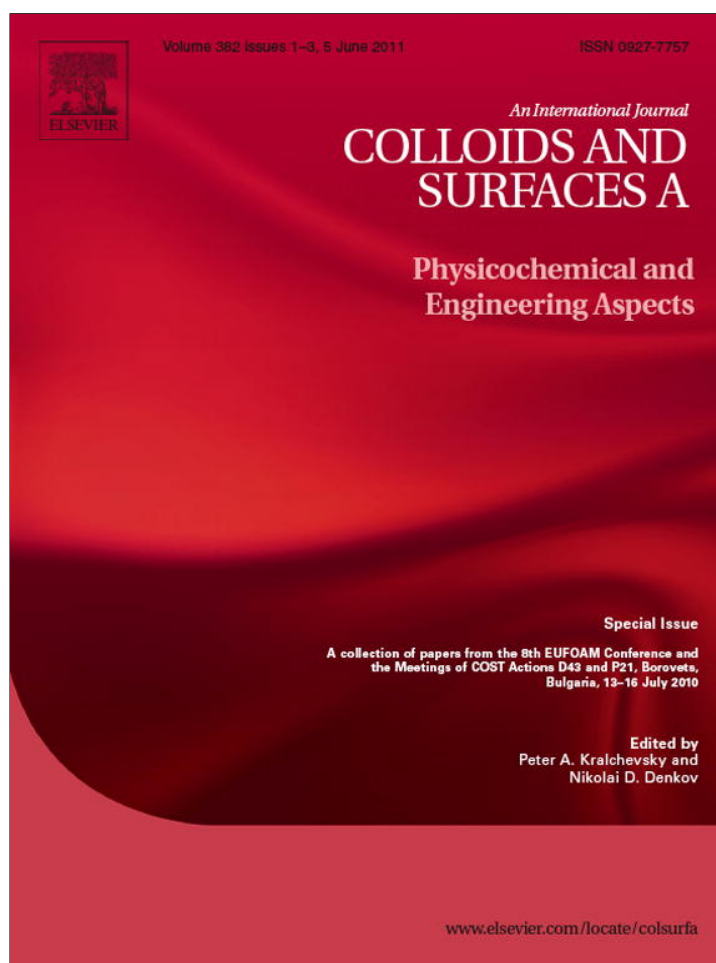


Provided for non-commercial research and education use.
Not for reproduction, distribution or commercial use.



This article appeared in a journal published by Elsevier. The attached copy is furnished to the author for internal non-commercial research and education use, including for instruction at the authors institution and sharing with colleagues.

Other uses, including reproduction and distribution, or selling or licensing copies, or posting to personal, institutional or third party websites are prohibited.

In most cases authors are permitted to post their version of the article (e.g. in Word or Tex form) to their personal website or institutional repository. Authors requiring further information regarding Elsevier's archiving and manuscript policies are encouraged to visit:

<http://www.elsevier.com/copyright>



Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa

Statistics of rupture in relation to the stability of thin liquid films with different size

Theodor D. Gurkov^{a,*}, Jana K. Angarska^b, Krassimir D. Tachev^b, Wolfgang Gaschler^c^a Department of Chemical Engineering, Faculty of Chemistry, University of Sofia, James Bourchier Avenue 1, 1164 Sofia, Bulgaria^b Faculty of Natural Sciences, University of Shumen, 9712 Shumen, Bulgaria^c BASF SE, 67065 Ludwigshafen am Rhein, Germany

ARTICLE INFO

Article history:

Received 30 September 2010

Received in revised form

29 November 2010

Accepted 2 December 2010

Available online 10 December 2010

Keywords:

Lifetime statistics

Probability for rupture

Coalescence

Thin liquid films

Drainage rate

Size dependence of stability

ABSTRACT

We study the stability and the thinning behavior of foam films in the presence of ionic surfactant. Using the method of capillary cell at low pressures (20–50 Pa), combined with interference microscopy, we measured the film thickness vs. time, the critical thickness of rupture, and the lifetime of films with different sizes. The film behavior is characterized by two separate stages: at first, there is a hydrodynamic thinning without rupture; afterwards, film rupture occurs as a stochastic process. The measured lifetimes in an ensemble of films are scattered in a certain range. We found that this statistical behavior is well described by a specific distribution, with cumulative probability $1 - \exp(-\beta t^2/2)$. By means of theoretical considerations, this distribution is derived from the time dependent differential probability for film rupture. Fitting of experimental data for the statistics of the film lifetimes is performed. This permits one to find the average transient lifetime at the stochastic stage; thus, thinning and rupture are distinguished. The size dependence of the drainage time is shown to comply with theories which describe the behavior of films with irregular thickness. The time for thinning, and the inverse drainage rate coefficient, scale with the film radius as $r_f^{4/5}$. This work may be relevant to understanding the stability of fluid dispersions in dependence of the particle size.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

The stability of fluid dispersions is governed to a large extent by the behavior of the thin liquid films which intervene between the bubbles or drops. For this reason, the films have been subject of both experimental and theoretical studies. Intrinsically unstable films, which live only very shortly (for seconds), are relevant to the problem of successful formulation of dispersions.

The film stability has been recognized to have a stochastic nature, as suggested by experimental observations—the measured lifetimes are usually scattered in a certain range [1,2]. Attempts to explain the origin of such a statistical behavior have not yet led to a final and commonly accepted conclusion. One source of random instability is related to the mechanism of film rupture by growth of capillary waves. The hydrodynamics of wave evolution, and its connection with the critical thickness of rupture and the film lifetime, have been investigated theoretically (see, e.g., Refs. [3–6]). The significance of this mechanism has recently been disputed [7], for bubbles in the 100 μm size range colliding in aqueous salt solutions. It was found that in all cases coalescence occurred at the

dimple rim that was also the thinnest part of the water film (where the local film thickness had minimum). The latter region was much smaller than the wavelength of an unstable (critical) fluctuation wave [7]. The film ruptured quickly when the local minimum in the thickness fell below about 5 nm, and therefore, went into the range of the attractive van der Waals–Lifshitz forces [7].

