MULTI-STEPWISE DRAINAGE AND VISCOSITY OF MACROSCOPIC FILMS FORMED FROM LATEX SUSPENSIONS

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Vertical, macroscopic thinning films formed from micellar solutions or latex suspensions exhibit a series of parallel, colored horizontal stripes of different thickness and, with time, of gradually increasing width. Such a step-wise profile can be explained by the existence of an ordered structure of spherical colloidal particles inside the film. It was established experimentally that, at a given temperature, the boundaries between the stripes are moving downwards with constant velocities. In addition, it was observed that colored circular spots, of lesser thickness than the surrounding film, are moving upwards in the lower stripes and, eventually, fuse with the corresponding colored stripe. The motion of the circular spots in a vertical stratifying film was used to determine the viscous properties of the ordered structure inside the film. It was found that the effective dynamic viscosity of the colloid crystal-like structure inside the film was about 100 times larger than the viscosity of the pure solvent.

INTRODUCTION

Step-wise thinning of liquid foam films was observed long ago by Johnnott and Perrin. This phenomenon, called stratification, was later observed and investigated by many authors, with both foam films and emulsion films. A possible explanation of the step-wise decrease of the film thickness, suggested in some works, is that a lamellar liquid crystal structure is formed inside the stratifying film. However, some recent experiments with both latexes and micellar solutions of ionic and nonionic surfactants revealed that stratification is observed with films formed from solutions containing monodisperse spherical colloid surfactants.
particles. These results lead us to the conclusion that surfactant micelles or latex particles inside the film form a colloid crystal structure which resembles the structures observed by Hachisu et al.\textsuperscript{13} for latex particles in bulk aqueous solutions. A theoretical model based on this idea provided a quantitative explanation of the metastable states of the film\textsuperscript{14} and of the mechanism of stratification.\textsuperscript{15}

The stratification of horizontal, microscopic liquid films represents a process of consecutive formation and expansion of spots having lesser thickness than the remaining part of the film\textsuperscript{11,12,15}. The appearance of stratification is quite different with macroscopic vertical or inclined films, which can be formed in a frame or in a test tube - Figure 1a. With films formed from latex suspensions, one observes a series of horizontal stripes of different, uniform colors at the upper part of the film\textsuperscript{10}. The different colors are due to interference of the common (polychromatic) light reflected by stripes of different, uniform thicknesses. The boundaries between the stripes are very sharp, a consequence of the stepwise profile of the film surface in this region (Figure 1b) and the liquid meniscus below the film appears as a region with gradually changing colors. Similar pictures with horizontal stripes can be observed with micellar solutions of nonionic surfactants\textsuperscript{10}. However, in the latter case, all stripes are gray in color, though with different intensity because the diameter of the micelles is smaller (about 10 nm in Ref.\textsuperscript{10}) than that of the latex particles.

According to the colloid crystal model, the stripes of different thicknesses contain different numbers of micellar layers inside the film (Figure 1b). In the case of charged particles (ionic surfactant micelles or latex particles) the height of a step is approximately equal to the effective particle diameter, i.e. the sum of the diameter of the particle itself and the thickness of its Debye atmosphere\textsuperscript{11,14}.

Similar detailed experimental studies of vertical stratifying films are still missing and the present paper is a first step in this direction. We measured both the velocity of the boundaries between the colored stripes of different thicknesses and the speed of rising circular spots. These data provide information about the viscosity and other properties of the colloid crystal structure inside the film. As a model system, we chose an aqueous solution of submicron latex particles and the results of these experiments are presented and discussed below.

EXPERIMENTAL SET-UP AND OBSERVATIONS

In our experiments we used a monodisperse, latex suspension of particles with a diameter of 156 nm (Dow Chemical) and were in a 44 wt% concentration. The concentration was determined by measuring the weight of a sample of the suspension before and after dehydration.

The suspension was placed in a cylindrical test-tube with an optical glass wall and the inner tube diameter was 2.5 cm. By shaking the test-tube one forms a flat, circular liquid film. The tube is then laid horizontally (Figure 1a) in a thermostated cell with a metal bottom and transparent walls made of optical glass. After being placed in a vertical position, the film was observed by means of a horizontal microscope and a set of horizontal stripes of different colors appear in the upper part of the film. The upper stripe is black when observed in reflected light and the next lower stripes have the following colors: white, yellow, blue and red. Following this, a sequence of alternating green and red stripes of different nuances were observed. Because the boundaries of the stripes are moving downwards with different velocities, the area of the stripes