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Comparative validation of the analytical models for the Marangoni effect on foam film drainage

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ABSTRACT

The aim of this paper is to evaluate four of the well-known models for drainage of thin liquid films, containing non-ionic surfactants, by applying them to different types of draining foam films stabilized by either strong or weak non-ionic surfactants.

The effect of non-ionic surfactants on the drainage of foam films under different conditions was studied. The following series of surfactants were employed: (1) methylisobutyl carbinol (MIBC), (2) Dowfroth 200, (3) pentaethyleneglycol monodecyl ether ($C_{10}E_5$), (4) pentaethyleneglycol monododecyl ether ($C_{12}E_5$), (5) hexaethyleneglycol monododecyl ether ($C_{12}E_6$), (6) octaethyleneglycol monododecyl ether ($C_{12}E_8$) and (7) tetraethyleneglycol monooctyl ether (C_8E_4). The experimental 'thickness' *vs* 'time' dependences were processed with four kinetic models: (1) the model developed by Scheludko on the basis of the Stefan–Reynolds lubrication theory (Scheludko model); (2) the model of Radoev, Dimitrov and Ivanov for foam films confined between partially mobile planar gas–liquid surfaces (RDI model); (3) the model of Ruckenstein and Sharma for foam films with surfaces wrinkled by capillary waves (RSh model); (4) the model of Manev–Tsekov–Radoev for foam films with surfaces corrugated by quasi-stationary inhomogeneities (MTR model). A systematic validation based on the statistical level of uncertainty of the model predictions, as compared to the experimental results was preformed. The test on the model kinetic equations confirmed their validations reported in the literature. In addition, cases in which none of the models is valid were identified as well. Ultimately, it was concluded that thin film drainage is a complex phenomenon, which should be studied further by different experimental techniques and modelling approaches.

1. Introduction

In colloid science, thin liquid films (TLF) were established during the past century as an efficient model for studying the behaviour of disperse systems like froths and emulsions [1–4], as their dynamic behaviour, evolution and transient stability depend on the film drainage and rupture [5–7]. In all of these applications, surface-active substances, used to control the behaviour of the TLF play a critical role [1–4,8–10].

In most cases experiments on TLF were conducted by the so-called "Scheludko cell" or vertical frames, exploiting micro-interferometry or light scattering [1,3,11–14]. Light scattering was exploited along with the micro-interferometry for studying soap films in vertical frames [13,14]. However, such films exhibit multiple inhomogeneities and are difficult to model, while "Scheludko" cell offers well-defined and convenient conditions for modelling. In the latter method, both the transient and equilibrium thicknesses of single films formed between two bubbles or between two oil droplets or between a bubble and a solid substrate is determined from the light intensities reflected from the two film surfaces (e.g., Refs. [1,15–30]). These works were focussed on the influence of the mechanical properties of the film surfaces (e.g., the Marangoni stress, the surface diffusivity and the surface viscosity), the film geometry, and the type and concentration of surfactants and electrolytes on the film drainage and stability.

Many developments have been introduces into the theory of foam film drainage during the past fifty years. For example, Lee and Hodgson [31] reviewed theoretically the basic features of thin films for the cases of a drop in contact to flat interface and to another drop as well. Based on the lubrication and quasi-steady approximations Scheludko [32] applied the Stefan–Reynolds lubrication theory [33,34], developed for drainage of the liquid between two parallel solid discs, pressed by external force, to describe the foam and emulsion film drainage. He considered films with planar rigid

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and immobile surfaces between bubbles or emulsion droplets. This assumption has been validated for foam films of small radii (below 0.05 mm) [25,35,36]. Radoev et al. [37,38] developed further the theory by considering mobile film surfaces. They obtained the exact analytical solution of the equation for the surfactant mass balance inside the film. According to the latter model, the velocity on the film surfaces is governed by the combined effects of the liquid outflow, Marangoni effect, and surfactant adsorption. Later on, Radoev et al. [16] incorporated into the theory the effect of the surface diffusion on the interfacial velocity.

Contribution to the theory was the introduction of the effect of surface viscosity on the film drainage firstly by Ivanov and Dimitrov and later re-established by Karakashev and Nguyen [39,40]. However, the surface viscosity appears to be less important when the Marangoni effect is dominant for typical surfactant systems even with low concentrations.

These theoretical models are valid for non-ionic surfactants and are based on the lubrication and steady-state approximations valid at very small Reynolds and Peclet numbers [2]. Yet, this restriction is due to the laminar outflow of the thinning films, despite any turbulence, in which bubbles in contact could be involved in (e.g., chemical reactor).