Breakdown of liquid films which happens along the circumference (the thinnest part, or the rim), has been considered also in the context of fluctuations in the local surfactant coverage [8,9]. Drop-to-drop variations in the adsorbate density were assumed to correspond to the normal distribution [8]. That premise led to an expression for the cumulative distribution of the coalescence times which was fitted to experimental data [2,9].

In this work we follow a simple approach, without entering into details about the physical mechanism of film instability. We consider the statistical behavior of the film lifetime in the frames of a model representation, based on the time-dependent differential probability, $p(t)$, for rupture within small time intervals Δt . A particular function $p(t)$ is used to derive the cumulative distribution of the lifetimes, which is found to be in good agreement with the experimental measurements. We have chosen a system (aqueous solution of ionic surfactant) in which the films are basically unstable, and evolve in two stages—continuous drainage, and stochastic rupture.

* Corresponding author. Tel.: +359 88 9777 441; fax: +359 2 962 5643.

E-mail address: tg@lcpe.uni-sofia.bg (T.D. Gurkov).

The thinning process is discussed in view of the role of the thickness inhomogeneity. The actual drainage is observed to be faster than that predicted by the Reynolds equation [10] for planar circular films with tangentially immobile surfaces. The influence of the interfacial mobility, as explicated in Ref. [11], is not important for surfactant concentrations sufficient to ensure good adsorption coverage. We find that the main factor determining the drainage behavior is the non-homogeneity of the thickness. The Manev–Tsekov–Radoev (MTR) theory [12] is confirmed to adequately describe the obtained data, as the drainage time and the inverse drainage rate coefficient both scale with the film size in the predicted form, $\propto r_f^{4/5}$.

2. Theory—statistics of film rupture

A simple model treatment is proposed below, with the goal to rationalize the apparent stochastic nature of the film lifetime. In particular, we derive an expression for the cumulative probability, $P_c(\tau)$, that the film ruptures within a certain finite time interval, τ . This provides a statistical distribution of the lifetimes, which is compared to experimental measurements in Section 4.

Let us consider small time intervals, Δt . With $p(t)$ we denote the probability that a film ruptures within the interval Δt around the time t . This probability originates from the physical processes causing instability in the film. In principle, rupture is not deterministic, in the sense that it cannot be predicted exactly, for example, by solving the hydrodynamic equations for the time evolution of the thinning film. This conclusion stems from practical observations. The reason for such an indeterminacy lies in the presence of inherent factors which bring about statistical behavior. The latter may originate, for example, from the following:

- Disturbances in the shapes of the menisci and the film surfaces, as these are perfectly symmetric only in theoretical calculations, but not in the real systems (where, e.g., the pressure may fluctuate, etc.);
- Variable density of surfactant adsorption layers, eventually caused by thermal fluctuations in the local concentration, or by accidental convections;
- Corrugations of the film surfaces, due to fluctuation capillary waves which may appear randomly; etc.

In any case, one may expect that the relevant probability $p(t)$ should be time-dependent, if there are any processes or physical changes in the film which go on with time. As a subject of our study, we consider films that are continuously thinning. Therefore, we have to take into account the functional dependence $p(t)$ explicitly. It can be represented by a model expression, for example, of polynomial type:

$$p(t) = B_1 t + B_2 t^2 + B_3 t^3 + \dots \quad (1)$$

A detailed calculation of the $p(t)$ relation can be a rather difficult task. It should involve theoretical analysis of the hydrodynamics of thinning, fluctuations, instabilities, etc. Such a treatment remains entirely out of the scope of the present work. We adopt an even simpler form of Eq. (1),

$$p(t) = Bt \quad (1a)$$

It will be shown below that Eq. (1a) is sufficient for obtaining a cumulative distribution that describes some experimental data well. A natural extension of the proposed approach is to take more terms in the polynomial expansion, Eq. (1), or select different type of function for $p(t)$. Then, a corresponding statistical distribution of the film lifetimes would result, and can be compared with real measurements.

During their time evolution, liquid films usually stay stable while the thickness remains large. Rupture starts happening after the thinning has led to a stage when instabilities occur. In Eqs. (1), (1a), the time $t=0$ corresponds to the moment when a possibility for film rupture first appears.

Now let us see how the probability $p(t)$ is related to the macroscopic statistical behavior of the film lifetime. We take a time interval τ which consists of $n = \tau/\Delta t$ number of pieces Δt . The quantity

$$p([k+1]\Delta t) \prod_{i=0}^k \{1 - p(i\Delta t)\} \quad (2)$$

specifies the probability for rupture exactly in the $(k+1)$ -st interval Δt , for arbitrary $k=0, 1, 2, \dots, (n-1)$. Here we mention that the film survives the first k intervals Δt when it breaks at the $(k+1)$ -st one. The next step in our derivation is to find the probability for film breakdown at any moment of time between 0 and τ , which means at any Δt between the first and the n -th. This (cumulative) probability, $P_c(n)$, is routinely obtained by summation over the constituent events [13,14].

$$P_c(n) = \sum_{k=0}^{n-1} p([k+1]\Delta t) \prod_{i=0}^k \{1 - p(i\Delta t)\} \quad (3)$$

Eq. (3) can be useful only in combination with an explicit formula for $p(t)$ —the probability that the film ruptures within Δt around t . We suppose Eq. (1a) is appropriate; this yields

$$P_c(n) = \sum_{k=0}^{n-1} B(k+1)\Delta t \prod_{i=0}^k \{1 - Bi\Delta t\} \quad (4)$$

Exact calculation according to Eq. (4) is to be performed numerically. However, under reasonable assumptions an analytical expression can be derived. For small Δt and small p , we set

$\prod_i = \exp\left(\ln \prod_i\right)$, replace the summation of logarithms by integration, and expand in series for small $(B\Delta t)$. The result reads

$$P_c(\tau) = 1 - \exp\left(-\frac{1}{2}\beta\tau^2\right) \quad (5)$$

(with $\beta=B/\Delta t$, $\tau=n\Delta t$). Eq. (5) gives the cumulative probability that the film ruptures at any time between 0 and τ ; it represents a particular case of the Weibull distribution. The function $P_c(\tau)$, Eq. (5), is used below for data fitting.

