Directly Experimental Evidence for Melting Process of Solid Domains in Monolayers of Fatty Acids at the Air-water Interface by a Brewster Angle Microscope

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(Received November 16, 1994)

First direct observation of the melting processes for fatty acid monolayer at the air-water interface has been successfully made by a Brewster angle microscope. The melting temperatures of solid domains in the monolayers of myristic, palmitic and stearic acids are around 6 $^{\circ}$C, 28 $^{\circ}$C and 46 $^{\circ}$C, respectively. Both the domain size and their distribution become homogeneous when the molten monolayer is cooled down back to the temperature below melting points.

A monolayer at the air-water interface has been generally considered to have gas, liquid expanded, liquid condensed and solid phases, which are usually given by its surface pressure *vs.* molecular area isotherms.[1] However, since Möhwald and his co-workers[2,3] made the new discovery of two dimensional domains floating on the water surface by using a fluorescence microscope in the early of 1980's, the above conception has met difficulties in explanation of such new phenomena obtained by using various novel experimental technologies. Now it is accepted that two dimensional solid domains exist in most kinds of monolayer systems even at the zero surface pressure right after spreading the solution on the water surface. The domains are accumulated together to form a condensed monolayer during the compression. On the other hand, some experiments aimed at the thermotropic behaviors of LB films have been made by Swalen and co-workers[4] with IR and Raman spectroscopies. Prior to the melting point, a pretransitional disordering of the hydrocarbon tails for cadmium arachidate layers was observed. Riegler[5] found a sharp decrease in electron diffraction peak intensities of cadmium stearate, arachidate, and behenate LB films at temperature below the bulk melting point. Recently, Kajiyama and co-workers[6,7] have suggested that the physical states of a fatty acid monolayer on the water surface can be classified simply into the two types: crystalline and amorphous states, which depended on the difference of the subphase temperature (T_{sp}) from its melting temperature (T_m). On the basis of both apparent decrease in the monolayer modulus *vs.* T_{sp} curve and the change of the electron diffraction pattern from a crystalline Debye ring to an amorphous halo for the transferred monolayers. Values of T_m for myristic, palmitic and stearic acids were evaluated to be 278, 301 and 317 K, respectively. However, the further direct evidences for the change of states in the monolayer on the water surface should be required.

Although the morphological change of a double-chain ammonium monolayer with heat treatment was reported by using a fluorescence probe,[8] a new optical microscope, Brewster angle microscope (BAM), has been invented,[9,10] which allows directly to observe a monolayer on the water surface without introduction of any fluorescence molecular probe. Several BAM investigations for the monolayer system have been already reported,[11,12] which include the monolayer phase transitions, the growth of two dimensional domains, and the monolayer collapsing processes etc.[13] In this letter the Brewster angle microscopy would be used to observe directly the melting process of the two dimensional solid domains in fatty acids monolayers on the water surface. These experiments have provided the positive supporting results to Kajiyama's data of the monolayer melting temperatures.

Myristic acid [$CH_3(CH_2)_{12}COOH$], palmitic acid [$CH_3(CH_2)_{14}COOH$] and stearic acid [$CH_3(CH_2)_{16}COOH$] were carefully recrystallized twice from ethanol, and dissolved in chloroform in a concentration below 10^{-3} M. Distilled water (pH 5.5) was used as a subphase. A PTFE covered 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 2.5 $^{\circ}$C to 50 $^{\circ}$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 aqeous subphase at the high temperature. The surface temperature of the subphase was taken with a precise mercury thermometer which was directly located at the air-water interface. The monolayer morphology on the water surface was detected with a Brewster angle microscope (BAM1, Nanofilm Technologie GmbH, FRG). The BAM observation for the monolayer melting process was carried out at the zero surface pressure (about the molecular area of 60 Å^2), and each observation was waiting at least 10 minutes after the subphase got to the given temperature so that the monolayer could have reached to the state near its thermodynamic equilibrium.

Figure 1 shows a set of BAM pictures of the melting process in a stearic acid monolayer during increasing T_{sp} up to 50 $^{\circ}$C. It is the first direct observation of a melting process in a two-dimensional monolayer system on the water surface. The domains are solid with a solid boundary at the T_{sp} below 25 $^{\circ}$C. When the T_{sp} increased gradually, the shape of the domains becomes flexible, and the reflectivity of the monolayer reduced, although they still have the clear boundaries, as shown in Figure 1(a). This kind of the domain might be called as a soft domain.

