Hopping Phenomena of [1-^{14}C]Octadecanoic Acid Molecules at the Surface of the Langmuir-Blodgett Film Regarded as an Extremely Thin Crystal

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The desorption of [1-^{14}C]octadecanoic acid molecules in vacuo from a Langmuir-Blodgett film, which is regarded as an extremely thin crystal, was studied by using three kinds of radioactive samples containing ten molecular layers: The first sample was labeled at the tenth (the outermost) layer; the second one, at the ninth layer and the third one, at both the ninth and tenth layers. From the initial slopes in the desorption curves for these samples it is suggested that most of the acid molecules desorb from the tenth layer and some acid molecules desorb as a dimer consisting of a pair of molecules from the ninth and tenth layers. The scanning electron micrographic observations were carried out for nonradioactive samples stored for a week at 298.2 or 278.2 K under atmospheric pressure; it was concluded that the fatty acid molecules jump back and forth between a boundary (stagnant) layer and the surface of the LB multilayer and coagulate into micron-size crystals.

Vapor pressure and heat of sublimation of long-chain fatty acid crystals at room temperature have been measured by only a few investigators in spite of their thermodynamical and practical utilities. This is attributable to the experimental difficulty in measuring the extremely low vapor pressure of the crystals. Some attempts[1–4)] have been made by Knudsen's method to determine the vapor pressure for the long-chain compounds but only near their melting points in which relatively high vapor pressures are available.

The highly oriented Langmuir–Blodgett (LB) multilayer of octadecanoic acid takes on a C-type (monoclinic) crystal structure in the upper monolayers other than the first monolayer.[5)] This is the most stable crystal form at room temperature. X-Ray diffraction and IR spectrum measurements indicated that the LB multilayer of octadecanoic acid consisted of its extremely small three-dimensional crystallites which are oriented so that their c-axes align with an angle of ca. 30° to the normal axis of the substrate plate.[5,6)] The desorption of the acid molecules from the LB film is therefore regarded as that from the extremely thin and small crystals. Accordingly, the measurement of the desorption for the acid molecules labeled radioactively from the LB multilayer will give us useful information about the mechanism of the desorption process from the crystal. In the present study the desorption from the surface of the fatty acid multilayer was investigated by using the ^{14}C-samples labeled at arbitrary layers; the desorption mechanism was estimated and confirmed also by scanning electron micrographic observations for the nonradioactive LB films.

Experimental

Materials. [1-^{14}C]Octadecanoic acid (specific activity of 59.0 Ci mol^{-1}) from New England Nuclear, Inc., and the purest grade sample of octadecanoic acid from Wako Chemical Industry were used for the built-up process. Ferrotype plates (20×15×0.5 mm) were used as the substrate plate. The plates were washed in aqueous ethanol solution (ethanol:water=1:1 in volume ratio) containing 5% of potassium hydroxide and rinsed in triple distilled water, and their surfaces were pretreated with iron (III) octadecanoate (the purest grade of Tokyo Kasei Industry Co., Tokyo) to be hydrophobic. The subphase solution was triple-distilled water[7)] whose pH was adjusted to 2 with twice distilled HCl. Under this pH condition, the monolayers consisting of only salt-free octadecanoic acid molecules are transfered onto the substrate plate even if some metal ions existed in the subphase solution.[8,9)]

Troughs and Movable Barriers. Two sizes of Teflon troughs were used: The small one had inside dimensions of 260 mm$^{\text{length}}$×25 mm$^{\text{width}}$×15 mm$^{\text{depth}}$ and large one, 282×155×5 mm. The large trough had a pocket (40×20×15 mm) in its bottom for vertical dipping of the substrate plate. The inside of the small trough was hydrophilic by the glow discharge in an oxigen atmosphere and the rims remained hydrophobic by protective adhesion tapes for a smooth movement[10)] of a thin glass plate (32×24×0.5 mm) coated with paraffin. For the large trough a paraffin-coated silk thread of ca.20 cm in length was used as a movable barrier for the compression of the monolayers.

