



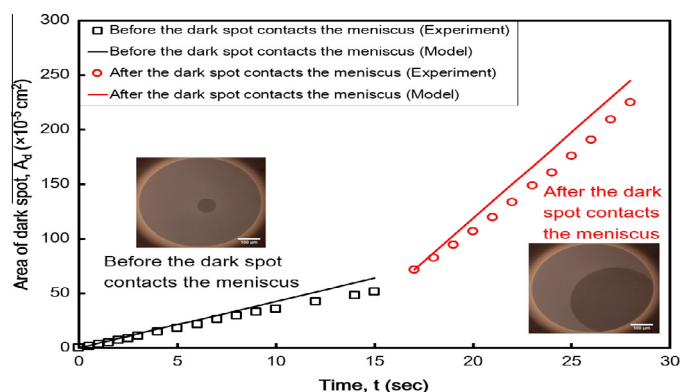
Stepwise thinning dynamics of a foam film formed from an anionic micellar solution



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GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 17 August 2016
Revised 14 October 2016
Accepted 18 October 2016
Available online 19 October 2016

Keywords:

Stratification
Foam film
Micelle
Dark spot
Anionic surfactant

ABSTRACT

Liquid films formed from a surfactant micellar solution thin in a stepwise fashion (stratify): the film thickness decreases layer-by-layer and dark spots appear (areas of the film with one micellar layer less than their surroundings). In a recent paper [*Langmuir* **2016**, 32, 4837–4847], we presented a two-dimensional diffusion model to explain the expansion of the dark spots inside the foam film formed from a nonionic surfactant micellar solution. Here, we apply the model to explain the dark spot expansion in the foam film formed from an anionic surfactant micellar solution of sodium dodecyl sulfate. We also apply this model to explain the expansion rate of the dark spot that makes contact with the meniscus. Our model adequately predicts the experimental measurements.

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1. Introduction

The foam film stratification phenomenon is the stepwise decrease in the thickness of a film containing layered particles between the confined film surfaces. The stratification is a universal phenomenon and has been observed in thin liquid films in the

presence of surfactant micelles [1–3], latex particles [4], silica particles [5], and polyelectrolyte surfactant mixtures [6,7]. During stepwise film thinning, dark spots (domains) that are one micellar layer less than the periphery appear inside the film. They reflect less incident light than the remaining part of the film and are seen as darker than their surroundings. Once a dark spot is formed, it radially expands and covers the film area. In the same manner, the film thickness decreases in regular steps with the formation and expansion of dark spots.

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Kralchevsky et al. [3] suggested in their vacancies condensation mechanism that the formation and expansion of the dark spots inside the film is controlled by the micellar self-diffusion between the film and meniscus. The gradient of the chemical potential causes the micelles to diffuse from the film to the meniscus, producing the vacancies as the film thins. The dark spots appear inside the film when the film reaches a sufficient concentration of vacancies to nucleate. The concentration of the vacancies inside the film depends on the effective micellar volume, film size, film thickness, and micellar polydispersity. Bergeron et al. [8] proposed a hydrodynamic model for the formation and early stage expansion of the dark spots (domain) in the foam film formed from sodium dodecyl sulfate (SDS) micellar solutions. The dynamics of the dark spot formation and expansion is driven by the equilibrium disjoining pressure that exhibits an unstable thickness region where the disjoining pressure isotherm has a positive slope. Their model explained the dark spot expansion dynamics in terms of the outward fluid flow within the inhomogeneous thin film as the radial pressure gradients develop from the curvature variations and viscous resistance to flow. However, their two-dimensional nonlinear hydrodynamic model is valid only for the formation of “holes” and a short period of expansion when the foam film thins under a constant capillary pressure. Their model does not predict the rate of the dark spot (or “hole”) expansion versus the film thickness and film size. The three-dimensional stability analysis is required to explain the rim breakup (the Rayleigh type of instability) during the “hole” expansion dynamics. Beltrán et al. [6] found that the foam film stratification phenomenon depends on the nature of the surfactant. They used an anionic surfactant and cationic surfactants with CarboxyMC solutions. For an anionic surfactant with the CarboxyMC solutions, the stratification was faster, showing the constant velocity of the domain’s rim movement. Slow stratification was found when the cationic surfactants were added to the CarboxyMC solutions. The stratification kinetics were the diffusive type (i.e., $R(t) \sim (4Dt)^{1/2}$). The charge and surfactant concentration affect the local viscosity or structural forces, and these are related to the stratification kinetics. However, there was a lack of a theoretical model to explain these differences and analyze the results. Later, Heinig and Langevin [9] studied the film formed from a mixture of an anionic polymer and a cationic surfactant. The shape relaxation of the coalescing domains was explained by the 2-D dissipation mechanism. They found that the film viscosity increases at least 30 times compared to the bulk, which was explained by the local molecular ordering and strong interactions with the film surfaces. However, their model cannot be applied when the domain’s coalescence is governed by the viscoelastic properties of the film or the Saffman length is too close to the length scale of the observed structures. Heinig et al. [10] suggested the local-diffusive mechanism to study the domain growth in stratifying foam films. The film tension gradient between the film and the domains causes the formation of a rim at the domain’s boundary. According to the local-diffusive mechanism, the film viscosity is 60 times larger than that of the bulk viscosity in their polyelectrolyte/surfactant mixture system. Unfortunately, the accuracy of the experimental disjoining pressure isotherm is very limited, so the validity of the proposed model to explain the domain growth dynamics in stratifying foam films is uncertain.