The Weibull distribution finds application in the engineering science for failure analysis, to describe the statistics of the lifetimes of units when effects of fatigue and wear-out are operative [15]. In the form $P_c(\tau) = 1 - \exp(-\text{const} \cdot \tau^\alpha)$, $\alpha = 1.0$ means random failures (independent of age), while $\alpha > 1.0$ indicates wear-out failures [15]. In our case $\alpha = 2$, which means that the probability for rupture increases with time; the latter feature is reflected in Eq. (1a).

It is convenient to characterize the distribution by the parameter $\tau_{1/2}$ —the time at which there is a probability of 0.5 for rupture:

$$P_c(\tau_{1/2}) = 0.5; \quad \beta\tau_{1/2}^2 = 2 \ln 2 \quad (6)$$

$\tau_{1/2}$ can be found from the statistics of measured lifetimes. The obtained results for $\tau_{1/2}$ allow us to distinguish what part of the overall film lifetime can be attributed to the stochastic process of rupture.

3. Experimental

We investigated thin liquid films stabilized by the surfactant Dowfax 2A1, which contains two different individual substances as

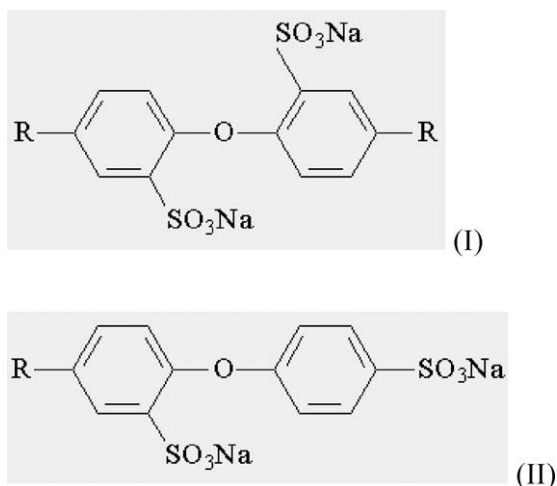


Fig. 1. Chemical components in the surfactant Dowfax 2A1: (I) 8–15%; (II) 28–36% active substance.

surface active ingredients in aqueous solution. The chemical composition [16] is depicted in Fig. 1. The surfactant was manufactured by Dow Europe SA, Horgen, Switzerland.

Films were made by sucking out aqueous phase from a biconcave meniscus held in a glass capillary. The cell was a modification of that proposed by Scheludko and Exerowa [17]. The experimental setup is presented schematically in Fig. 2. The method has been described previously [18,19], so that the full details will not be given here. The film size was controlled by means of a syringe to maintain the air pressure.

The observations were carried out in reflected monochromatic light (with wavelength $\lambda = 551 \text{ nm}$), so that the interference picture gave information about the local film thickness. The latter was expressed as equivalent water thickness, h_w , determined from the formula

$$h_w = \frac{\lambda}{2\pi n} \arcsin \left\{ \frac{\Delta}{1 + [4R/(1 - R^2)](1 - \Delta)} \right\}^{1/2} \quad (7)$$

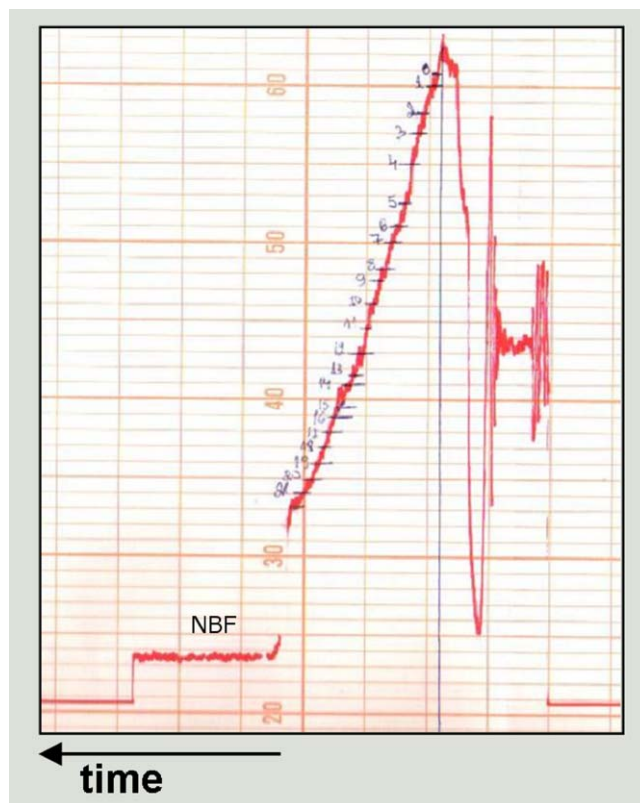


Fig. 3. Sample interferogram, that is, the reflected light intensity (a.u.) vs. time.

h_w is calculated assuming a homogeneous refractive index, n , of the bulk solution in the film interior; $R = (n - 1)^2 / (n + 1)^2$, and $\Delta = (I - I_{\min}) / (I_{\max} - I_{\min})$. Here I is the instantaneous intensity of the light reflected from the film; I_{\min} , I_{\max} correspond to the minimum and maximum values of I . I is obtained by recording the photo-current from a small part of the film around the periphery. The measurements of I were performed contin-