Built-up Procedure. A benzene solution (1×10^{-3} mol dm^{-3}) of nonradioactive octadecanoic acid was used as spreading solution for the large trough and hexane solutions (1×10^{-4} mol dm^{-3}) of radioactive or nonradioac-

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tive sample, for the small trough. The purest grade ethyl tetradecanoate (Wako Chemical Industry) as used as a piston oil whose surface pressure was about 20.7 mN m^{-1}.

The samples of LB film containing eight monomolecular layers of the nonradioactive acid were prepared by the conventional vertical-dipping method, using the large Teflon trough, at 285—290 K. Let us term the samples thus obtained LB-8 plates.

The substrate plate as dipped to a depth of 15 mm in the subphase solution and withdrawn through the nonradioactive monolayer at a velocity of 0.1—0.5 cm s^{-1} by means of a synchronous motor. In order to know the transfer ratio of the monolayer onto the substrate plate, we used the small Teflon trough and the floating glass plate (movable barrier) coated with paraffin. From the movement of the glass plate in the transfer process we evaluated the transfer ratio of the monolayer. The ratios for both upward and downward strokes were almost unity (0.97—1.00).

A modified horizontal-lifting method[10)] was employed for the transfer of the additional two radioactive and/or nonradioactive monolayers on the LB-8 plates by using the small Teflon trough. The transfer process by the method is schematically shown in Fig. 1. After the solution surface was swept with Teflon barriers, the surface was divided into two equal parts with a narrow glass barrier **A** which was made hydrophobic by treatment with dimethyldichlorosilane. In order to prepare a radioactive sample labeled at the tenth layer, a nonradioactive octadecanoic acid monolayer was spread on one part of the divided surface. The monolayer was compressed with the floating glass plate by piston oil pressure. Then, the LB-8 plate on the monolayer (Fig. 1-a) was touched almost horizontally. A new glass barrier **B** was then placed near the end of the plate (Fig. 1-b), and the monolayer remaining around the plate was cleaned out with several hydrophobic glass barriers and an aspirator. Subsequently a [1-^{14}*C*]octadecanoic acid monolayer was spread on the other surface. The monolayer was also compressed with the second floating glass plate by a piston oil pressure. On removing the glass barrier **A** from the solution surface, the radioactive monolayer came from one part of the divided surface and spread around the plate (Fig. 1-d). The plate was then turned gradually by a mechanical operation controlled with a personal computer (NEC model PC-8001 MKII), lifted and finally removed from the surface (see Fig. 1-e and f). One molecular layer of the nonradioactive octadecanoic acid and an additional layer of [1-^{14}*C*]octadecanoic acid were transferred onto the LB-8 plate by this process. In order to prepare a sample labeled at the ninth layer, the LB-8 plate should be initially attached to the radioactive monolayer. For the preparation of a sample labeled simultaneously at both the ninth and tenth layer, the water surface should be occupied only by the radioactive monolayer: It is not necessary to use the glass barrier **A** to devide the solution surface into two parts. This depositing process gave Y-type films for the octadecanoic acid monolayer and the transfer ratios by this method were also almost unity.

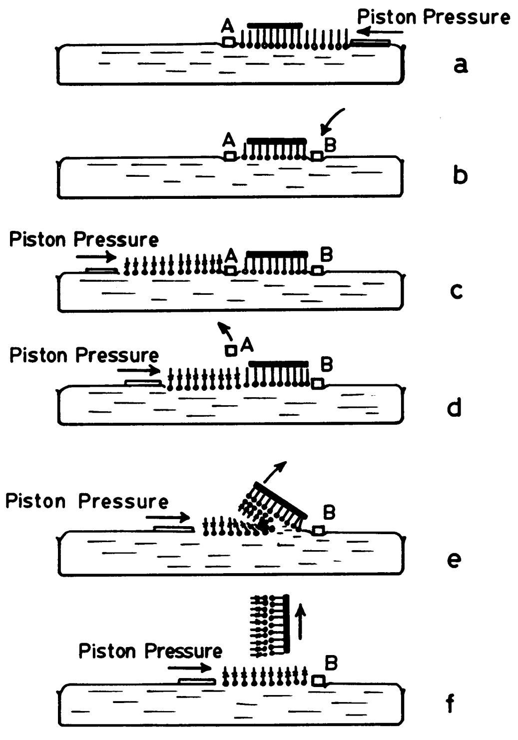

Fig. 1. Scheme of the transfer process of radioactive and/or nonradioactive monolayer onto LB-8 plate.

