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A Nano-scale Study on Film Stability

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Abstract: Thickness and stability of films formed by different surfactants are studied by means of thin film balance (TFB) technique to observe the formation and stability of the films. It is demonstrated that stable Newton black films (NBFs) can be easily obtained with non-ionic surfactants (C12E5, C12G2) than ionic surfactants (C12TAB, C16TAB). Common black film (CBF) was obtained with C16TAB at 5×10-3 mol/L, while the film of C12TAB is unstable. It has been demonstrated that the horizontal forces should also be taken into consideration for explaining film stability.

Keywords: Nano-film, surfactant, film stability.

Films are often used to study molecular self-assemblies and colloidal particles stratification[1, 2]. Thickness and stability of films are two important key parameters for studying foam properties and behaviours[3]. Usually it is believed that both film thickness and stability depend on the balance of attractive van der Waals component Π_{vw} and the repulsive electrostatic term Π_{el} and/or hydration and steric repulsion terms of the disjoining pressure in normal direction of films. Film stability is traditionally studied by observing the volume change of foam with time. Although it is convenient, the method cannot offer detailed information of the mechanisms and interactions of surface layers. Thin film balance (TFB) approach is effective to investigate the stability of the freestanding film at a near-molecular level[4]. The advantage of TFB method is that film can be investigated in nano-scale and disjoining pressure can be measured. With TFB, film structure and drainage mechanism can be presented; the force between layers can be calculated from the relationship between thickness and pressure; and the stability of film (or foam) can be compared with other systems from pressure at which film breaks. Here we report the investigation of thickness and stability of the films formed by different non-ionic and cationic surfactants, respectively.

Dodecyltrimethlyammonium bromide ($C_{12}TAB$, > 99%, 25°C, CMC=1.6×10^{-2} mol/L), hexadecyltrimethylammonium bromide ($C_{16}TAB$, > 99%, 25°C, CMC=9.2×10^{-4}

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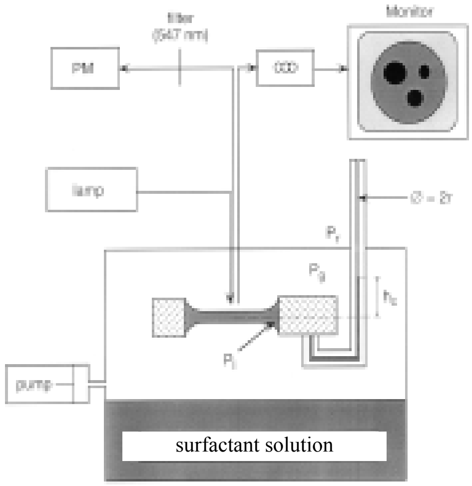
mol/L), pentaethylene glycol monododecyl ether ($C_{12}E_5$, 25˚C, ≥ 97%, CMC=7.1×10^{-6} mol/L), and *n*-dodecyl-α- D-maltoside ($C_{12}G_2$, ≥ 97%, 25˚C, CMC=1.2×10^{-4} mol/L) were employed to form films at 24˚C, respectively.

The schematic diagram of TFB instrument is presented in **Figure 1**. The small hole (diameter *ca.* 2 mm) drilled in a porous glass plate is used for the formation of a freestanding surfactant film. The glass plate and film are hanging in the isolated cell, which has an observing window. For a measurement, the porous glass plate is immerged in bulk solution in the isolated cell. After the equilibrium of solution with its vapour in the cell (*ca*. 2 h), the plate is taken out from the solution. After a new equilibrium of liquid and vapour is reached, the capillary pressure compensates the disjoining pressure. Two monolayers are relative far away and the film is very thick with a lot of solution in between. To start the measurement, the attached pump adds pressure into the cell accurately. The film thickness is obtained by the interferometrical method by a photo meter with a filter of 547 nm proposed by Scheludko[5]. Through the observing window, CCD camera records the images shown in the microscopy. Thus the pressure and film thickness are measured. The pressure at which the film breaks is considered to evaluate the stability of the films.

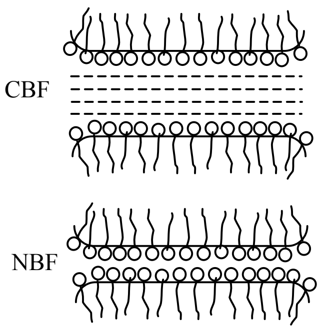
There are three equilibrium types of films-thick common films (colored), thinner common black films (CBF) and thinnest Newton black films (NBF). CBF contains micelles or water inside because of stronger repulsive force, particles stratification and other interactions. Its thickness depends on disjoining pressure, which is a sum of all vertical forces. In some cases, the repulsive force is too weak to keep two monolayers in a distance. Such film without solvent and other molecules in between is consisted of only double surfactant layers, which reflects nearly no light, and is called Newton black film (NBF)[6]. CBF and NBF are illustrated in **Figure 2**.

