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Collapsing Processes in Stearic Acid Monolayer Studied by Brewster Angle Microscope

Zuhong LU† and Hiroo NAKAHARA*
Faculty of Science, Saitama University, Shimo-okubo 255, Urawa 338
†National Laboratory of Molecular and Biomolecular Electronics,
Southeast University, Nanjing, 210018, China

Collapsing processes of a stearic acid monolayer have been studied on the different subphases by a Brewster angle microscope. It has been suggested that the collapsing processes can be classified into three basic models: nucleation, straight ridge-like catastrophe, and ultrafine particle accumulation. The collapsing structures depend on the interaction between the head groups and the aqueous subphase.

When an insoluble monolayer at the air-water interface is over-compressed, an irreversible collapse will occur. The collapsing processes of a monolayer has been a research subject for several decades.1,2) The earliest direct observations of an collapsed monolayer on the water surface using an optical dark field microscope were reported by Zocher and Stiebel,3) and by Langmuir and Schaeffer,4) who found a number of structures including nuclei, clumps, and striations. However, since an ordinary optical microscope has a limited sensitivity, it is difficult to see a monolayer at the beginning of a collapsing process. Further studies for a collapsed monolayer were carried out by means of electron microscopes. Based on the electron microscopic photographs of the transferred monolayers, several well known collapsed patterns have been reported.5,6) Recently, a theoretical model for a nucleation process has been established by Vollhardt and co-workers,7-9) which fits well their experimental data obtained from the monolayer area relaxation process at a constant pressure on an acidic subphase. However, it is generally considered that a collapse process depends on nature of the substances and various experimental parameters, such as compression rates, temperature, and prehistory of the monolayer itself. Although many different collapsing structures have been reported by several researches, a completely clear picture of a monolayer collapsing processes is far from fully understood. Recently, a new optical microscope with a very high sensitivity, a Brewster angle microscope (BAM), has been invented,10,11) which allows directly to visualize a monolayer on the water surface. Hellon and co-workers 12) has used BAM to observe a metastable monolayer directly at a constant surface pressure, and their results have given the direct experimental evidence of the nucleation model. Although the other powerful microscopic techniques (such as scanning probe microscopy, electron microscopy, and fluorescence microscopy etc.) may provide some important information, BAM has its own particular advantages in studying the dynamic process of a monolayer during compression without introducing any probe molecule into the monolayer.

In this letter the intrinsic relationship between the collapsing processes of a stearic acid monolayer and the monolayer formation conditions (specially subphase pH value and its temperature) was explored by use of a Brewster angle microscope. Three basic structures have been identified from collapsed monolayers, which strongly depend on the interaction between the monolayer and the aqueous subphase.

Commercial stearic acid (octadecanoic acid) was carefully recrystallized twice from ethanol, and dissolved in chloroform in the concentration below 10^{-3} M. Distilled water (pH 5.5), acidic aqueous solution (pH 3, adjusted by H_2SO_4), alkaline aqueous solution (pH 10, adjusted by NaOH), and cadmium salt solution (3×10^{-4} M $CdCl_2$ and 5×10^{-5} M $NaHCO_3$, pH 6.3) were used as subphases, respectively. A PTFE coated rectangle stainless steel trough with a total surface area of 3.5 cm x 100 cm was used, in which the surface temperature of the subphase could be controlled from 5 °C to 50 °C by a water circulation system. A water dropping system has been used to add water continuously into the subphase and to complement the evaporated water from the subphase at high temperature. The surface pressure of a monolayer was monitored by a Wilhelmy-type film balance. The morphology of a monolayer on the water surface was obtained with a Brewster angle microscope (BAM1, Nanofilm Technologie GmbH, FRG). The monolayer compression rate was in the range of 1–5 cm^2 / min.

Figure 1 shows the typical bulk structures of a collapsed monolayer of stearic acid on the different subphases. When the monolayer on an acidic subphase at the temperature of 25 ± 1 °C is compressed over a critical point about 19 Å^2/molecule, some small nuclei are going to appear at the beginning. Those nuclei will grow up through the further compression, while the number of the nuclei almost keeps constant, as shown in Fig.1(a). This collapsing process probably fits the nucleation model suggested by Smith et al.$^{2)}$ and Vollhardt et al.,$^{7)}$ in which stearic acid molecules tend to be formed into amorphous bulk structures. However, when a monolayer spreads on an alkaline subphase, the other two structures of the collapsed monolayers will be seen. In Fig.1(b) a long narrow ridge-like structure of the collapsed film, which is formed in a catastrophic way, seems to fit the collapsing model proposed by Ries et al.$^{5)}$ The rough surface shown in Fig.1 (c) can be considered as a number of micro-particles which accumulated to form a thick layer during over-compression. This might be consistent with the electron microscopic studies made by Neuman.$^{6,13)}$