The Measurement of the Desorption in Vacuo. The radioactive samples thus obtained were set in the vacuum chamber thermostated at ±0.1 K. After the samples had been set in the chamber, it took about 3 minutes to reach a pressure of 1×10^{-2} Pa with rotary and diffusion pumps. Isothermal desorption experiments were performed under this pressure and at a number of different temperatures (288—303.9 K). The radioactivity of each sample, being proportional to the remaining amount of [1-^{14}*C*]octadecanoic acid, was measured batchwise with a thin end-window Geiger-Müller tube, with a mica window of thickness 1.4 mg cm^{-2} at any given time.

Observation with Scanning Electron Micrographs. Scanning electron micrographic observation (SEM) of the nonradioactive samples containing ten monomolecular layers either freshly prepared or stored for a week under atmospheric pressure at 298.2 or 278.2 K were carried out with a JOEL JXA-840 scanning electron microscope.

Results and Discussion

Figure 2 shows the relative desorption profiles, $\ln(R/R_0)-t$, for the [1-^{14}*C*]octadecanoic acid from the LB films labeled at the tenth layer under the conditions of 1×10^{-2} Pa and various temperatures (288.6—303.8 K). R denotes the radioactivity due to the labeled molecules remaining in the LB film at time t and R_0, that at t=0. By assuming a first-order reaction for the desorption process, initial slopes in the curves were adopted to obtain the rate constants k_1 for the desorption of the acid molecules. Figure 3 show the Arrhenius plots for the rate constants. Five plots at lower temperatures (288.6—298.2 K) show good linearity, while a plot at 303.8 K deviates from this line. Not only desorption but also molecular exchange reactions most likely occur from and among monolayers at the higher temperature. The apparent activation energy, 191.2 kJ mol^{-1}, for the desorption was obtained from the linear portion of the Arrheneus plots. This value is somewhat larger than the heat of sublimation for the octadecanoic acid crystal.[2] The heat of sublimation was calculated from the temperature dependence of its vapor pressure, which was obtained by Knudsen's method, near the melting point (342.2 K) of the crystal.

Figure 4 shows the desorption profiles for three kinds of samples in vacuo at 298.2 K. The first sample (▽) as labeled at the 9th layer, the second one (○), at the 10th layer, and the third one (□), at both the 9th and 10th layers. The desorption rate for the first sample is slower than that for the second one, but not zero. Some acid molecules seem to escape from the 9th layer as well as from the 10th layer even at the initial stage in spite of the existence of an additional monolayer on the 9th layer. The molecules is therefore thought to desorb as a dimer consisting of a pair of molecules across the 9th and 10th layers. One-half the sum (▲) of the relative radioactivities of the first and the second samples should be equal to the relative radioactivity of the third sample (□). However, the former was always larger than the latter.

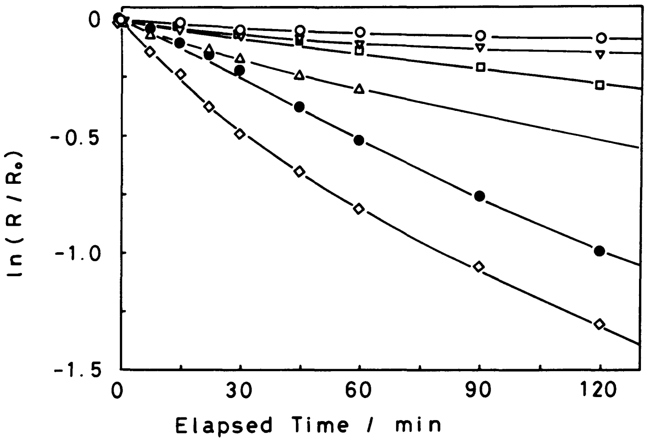

Fig. 2. Relationship between logarithm of relative radioactivity and evacuation time for the ^{14}C-sample labeled at the 10th layer under a pressure of 1X 10^{-2} Pa and various temperature. The mark ○ is at 288.7 K, ▽, at 290.7 K, □, at 293.4 K, △, at 296.3 K, ●, at 298.2 K, and ◇, at 303.9 K.