Figure 1 Schematic diagram of the thin-film balance



$$\Pi=Pg-Pr+2\sigma/r-\Delta\rho gh_c$$

Figure 2 Schematic illustration of CBF and NBF

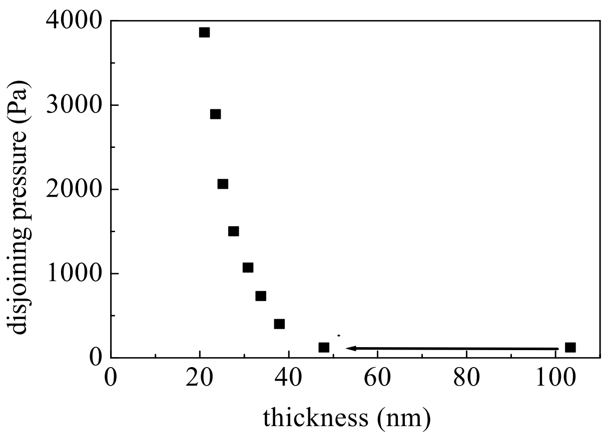


For $C_{12}TAB$, only thick common films have been observed with concentration varied from 1×10^{-5} to 1×10^{-2} mol/L without extra pressure. Films break after drainage at very low pressure. Relative stable film can be acquired with $C_{16}TAB$ at a relatively high concentration. The difference in the stability of $C_{12}TAB$ and $C_{16}TAB$ is due to their difference in molecular structures. The molecular interaction force of hydrophobic part is considered as van der Waals attractive force, which contributes to horizontal strength of the film instead of vertical. Compared with $C_{12}TAB$, a longer hydrophobic chain of $C_{16}TAB$ is responsible for higher strength of the film.

Figure 3 shows the disjoining pressure isotherm (disjoining pressure as a function of the film thickness) of the $C_{16}TAB$ film at a concentration of 5×10^{-3} mol/L. The isotherm is obtained in equilibrium. It indicates the film thins continuously when the disjoining pressure increased after jump to around 50 nm. The step with a width of 50 nm can be found in **Figure 3.** After solution drainage, film thickness reduces as disjoining pressure increases. It is the increase of electrostatic repulsive force that keeps two layers of film apart.

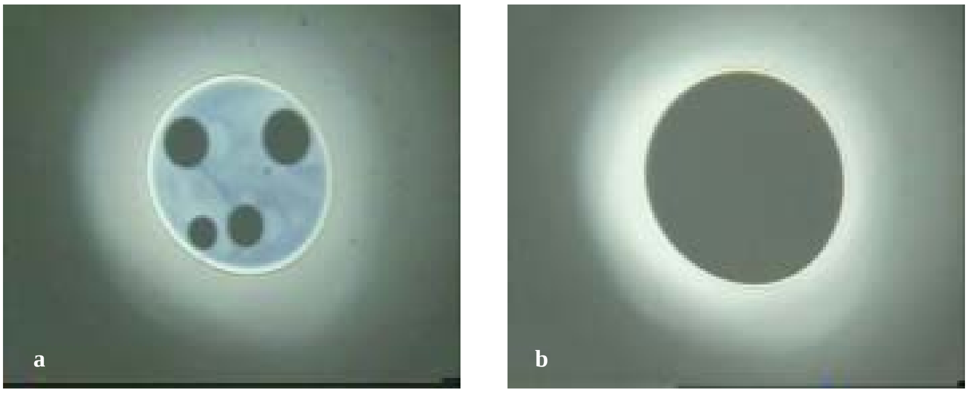
For the non-ionic surfactant $C_{12}E_5$, at low concentration, films break quickly after jump to NBF. Stable NBF with a thickness of nearly 6 nm can be obtained at the concentration of 2×10^{-4} mol/L or higher. The images in **Figure 4** show the film stepwise thinning process with time. The circular area in the middle of each image is the plane parallel part of the film, which is surrounded by the Plateau border. The four spots with different intensity (in **Figure 4a**) from the main circular area show hydrodynamic process of film forming: drainage of the solution from film. Such instabilities are due to the rate of extension of the smaller new thickness is faster than the liquid can be pressed out of the film. The film reached a homogeneous thickness after a while (see **Figure 4b**), certified by the uniform intensity. At the early stage, the film is thick with bulk solution in between. The thickness is controlled by the equilibrium of disjoining pressure and electrostatic repulsive force, van der Waals force, etc, according to the postulations of DLVO theory[7, 8]. After solvent drains out, the film thickness is thinning to offer a NBF.

Figure 3 Disjoining pressure isotherm (disjoining pressure in dependence on the film thickness)



C16TAB concentration 5.0×10-3 mol/L

Figure 4 Images of thinning process of $C_{12}E_5$ NBF



(a) early stage showing drops in the film (b) later stage showing homogeneous film

Similar NBF has also been obtained with $C_{12}G_2$, but only when the surfactant concentration reach 1×10^{-3} mol/L or higher. The fact that stable films could be formed at different concentrations with $C_{12}E_5$ and $C_{12}G_2$ is caused by their molecular structures and CMCs. The reason for both obtaining NBF with $C_{12}E_5$ and $C_{12}G_2$ is that non-ionic surfactants have no stronger repulsive force in both horizontal and vertical directions. Van der Waals attractive force makes film stronger and small vertical repulsive force makes two layers close to form NBF. $C_{12}E_5$ can form NBF as well as $C_{12}G_2$ because of the weak repulsive force in vertical direction, which means film thickness is controlled by vertical forces, as described by DLVO theory. Because film can collapse at different thicknesses, the stability is independent of thickness.

In summary, by means of TBF, CBFs are obtained with C_{12}TAB and C_{16}TAB, respectively. C_{16}TAB film is more stable than C_{12}TAB because of existence of stronger Van der Waals force in horizontal direction, which gives certain contribution to the stability of films in addition to classical DLVO theory in vertical direction.

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