During the foam film’s stepwise thinning, droplets surrounding the dark spot (i.e., the Rayleigh type of instability) are formed in some systems [7,8,11,12]. Sorin and Langevin [11] noted that the expansion rate of the stratification domain (or dark spot) is changed depending on the presence of droplets surrounding the domain (the Rayleigh type of instability) when using the cationic surfactant, dodecyltrimethylammonium bromide (DTAB). When the droplets appear near the boundary of the domain, the diameter

of the domain grows linearly with time. For a domain without droplets (the rim instability), the domain diameter is proportional to the square root of the time (i.e., the domain expansion is governed by the diffusion process). They found that the droplets surrounding the domain appear at the last film thickness transition corresponding to the thinnest domains. Depending on the film thickness, the domain changes the kinetics of its expansion. Beltrán and Langevin [7] studied the kinetics of the stratification of liquid films formed from mixed solutions of a polyelectrolyte (carboxymethylcellulose) and sodium dioctyl sulfosuccinate (AOT). They also found that the droplets surrounding the domain (a Rayleigh type of instability) are related to the dynamic change in the domain’s expansion. However, the dynamic change occurs at the same thickness of the film before and after the formation of the rim’s instability droplets. Before the formation of the instability droplets, the radius of the dark spot, $R(t)$, shows diffusive scaling (i.e., $R(t)$ scales as $t^{1/2}$). The radius of the dark spot expands linearly with time in the presence of the instability droplets. The fast expansion of the domain accompanies the rim-instability-formed droplets surrounding the domain and results from charged particles (e.g., anionic surfactant micelles) as well as the film’s surfaces.

Based on the vacancies condensation mechanism [3], the rate increase in the dark spot expansion when the droplets surrounding the dark spot appear can be explained by the fact that the droplets (which are thicker than the dark spot) supply more vacancies to the dark spot. Zhang and Sharma [12] observed the change in the dark spot (domain) expansion kinetics with the formation of the droplets between the thinner expanding domain and the surrounding film for the foam film formed from sodium dodecyl sulfate (SDS) micellar solutions. They found the very close apparent velocities of the dark spot expansion between the expansion dynamics observed after the formation of the droplets near the dark spot and after the dark spot contacts the meniscus. Recently, Zhang et al. [13] analyzed the freely standing thin film stratification phenomenon using Interferometry Digital Imaging Optical Microscopy (IDIOM) protocols. They visualized the stepwise decrease of the film thickness, growth of the dark spot, and topological transitions that created non-flat structures in thin films such as ridges and mesas (the Rayleigh type of instability). For a foam film formed from the 0.08 M SDS micellar solution, they reported that the thickness of the droplets surrounding the dark spot is ~ 60 nm. Therefore, the droplets surrounding the dark spot are thick enough to supply more vacancies to the dark spot, just like how the dark spot contacts the meniscus, resulting in the similar apparent velocities in the dark spot expansion.

We have previously reported our observations on the stepwise layer-by-layer decrease of the film thickness, as well the appearance and growth of the dark spot of one layer less than the film thickness for the film formed from a nonionic micellar surfactant solution [14]. We also recently developed a theoretical model to rationalize these data.

Our theoretical model for the dynamics of the dark spot expansion used the two-dimensional Fickian diffusion equation in cylindrical coordinates for the thin liquid film with the appropriate moving boundary conditions. We derived the following equation [14]:

$$R(t)_n^2 = 4\lambda^2 (D_f) \left(\frac{D_n}{D_f} \right) \left(\frac{V_n}{V_f} \right) t \quad (1)$$

where t is the time, $R(t)_n^2$ is the squared dark spot radius, D_n is the apparent micelle diffusion coefficient, and V_n is the volume of the film containing “n” micellar layers. D_f and V_f are the apparent micelle diffusion coefficient and the film volume for the reference micellar layer, respectively. λ^2 is a constant obtained from the experimental measurements of the squared dark spot radius versus

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