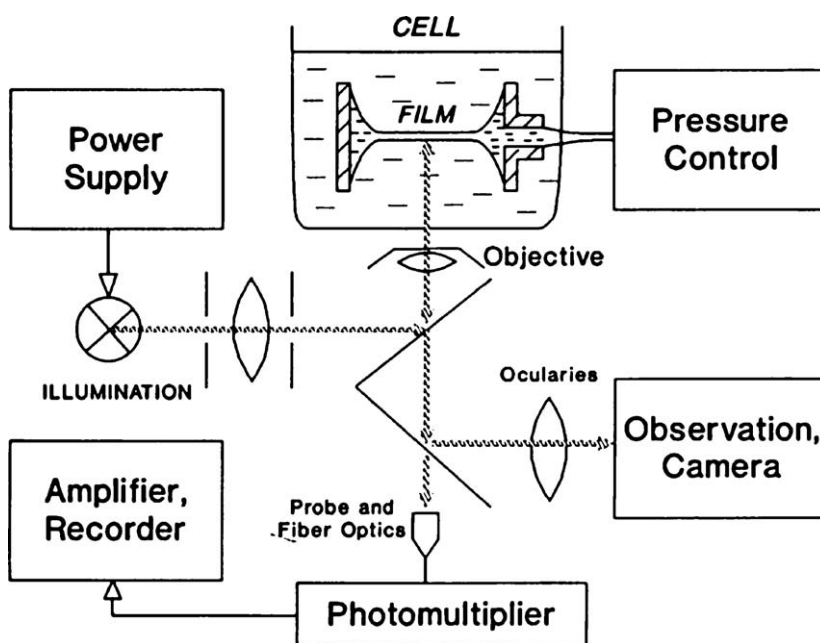


Fig. 2. Sketch of the experimental setup for thin liquid film measurements.

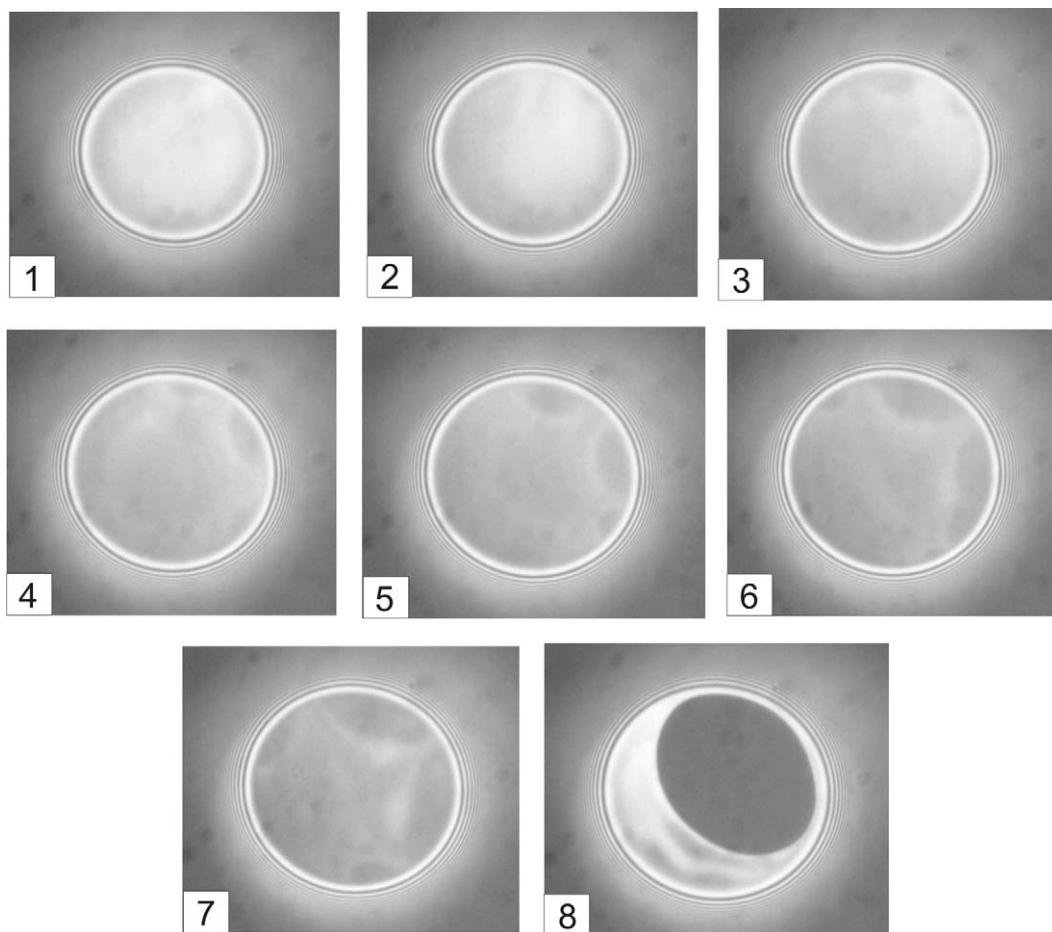


Fig. 4. Sequence of images illustrating the time evolution of a foam film; the pictures correspond to the following times: (1) 76 s, (2) 81.2 s, (3) 86.1 s, (4) 91 s, (5) 95 s, (6) 99 s, (7) 103 s, and (8) 110 s after the film formation.

uously as the film was thinning, so the kinetics of drainage was monitored as a function of time. Fig. 3 shows an example of the $I(t)$ dependence, which is converted to $h(t)$ using Eq. (7).

We studied systems with 0.005% and 0.05% Dowfax, in the presence of 0.5 M NaCl, at the temperature of 40 °C. The conditions were selected in such a way that the films should be unstable, in the sense of not reaching a constant equilibrium thickness. All films were draining, until a transition occurred; the latter was either rupture or formation of a very thin Newton Black Film (NBF). The cases illustrated in Figs. 3 and 4 include appearance of NBF at the end of the film lifetime. In other cases the films ruptured directly, without NBF. We were interested in the thinning stage (before the transition); the critical thickness of the transition, h_{cr} , was also measured. The lifetime, τ_{total} , is defined as the time elapsed between the moment when the film thickness corresponds to a point around the interference maximum (Fig. 3, $h \approx 95$ nm), until the transition happens. The statistical nature of the lifetime is discussed below in view of the theoretical considerations from Section 2.

We formed films which had three different sizes, with radii $r_f = 0.0050, 0.0100, 0.0150$ cm. Our purpose was to explore how the drainage time depended upon r_f .

From Fig. 4 one sees that the film thickness is irregular, in other words, the two opposing surfaces are not exactly plane parallel, there are asymmetric thinner and thicker parts which change with time. This fact bears relevance to the drainage rate, and its size dependence.