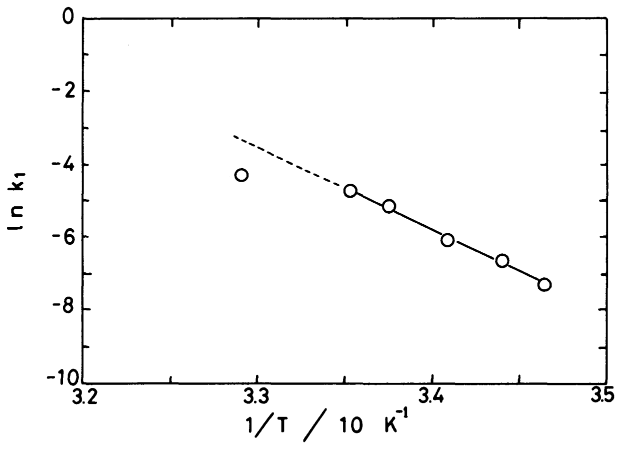

Fig. 3. The logarithm of the desorption rate for octadecanoic acid LB film labeled at the 10th layer vs. reciprocal temperature.

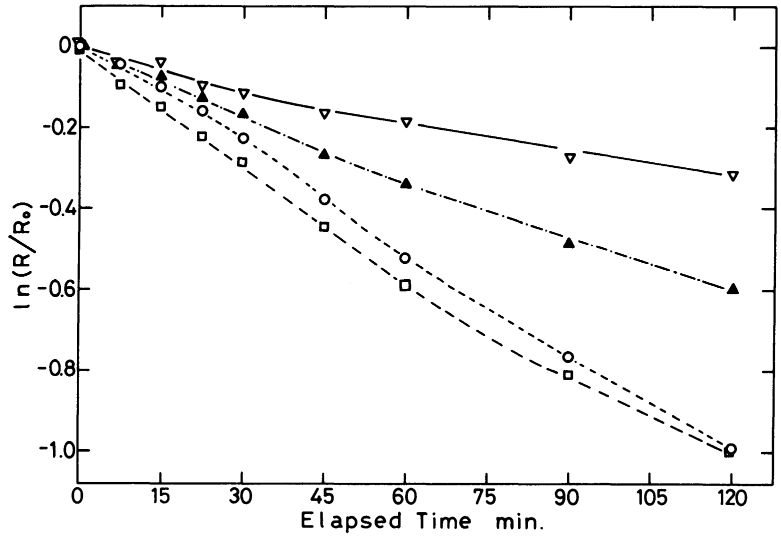

Fig. 4. Relationship between logarithm of relative radioactivity and evacuation time for various samples under a pressure of 1×10^{-2} Pa and at 298.2 K. ▽ denotes the sample labeled at the 9th layer, ○, the sample labeled at the 10th layer; □, the sample labeled simultaneously at the 9th and 10th layers; and ▲ one-half the sum of ▽ and ○.

Moreover, the relative radioactivity for the sample decreases significantly more than the relative radioactivities for the first and second samples. Consequently, the ^{14}C-labeled molecules appear to migrate among the layers even during the evacuation.