With the development of computers, the general differential equation for drainage of films with deformable surfaces was solved numerically in a number of works (e.g., Refs. [41–44]). Thus, the corrugation of the film surfaces was explained [42,43] later with the formation of surface instability caused by the Marangoni effect. Numerical simulation of this instability causing asymmetric drainage of foam film was performed by Joye, Hirasaki and Miller [42,43]. They indicated that asymmetric film drainage is faster than axisymmetric. Valkovska and Danov [45] included an electrical term into the bulk pressure stress tensor and the electrostatic potential into the film, thus making the theory valid for ionic surfactants. Due to the complexity of the problem the differential equations were solved only numerically.

Manev and Nguyen [46] observed experimentally that the increase in the film radius correlates with the film thickness inhomogeneities, which accelerate the film drainage. Analytical solutions for the limiting cases of small and large deformation of the bubble caps were also obtained by Ivanov et al. [47]. The evolution of thin film with dimple was analytically obtained by Tsekov and Ruckenstein [48]. Empirical equations along with numerical solutions on film thinning between approaching drops were obtained by Davies et al. [49] and Jeelani and Hartland [50].

Moreover, experiments performed by Manev [51,52] established that the thinning rate of films with radius larger then 50 μm is inversely proportional to the film radius raised to the power 4/5, instead of power 2 as in the Stefan–Reynolds equation. This problem was analysed in different ways in the literature. Malhotra and Wasan [53] attributed the experimentally established dependence to the modulation of the pressure distribution in the adjacent meniscus by the film drainage, while Ruckenstein and Sharma [20] tried to explain it with the peristaltic action of surface hydrodynamic waves, formed during the film drainage and derived analytical kinetic equation (containing an empirical term). The problem was attacked from a different angle by Manev, Tsekov and Radoev [25], who assumed that quasi-stationary steady and static thickness inhomogeneities are the driving force for the faster film drainage. They solved the problem analytically and obtained another kinetic equation for the film drainage.

The above scrutiny on the literature shows that surfactant adsorption at the film surfaces plays a critical role in foam film drainage. In many cases, the effect of surfactant adsorption can be adequately accounted for by considering the Marangoni stress. The available theories for the Marangoni effect on foam film drainage can be represented by four models specified as follows:

1. The model of Scheludko [1,54] which is based on the Stefan–Reynolds lubrication theory [55]. A capillary "squeezing" force presses the film surfaces towards each other. The surfaces are assumed to be planar, rigid and tangentially immobile.
2. The model of Radoev, Dimitrov and Ivanov (RDI) [16]. The film drainage driven by the capillary pressure is controlled by the mobile but planar rigid film surfaces. The mobility of the film surfaces depends on the Marangoni stress, surface diffusion and surfactant adsorption.
3. The model of Ruckenstein and Sharma (RSh) [20]. The capillary pressure pushes the two immobile film surfaces towards each other. The surfaces are wrinkled by capillary waves pumping the liquid out peristaltically towards the film periphery, thus making the film draining faster.
4. The model of Manev, Tsekov and Radoev (MTR) [25]. The tangentially immobile film surfaces are corrugated by quasi-stationary inhomogeneities in film thickness which reduce the hydrodynamic repulsion between the film surfaces and, therefore, accelerate film drainage.

These models do not account for the dynamic effects produced by the electrical double layer, which can arise in TLF with ionic surfactants. For this reason, non-ionic surfactants are used for stabilizing the foam films here.

The aim of this paper is to evaluate these models by applying them to different types of draining foam films stabilized by either strong or weak non-ionic surfactants.

2. Foam film drainage theories

The key considerations and assumptions used to establish the foam film drainage theories can be summarized as follows [2]:

- Cylindrical coordinate system has been chosen (Fig. 1).
- The liquid is an incompressible Newtonian fluid.
- The lubrication approximation is assumed, i.e., $(h_0/R_0) \ll 1$, where h_0 is the initial thickness at the film centre and R_0 is the film radius (the Reynolds number $\ll 1$).
- The local variation of film thickness with radial coordinate is weak, i.e., $\partial h/\partial r \ll 1$.
- The contribution of the convective term is significantly smaller as compared to the contribution of the diffusive term in the film mass balance equation (the Peclet number $\ll 1$). Therefore the convective and time derivative terms in the film mass balance equation are neglected. This is the so-called "quasi-steady" approximation, imposing that the time dependences of all quantities can be expressed through the thickness h alone.
- The surfactant adsorption layers on the film surfaces are close to equilibrium.
- The effect from the surface viscosity is negligible compared to the Marangoni effect.

All of the above assumptions lead to a simplified system of differential equations solvable analytically with appropriate boundary conditions [2,10] as follows:

- Radial component of the Navier–Stokes equation with omitted convective and time derivative terms.
- Normal component of the Navier–Stokes equation in the lubrication approximation: $\partial P/\partial z = 0$.
- Continuity equation, mass balance equation in the film with omitted convective and time derivative terms.
- Mass balance equation on film surfaces and tangential stress boundary equation with omitted surface viscosity term.