4. Results and discussion

Fig. 5 summarizes the results for the lifetime and the critical thickness of the studied films. In each particular system, the correlation plot $h_{cr}(\tau_{total})$ produces no evidence of any specific relation between these two quantities; the experimental points lie in scattered clouds. This confirms the statistical nature of the film behavior—both the critical thickness and the drainage rate can fluctuate.

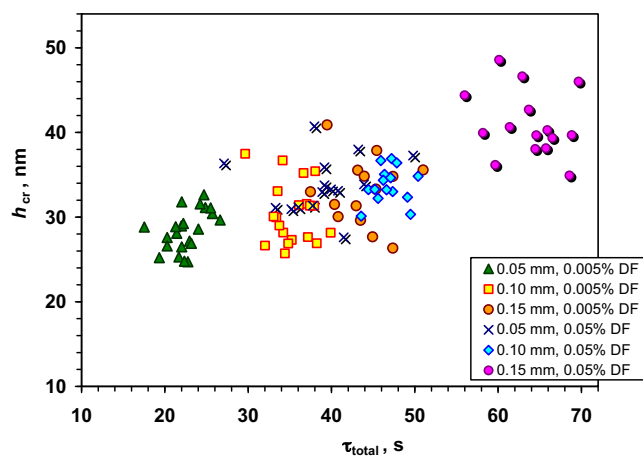


Fig. 5. Correlation plot of the measured critical thickness, h_{cr} , and the lifetime, τ_{total} .

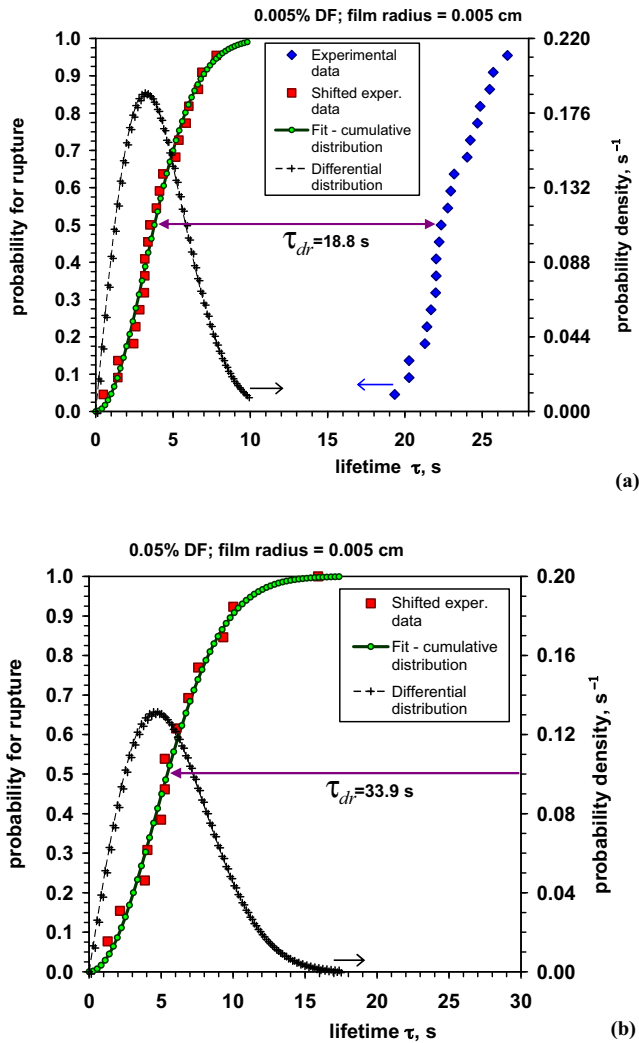


Fig. 6. (a, b) Sample statistical data: Fraction of films that rupture until the moment τ (diamonds and squares), fitted with the model distribution. The measured τ is shifted on the time axis, so that the theoretical curve can fit the experimental points with one adjustable parameter.

In Fig. 5, a marked trend is noticed in dependence of the film radius: larger r_f leads to longer lifetime τ_{total} . On the other hand, the influence of the film size on h_{cr} is relatively weak. In general, higher surfactant concentration brings about an increase of the lifetime. In order to rationalize these features of the stability, it is important to recognize the existence of two distinct stages in the evolution of the films. First, there is a process of drainage during which no rupture can occur; then, a second stage comes, when the film breakdown happens stochastically, and the rupture events are governed by certain probability. Below, after analyzing the statistics of rupture, we will separate the contribution of the pure drainage, τ_{dr} , in the total lifetime, τ_{total} . Next, we will comment on the role of the film size for the drainage time, that is, how τ_{dr} scales with r_f .

4.1. Statistics of film rupture

The scattered data from Fig. 5 are fitted for each system with the cumulative probability function $P_c(\tau)$, Eq. (5). For this purpose, the number of films which have disappeared within a time period τ , divided by the number of all measured films in a given series, is taken to represent approximately the cumulative probability for rupture. In such a way the ordinates of the data points in Fig. 6a, b are obtained. The time on the abscissa is shifted to the left with an

Table 1
Parameters of film behavior in systems containing Dowfax 2A1 (+0.5 M NaCl, 40 °C).

Film radius, r_f (cm)→	0.005	0.010	0.015
0.005 wt% Dowfax			
τ_{total} (s)	22.64	35.51	44.54
$\tau_{1/2}$ (s)	3.80	3.87	4.80
τ_{dr} (s)	18.84	31.64	39.74
h_{cr} (nm)	28.4 ± 2.4	30.5 ± 3.6	33.0 ± 3.9
0.05 wt% Dowfax			
τ_{total} (s)	39.32	46.82	63.95
$\tau_{1/2}$ (s)	5.43	3.56	7.21
τ_{dr} (s)	33.89	43.26	56.74
h_{cr} (nm)	33.6 ± 3.4	33.8 ± 2.1	41.0 ± 3.9

equal interval, τ_{dr} , for all points, as shown in Fig. 6a. From the total time (diamonds, Fig. 6a) we subtract the time of the drainage stage, τ_{dr} , during which the probability for rupture is equal to zero. The resulting shifted experimental curve is well fitted by the theoretical $P_c(\tau)$, Eq. (5). The adjustable parameter is β , or equivalently, $\tau_{1/2}$, Eq. (6). τ_{dr} is also varied to achieve precise horizontal alignment of the data with the fit; in other words, τ_{dr} is found from the fit as well.