The radioactivity of another sample labeled at the 10 th layer was not altered after one-week storage under the conditions of atmospheric pressure and room temperature (298.2 K). The acid molecules, therefore, do not evaporate, but might migrate among and/or in layers under the above conditions. Fujihira et al.[11] observed the translayer diffusion in LB films by measuring the mobility of dyes. Such a translayer diffusion can be attributed to molecular exchange among the layers. To confirm the possibility of molecular exchange, four kinds of samples were prepared by the following procedure: Sample **a** was a LB film labeled at the 10 th layer; sample **b**, same as sample **a**, but stored for a week at 298.2 K and atmospheric pressure; sample **c**, a LB film labeled at the 9 th layer; sample **d**, same as sample **c**, but stored for a week at 298.2 K and atmospheric pressure. Desorption in vacuo for these four samples was observed. The $\ln(R/R_0)$–t relationship obtained is shown in Fig. 5. The desorption from sample **a** (◇) was faster than that from sample **b** (○), while the desorptions from the other samples **c** (□) and **d** (▽) were almost equal with that for sample **b** (○). Apparently, the acid molecules exchange their positions in and/or among monomolecular layers during the storage of the samples.

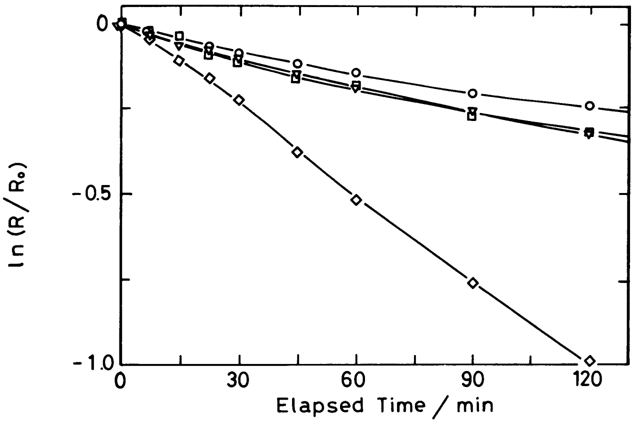

Fig. 5. Relationship between relative radioactivity and evacuation time for the various samples under a pressure of 10^{-2} Pa and 298.2 K. ◇ denotes sample **a** which is a LB film labeled at the 10th layer; ○, sample **b**, same as sample **a**, but stored for a week at 298.2 K and atmospheric pressure; □, sample **c**, LB film labeled at the 9th layer; ▽ sample **d**, same as sample **c**, but stored for a week at 298.2 K and atmospheric pressure.

The samples **b** and **d** stored for a week at 298.2 K and atmospheric pressure, showed a powdery appearance at their surfaces, while the sample just prepared or stored at lower temperature (278.2 K) did not have such an appearance. Figures 6-a and -b show the SEM pictures for two samples containing 10-monolayers of nonradioactive acid stored for a week at 278.2 K and at 298.2 K, respectively, under atmospheric pressure. The picture for the sample stored at 278.2 K (Fig.6-a) was as smooth as that for the sample just prepared, while that of the sample stored at 298.2 K (Fig. 6-b) had many white clusters having a diameter in the range of 0.2 to 3 μm. The clusters seem to be micron-