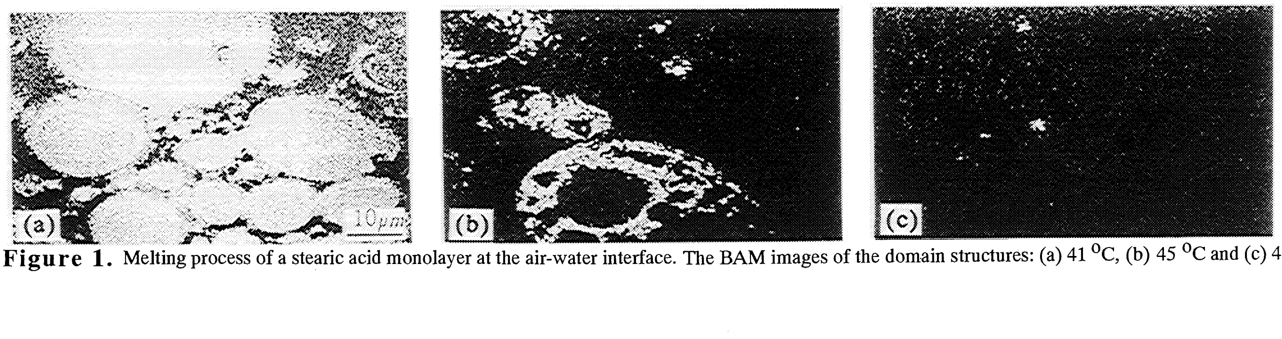

Figure 1. Melting process of a stearic acid monolayer at the air-water interface. The BAM images of the domain structures: (a) 41 $^{\circ}$C, (b) 45 $^{\circ}$C and (c) 47 $^{\circ}$C.

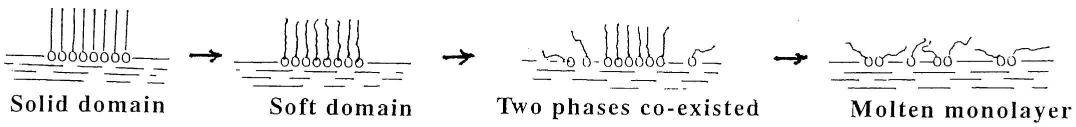

Figure 2. The schematic pictures of the monolayer melting process.

After the T_{sp} is above 45 °C, the domains become smaller and the boundaries become vaguer, some part of the monolayer material is melted from the domains, as shown in Figure 1(b), where both soft domain phase and melted monolayer phase are coexisted. The two dimensional domains are dissolved completely and the monolayer becomes dark and homogeneous above 47 °C, as shown in Figure 1(c).

The high contrast BAM picture of a monolayer structure is due to the differential reflectivity of the monolayer on the water surface at the Brewster angle. The reflectivity of a monolayer strongly depends on their thickness. When a monolayer is too thin to modify the local reflectivity of the air-water interface, one can hardly observed the BAM image of the monolayer structure. For most polymer monolayers, such as polymethylmethacrylate (the monolayer thickness is about 8 Å[14]), it is very difficult to obtain their BAM images of the monolayer structures on the water surface. In Figure 1, we have seen that the melted monolayer has low reflectivity. It could be deduced that the melted monolayer had a low thickness. Therefore, the following melting model of a fatty acid monolayer could be suggested during increase of the temperature: Solid domains → Soft domains → Two co-existed phases between domains and melted monolayer → completely melted monolayer, as shown in Figure 2.

The similar melting processes for the monolayers of myristic and palmitic acids have been studied. But the melting temperature decreases rapidly with decreasing the chain length. The ranges of Tm for myristic and palmitic acids are 5 - 7 °C and 27 - 29 °C, respectively. In comparison with the data obtained from the monolayer at the condensed state by Kajiyama et al., our values obtained at the zero surface pressure are well consistent with Kajiyama's. It has provided the strong evidence for the Kajiyama's comment about the monolayer melted state. Furthermore, it might imply that the surface pressure has little effect on the T_m of a monolayer. The thermodynamical properties in the two dimensional system of a monolayer on the water surface depends on its three dimensional environment, and the dependence of the carbon chain on the T_m of the fatty acid monolayer could be due to the interaction between the water molecules and the head group of fatty acid.

Melting process of a monolayer might be fundamental in explanation of the annealing effect of a monolayer on the water surface, which is able to reduce the defect density effectively in the monolayer by several orders of magnitude[15,16]. The defects in the Langmuir-Blodgett films originate from the irregular solid domain on the water surface during compression, and be conserved on deposition. Figure 3 shows that the size of the domains become uniform and their distribution becomes homogeneous after a stearic acid monolayer is cooled down back to the room temperature after melting. If a monolayer in a condensed state is annealed at the temperature above T_m, it is expected that the homogeneous solid monolayer almost without any structural defect can be formed.

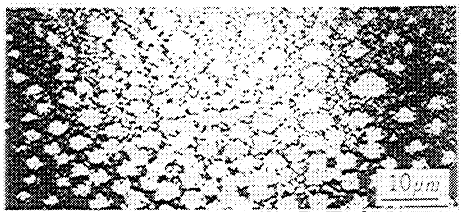

Figure 3. BAM image of a stearic acid monolayer on the water surface at 20 °C after melting.

In conclusion, the monolayer melting processes of myristic, palmitic and stearic acids were studied in the range of the temperature between 2.5 °C and 50 °C by use of a Brewster angle microscope. Since the strong evaporation of the subphase, it is difficult to observe the melting process at the temperature above 50 °C. Two different states of the monolayer (domain and melted monolayer) have been distinguished by the melting temperature of T_m during increasing the subphase temperature of T_{sp}. The melting temperatures for myristic, palmitic and stearic acids have been determined to be about 279, 301 and 340 K, respectively, which are in agreement with the data given by Kajiyama et al.. This experiment has directly proved that the solid domains formed in a fatty acid monolayer can be melted at the temperature above T_m. This conclusion can be extended to the some other monolayer systems.

Authors are greatly appreciated that the State Education Commission of China and Chinese Young Scholarship Foundation of Huo Yingdong to provide financial supports for Lu's doing six-month research in Saitama University.

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