For all cases in the present study (Fig. 5), the cumulative probability function $P_c(\tau)$ from Eq. (5) turns out to adequately represent the statistical behavior of the film rupture. Therefore, we infer that even the simple dependence $p = Bt$ (Eq. (1a)) can be relevant for the description of a specific system—perhaps because the times are short, the $p(t)$ relation can be approximated to a line. On the other hand, in a recent work (Ref. [20]) the lifetime statistics of very long living films was analyzed. It was found that the cumulative distribution was of Weibull type (cf. Eq. 5), but with a power index of 1.55 in the exponent [20], while in our work, Eq. (5), the power index is 2. Such a difference is likely to originate from the $p(t)$ dependence, which can be complicated for long times.

Actually, the Weibull distribution should not be regarded as universal or unique, as far as other possible choices for interpretation of the film stochasticity have also been discussed in the literature. In Ref. [21], the log-normal distribution was employed to describe data for the coalescence efficiency of micron-sized emulsion drops. On the other hand, a theoretical distribution [8] which resembles the normal (Gaussian) one was utilized in Refs. [8,9] to fit experimental results for the lifetimes of millimeter-sized drops and bubbles. It seems plausible to infer that specific features of the investigated system, connected with relevant physical factors, may influence the macroscopic manifestation of the statistical coalescence behavior. Hence, the applicability of a given theoretical function can be proven by fitting of concrete data.

Our results for the film lifetimes, including the contributions of the unstable stage with the statistically averaged time for rupture, $\tau_{1/2}$, and the thinning stage of duration τ_{dr} , are collected in Table 1.

$$\tau_{total} = \tau_{1/2} + \tau_{dr} \quad (8)$$

One can discern a well pronounced trend of increasing lifetime, τ_{total} , with the film radius r_f , which is due to the increase of the drainage time, τ_{dr} (see Table 1).

4.2. Film drainage behavior

Thinning of films with irregular thickness was considered by Manev, Tsekov and Radoev [12]; quantitative description of the non-homogeneities associated with accelerated drainage led to the following equation for the thinning velocity:

$$V_{MTR} = \frac{1}{6\mu} \sqrt[5]{\frac{h^{12}(P_\sigma - \Pi)^8}{4\sigma^3 r_f^4}} = -\frac{dh}{dt} \quad (9)$$

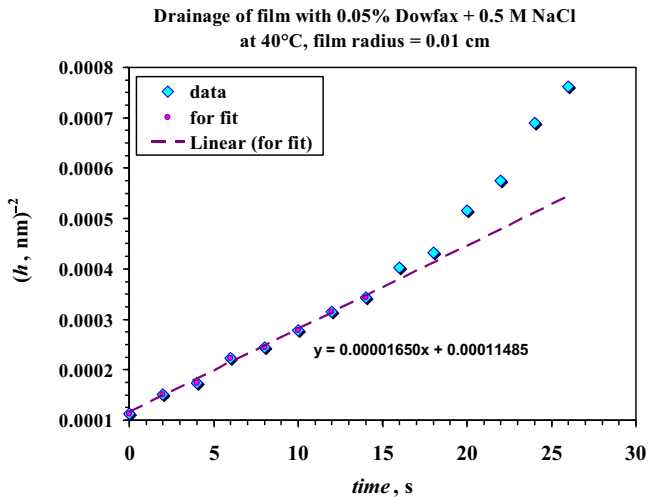


Fig. 7. Attempt for scaling of the film drainage according to the Reynolds equation.

where μ is the liquid viscosity, σ is the surface tension, P_σ is the capillary pressure (that sucks the liquid from the film), and Π is the disjoining pressure (due to molecular forces between the film surfaces). In our systems the thinning happens at constant film radius, so r_f in Eq. (9) can be factored out; the integration over the time, from 0 to τ_{dr} , then yields

$$r_f^{4/5} F(h) = \text{const.} \tau_{dr} \quad (10)$$

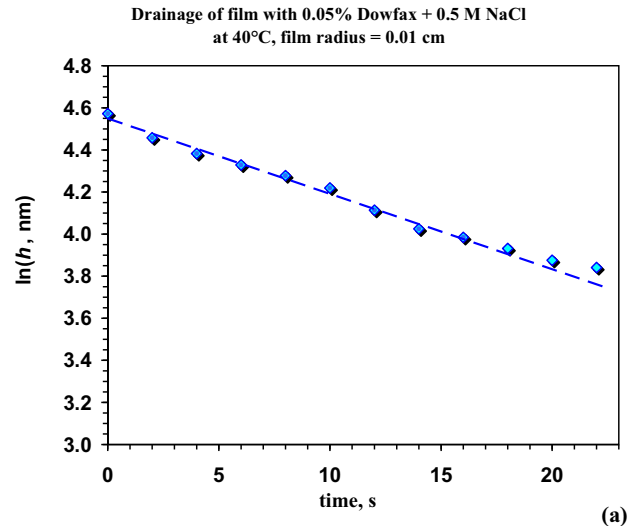
Here $F(h)$ incorporates the effect of the disjoining pressure, $\Pi(h)$, which is expected to affect the drainage as far as the thickness falls below ~ 100 nm. Eq. (10) suggests that the thinning time should scale as $r_f^{4/5}$. We check if this is true with the data for τ_{dr} from Table 1; they are plotted in Fig. 9. The results prove that the scaling predicted by Eq. (10) really holds. Other authors have also observed good agreement between experimental measurements and the MTR Eq. (9)—examples are presented in Refs. [22,23].

Let us comment briefly on the drainage rate of the investigated films. The Reynolds Eq. (11) describes the case of a circular film with perfectly plane-parallel surfaces which are tangentially immobile. If Π is negligible (for thicker films), Eq. (11) can be cast into integrated form, Eq. (11a). The latter can be used for data chart—see Fig. 7.