A general nucleation process should involve both the size growth of the nuclei and the increase of the number. Both of the temperature and the pH value of the subphase can influence the nucleation process and produce very different collapsing

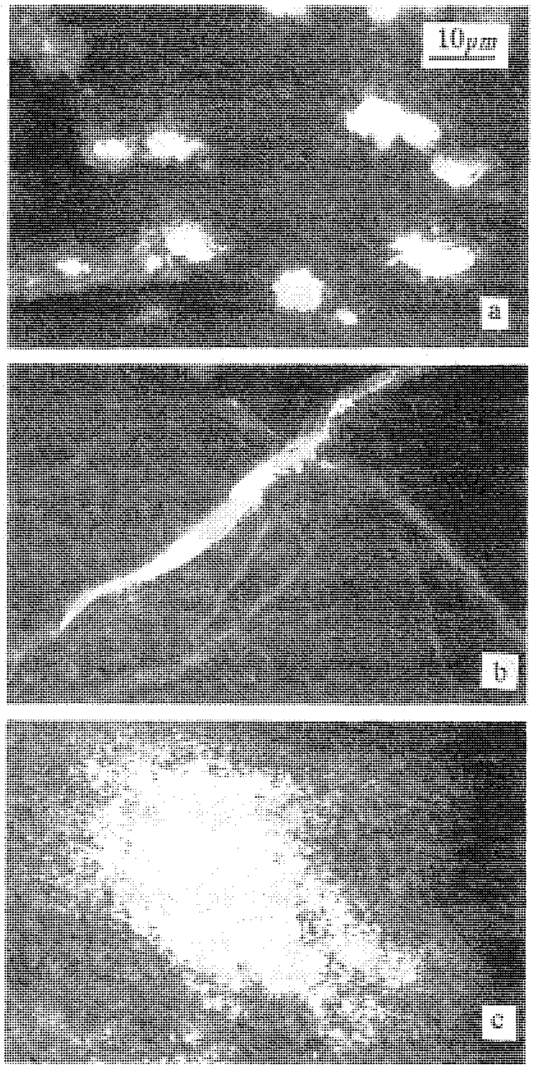

Fig.1. The typical structures of a collapsed monolayer of stearic acid. (a) Bulk nuclei on an acidic subphase at temperature at 25 ± 1 °C, (b) Long ridges on an alkaline subphase and (c) Fine particle accumulation pattern on an alkaline subphase.

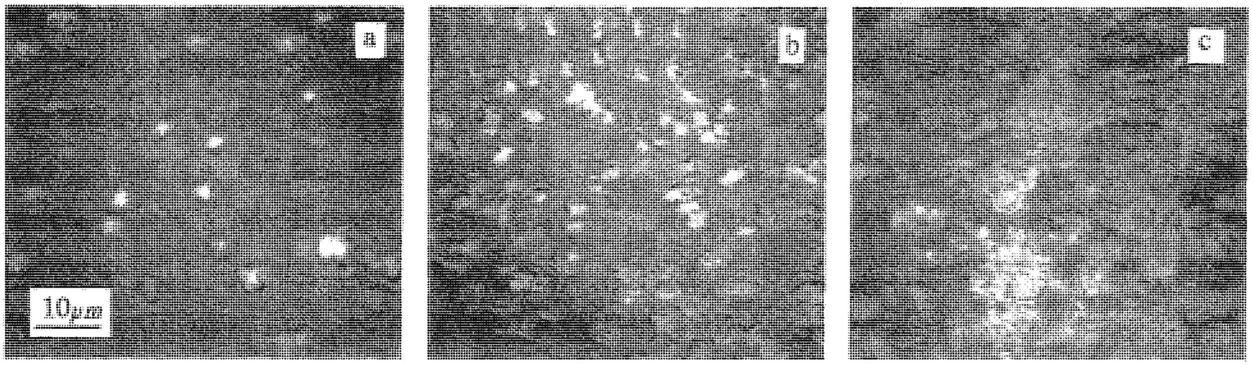

Fig.2. The nucleation process of the collapsed monolayer of stearic acid on an acidic subphase at 15 °C during over-compression process from (a)19.5 to (c)18.5 Å^2/molecule.

patterns. In the case of an acidic subphase at the temperature below 20 °C, both the number of the nuclei and their size increase during over-compression, as shown in Figs.2 (a) and (b). If the monolayer was compressed further, some neighbouring nuclei tend to unite with each other, and become large irregular clump-like nuclei shown in Fig.2 (c). The lower the temperature is, the more important the number-increase nucleation process is. Slight increase of the pH value of the subphase has the similar effect to the nucleation process. When distilled water is used as a subphase, the monolayer tends to the number-increase nucleation process. Moreover, it can be expected that a slow compression speed makes a larger nucleus in the monolayer, which has been supported by the BAM observation made by Henon et al.[12] In the nucleation process the nuclei might be originated from the impurities and / or the structural defects in a monolayer.