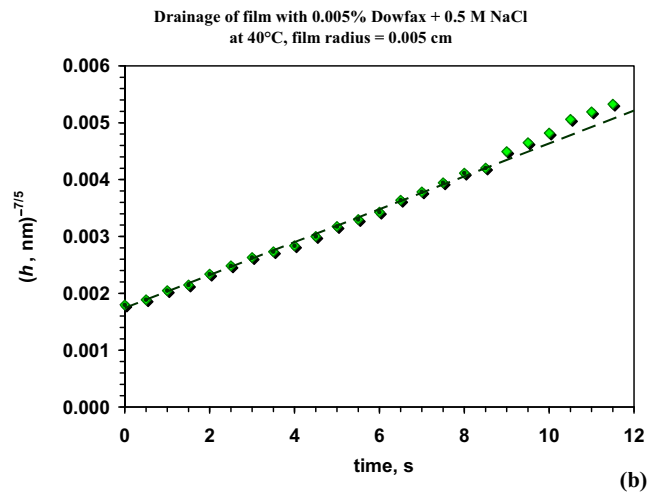
$$V_{Re} = -\frac{dh}{dt} = \frac{2h^3}{3\mu r_f^2} (P_\sigma - \Pi) \quad (11)$$

$$\frac{1}{h^2} = \frac{1}{h_0^2} + \frac{4P_\sigma}{3\mu r_f^2} t \quad (11a)$$

The initial portion of the $h^{-2}(t)$ dependence is indeed a straight line (Eq. (11a)). At smaller thicknesses, the influence of the van der Waals attraction (negative Π) would lead to accelerated drainage, so the points deviate from the line. The slope in Fig. 7 can be evaluated, knowing that $P_\sigma = 30.1$ Pa in our case. The expected slope according to Eq. (11a) is $4 \times 10^{-6} (\text{nm}^2 \text{s})^{-1}$, while the real one, determined from Fig. 7, is $1.65 \times 10^{-5} (\text{nm}^2 \text{s})^{-1}$. The observed faster thinning can in principle be due to surface mobility; however, this is unlikely to be so in the concrete case, because the surfactant concentration is high (above the Critical Micellization Concentration). Therefore, the interfaces should be immobilized by the dense layer of adsorbed surfactant. The most plausible cause for the fast drainage is the inhomogeneous thickness. Such a conclusion is strongly supported by the fact that τ_{dr} scales as $r_f^{4/5}$ (Fig. 9, Eq. (10)), and we do not have $\tau_{dr} \propto r_f^2$ as Eq. (11a) would suggest.



(a)



(b)

Fig. 8. The initial film thinning [starting from a thickness $h(t=0)$ close to that at the first interference maximum], described as (a) $\ln(h) \propto t$, and (b) $h^{-7/5} \propto t$.

Fig. 8 further illustrates the process of thinning. The simple empirical dependence

$$V = -\frac{dh}{dt} = \alpha h \quad (12)$$

is applied to prepare the plot in Fig. 8a; $\ln h(t) = \ln h(0) - \alpha t$. Eq. (12) was found to be in accord with experimentally measured $h(t)$ in Ref. [24]. In Fig. 8a, the validity of Eq. (12) cannot be anticipated to extend (with the same rate coefficient) in the whole range of thicknesses down to h_{cr} , because of the influence of $\Pi(h)$. Still, the initial part of the $h(t)$ dependence is well fitted by Eq. (12). We determine α from the experimental curves $\ln h \propto t$ for all studied systems.

From Eq. (12) it follows that α^{-1} should scale with the film radius r_f in the same way as the drainage time does. Having in mind Eq. (10), we reach the surmise that

$$\frac{1}{\alpha} \propto r_f^{4/5} \quad (13)$$

The latter relation is verified by plotting the available values of α^{-1} in Fig. 9 (see the right-hand ordinate axis). Evidently, the scaling of $1/\alpha$ according to Eq. (13) is confirmed.

For the sake of completeness, we checked also the law of thinning predicted by Eq. (9)—in absence of Π there has to be $h^{-7/5} \propto t$. Fig. 8b shows this to be true, in a limited interval with thicker films.

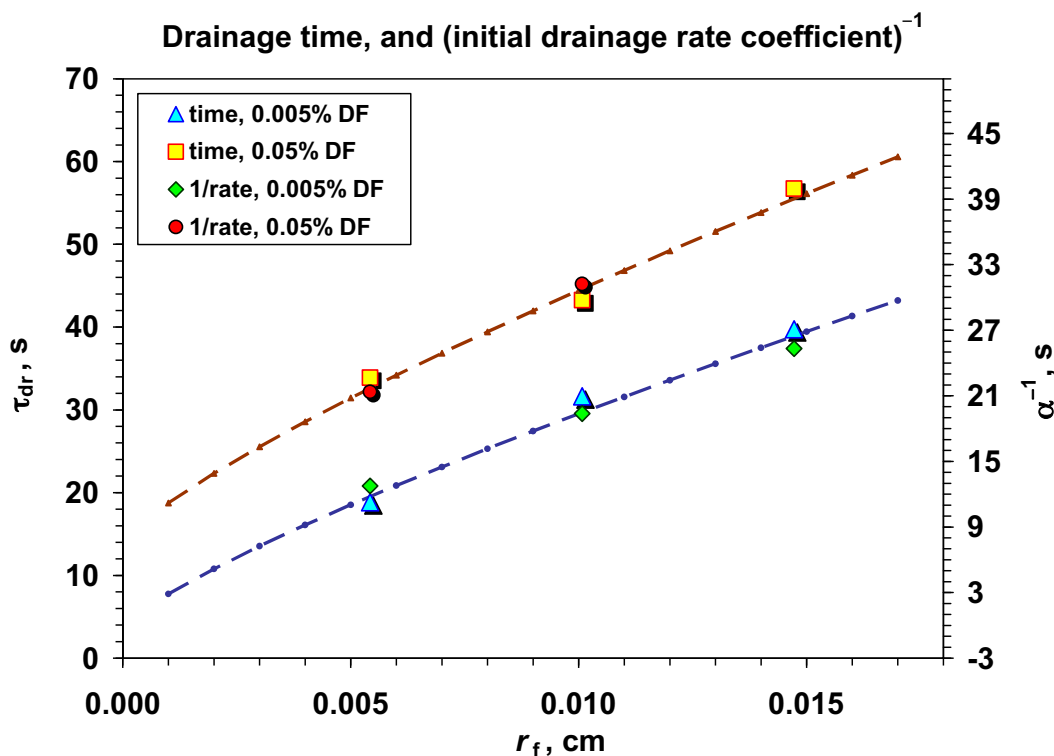


Fig. 9. The characteristic parameters of film thinning (τ_{dr} , α^{-1}) scale as $r_f^{4/5}$: the dashed lines correspond to $3.65 + 1030 \times r_f^{4/5}$ for 0.005% DF; $13.9 + 1215 \times r_f^{4/5}$ for 0.05% DF.

Of course, for a full comparison with the theory, the disjoining pressure $\Pi(h)$ should be taken into account. That task, however, may be complicated for films whose thickness is irregular.

5. Conclusions

We have investigated unstable liquid films, with time evolution that consists of thinning and stochastic rupture stages. The statistics of the film lifetime is described by a simple model which does not consider in detail the mechanism of rupture and the underlying physical phenomena. Instead, the cumulative distribution function is derived from a model time dependence of the probability, $p(t)$, for film rupture within a small interval Δt around a time t . It is assumed that the $p(t)$ relation is linear, which is reasonable for short times. The obtained peculiar integral distribution $P_c(t)$ is in good agreement with the measurements. From the fits with the model cumulative curve, we determine the average transient lifetime $\tau_{1/2}$ pertaining to the stage when rupture is possible. The total lifetime is a sum of $\tau_{1/2}$ and the drainage time.

The drainage time, and the inverse thinning rate coefficient, scale with the film radius as $r_f^{4/5}$. This is in accord with the expectations which follow from the MTR theory for films with irregular thickness.

Acknowledgements

This work was funded in part by BASF AG, Ludwigshafen, Deutschland. T.G. also wishes to acknowledge financial support from the EU program COST, Action D43—“Colloid and Interface Chemistry for Nanotechnology”.

References

- [1] G.E. Charles, S.G. Mason, *J. Colloid Sci.* 15 (1960) 236–267.
- [2] S.M. Reddy, P. Ghosh, *Chem. Eng. Sci.* 65 (2010) 4141–4153.
- [3] J.E. Coons, P.J. Halley, S.A. McGlashan, T. Tran-Cong, *Adv. Colloid Interface Sci.* 105 (2003) 3–62.
- [4] A. Oron, S.H. Davis, S.G. Bankoff, *Rev. Mod. Phys.* 69 (1997) 931–980.
- [5] T. Erneux, S.H. Davis, *Phys. Fluids A* 5 (1993) 1117–1122.
- [6] I.B. Ivanov, K.D. Danov, P.A. Kralchevsky, *Colloids Surf. A* 152 (1999) 161–182.
- [7] I.U. Vakarelski, R. Manica, X. Tang, S.J. O’Shea, G.W. Stevens, F. Grieser, R.R. Dagastine, D.Y.C. Chan, *Proc. Natl. Acad. Sci. U.S.A.* 107 (2010) 11177–11182.
- [8] P. Ghosh, V.A. Juvekar, *Trans. IChemE, Part A* 80 (2002) 715–728.
- [9] K. Giribabu, P. Ghosh, *Chem. Eng. Sci.* 62 (2007) 3057–3067.
- [10] L.D. Landau, E.M. Lifshitz, *Fluid Mechanics*, Pergamon Press, Oxford, 1984.
- [11] I.B. Ivanov, *Pure Appl. Chem.* 52 (1980) 1241–1262.
- [12] E.D. Manev, R. Tsekov, B. Radoev, *J. Dispersion Sci. Technol.* 18 (1997) 769–788.
- [13] T.T. Soong, *Fundamentals of Probability and Statistics for Engineers*, Wiley, Chichester, UK, 2004.
- [14] B.V. Gnedenko, *Theory of Probability*, 6th ed., Gordon & Breach, Amsterdam, 1997.
- [15] R.B. Abernethy, *The New Weibull Handbook*, fourth ed., North Palm Beach, FL, USA, 2000, ISBN 0-9653062-1-6.
- [16] M.J. Rosen, *Surfactants and Interfacial Phenomena*, 3rd ed., Wiley-Interscience, Hoboken, New Jersey, 2004.
- [17] A. Scheludko, D. Exerowa, *Kolloid-Z* 165 (1959) 148–151.
- [18] K.G. Marinova, T.D. Gurkov, O.D. Velev, I.B. Ivanov, B. Campbell, R.P. Borwankar, *Colloids Surf. A* 123–124 (1997) 155–167.
- [19] V. Simulescu, J.K. Angarska, E.D. Manev, *Colloids Surf. A* 319 (2008) 21–28.
- [20] S.T. Tobin, A. Meagher, B. Bulfin, M.E. Moebius, D. Weaire, S. Hutzler, A public study of the lifetime distribution of soap films, in: Poster PE11, Presented at the EUFOAM 2010 Conference, Borovets, Bulgaria, 14–16 July, 2010.
- [21] A. Nandi, A. Mehra, D.V. Khakhar, *Phys. Rev. Lett.* 83 (1999) 2461–2464.
- [22] J.E. Coons, P.J. Halley, S.A. McGlashan, T. Tran-Cong, *Colloids Surf. A* 263 (2005) 197–204; J.E. Coons, P.J. Halley, S.A. McGlashan, T. Tran-Cong, Drainage of emulsion and foam films in Scheludko-Exerowa cells, in: Proceedings of the XXI-*st* ICTAM, 15–21 August, Warsaw, Poland, 2004.
- [23] J.K. Angarska, C. Stubenrauch, E.D. Manev, *Colloids Surf. A* 309 (2007) 189–197.
- [24] J.K. Angarska, E.D. Manev, *Colloids Surf. A* 223 (2003) 27–34.