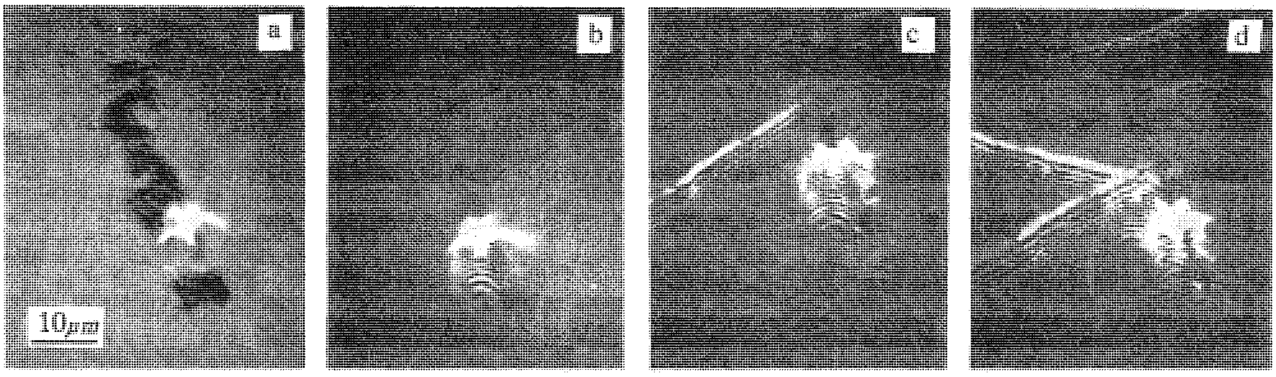

Fig. 3. The BAM pictures for the production process of the straight ridge-like catastrophic structure of the collapsed film from a structural defect in a stearic acid monolayer on an alkaline subphase surface (from a: 19.5 to d: 18.5 Å^2/molecule).

When an alkaline solution is used as a subphase, the ionized carboxyl groups of stearic acids have the strong interaction with the subphase, two kinds of collapse processes are observed (long straight-ridge catastrophe and micro-particle accumulation). The ridge structure commonly originates from the edges of the monolayer close to the moving barriers and the boundaries between domains, where highly strain force is easily produced during compression. Figure 3 shows a collapsing process of the long straight ridge-like structure at the edge of a hole during compression. The hole in a monolayer was formed immediately after spreading the stearic acid solution onto the water surface, and became smaller during compression until its edge met together (Figs.3 (a) and (b)).

Further compression produced a strain so highly that the monolayer could have hardly kept its stable state. The monolayer burst out suddenly into a ridge structure at last in the way firstly suggested by Ries$^{5)}$(Figs.3(c) and (d)). Moreover, the ridge bulk structure could produce some new strains in the monolayer, and produce some new catastrophe collapse if the compression continues. These long narrow straight ridges could be further compressed into a striation-like pattern due to the inhomogeneous flow in the monolayer. According to Ries' model, a ridge should have an ordered triple-layered structure, which has been supported additionally by AFM observation of a collapsed structure of a calcium stearate monolayer on HOPG by Birdi and Vu.$^{14)}$ However, a ultrafine particle accumulation seems more intrinsic process than the catastrophe. Neuman$^{6,13)}$has explained these ultrafine particles as both micelles and crystals according to his electron microscopic pictures. A monolayer on a cadmium salt solution shows the similar collapsing phenomena as on an alkaline subphase. It could be concluded that a strong interaction between the molecules and its aqueous subphase plays an important role in forming these ultrafine bulk particles.

In conclusion, three fundamental collapsing processes, which are nucleation, ridge catastrophe and ultrafine particle accumulation, have been concluded experimentally through direct observation of a stearic acid monolayer on the aqueous solution by using a Brewster angle microscope. These collapsing processes are strongly dependent on the pH value and/or ionic strength of the subphase. Although the other factors, such as subphase temperature and compression rate, influence the collapsing pattern of a monolayer, it has been found that they have little influence on the basic collapsing model. The strong electrical interaction between the carboxyl groups of the stearic acid and the subphase should play an important role in the monolayer collapse processes.

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