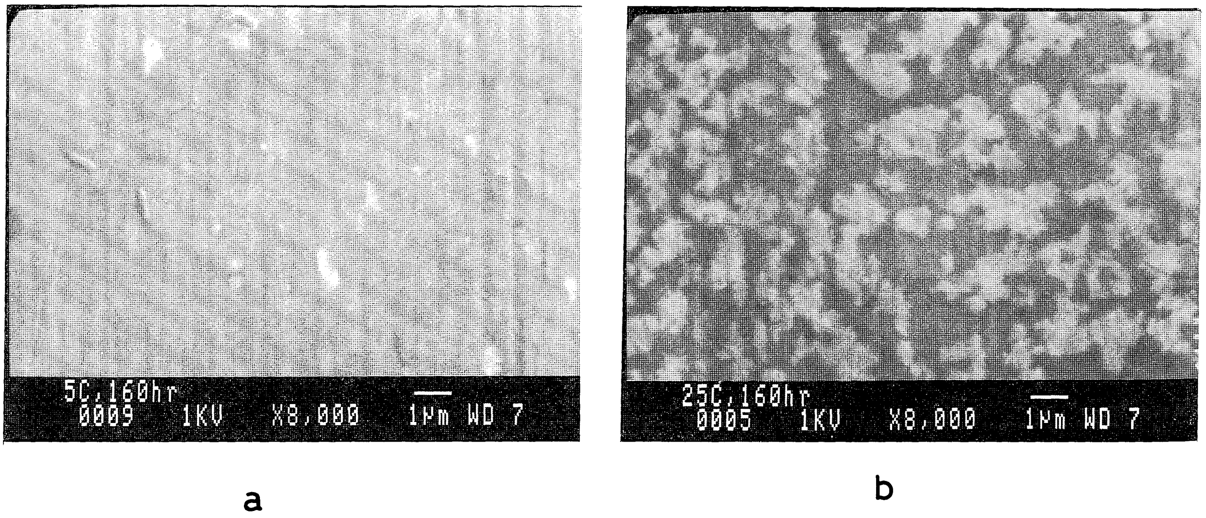

Fig. 6. Scanning electron micrographic (X5200) of the two samples containing 10 molecular layers of nonradioactive acid stored for a week under atmospheric pressure at 278.2 and 298.2 K. Photograph **a** is the sample stored at 278.2 K and photograph **b**, the sample stored at 298.2 K.

size crystals. The acid molecules in the LB film appear to migrate and aggregate to form the micron-size crystals during the storage at room temperature and under the atmospheric pressure. Let us examine the mechanism to produce such crystals.

The desorption of octadecanoic acid molecules in vacuo from its LB film is considerable:[12,13] Almost 90% of the [1-^{14}C]octadecanoic acid molecules in its monolayer on a quartz backing was evaporated after one hour evacuation at a pressure of 10^{-4} Pa.[12] Under atmospheric pressure, however, the radioactivity of the LB film of ^{14}C-labeled acid did not alter for a long time: There hardly occured any desorption of the acid molecules from the LB film under these conditions. The above two contradictory facts suggest the following for consideration: A thin boundary layer (stagnant layer) of the acid vapor occurs near the surface of the LB film as illustrated schematically in Fig. 7. In vacuo the molecules have a long mean-free path and can escape easily from the layer, while in air under the conditions of atmospheric pressure and room temperature the molecules, colliding frequently with air molecules or one another, have a short mean free path (10^{-7} m) and rarely escape (diffuse) from the layer into the air. Consequently, the desorption and adsorption of the molecules are continuously repeated between the LB film and the stagnant layer; the rates in the above two processes are in balance with one another. By repeated processes, an isothermal distillation[14] may occur from the extremely small crystallites (the LB film of multilayer of octadecanoic acid is, as mentioned before, an assembly of the extremely small crystallites),[6] to slightly larger crystallites. The extremely small crystallites would evaporate and disappear, while the slightly larger crystallites would become larger and larger during the one-week storage of the LB film. Thus film molecules can transfer over a long distance and coagulate into micron-size crystals. The "overturning" of octadecanoic acid molecules in monolayer[15,16] and the transference of ^{14}C-labeled acid from its LB film deposited on a solid surface onto other solid when the former solid was contacted with the latter one[17] might be due to the molecular migration by the desorption/adsorption process. Beischer,[18] and Rideal and Tadayon[19] reported the surface diffusion for the octadecanoic acid molecules in the monolayer deposited on mica surface the mobility of the molecules on the surface was found to be much greater than inside the bulk substance. The surface diffusion also seems to be attributed mainly to the desorption/adsorption process.

Estimation of Equilibrium Vapor Pressure. The desorption rate of an acid molecule from the LB film at time t is expressed as

$$-(\mathrm{d}\Gamma/\mathrm{d}t)_{\mathrm{des}} = k_1\Gamma, \qquad (1)$$

where Γ is the amount of radioactive octadecanoic acid in the LB film; k_1, the rate constant for the desorption. For the adsorption of molecules from the vapor layer onto a solid surface, the following equation is applicable,[20]

$$(\mathrm{d}\Gamma/\mathrm{d}t)_{\mathrm{ads}} = k_2PS_o \qquad (2)$$

where k_2 is the rate constant for the adsorption; P, the vapor pressure and S_o, the number of sites available for the adsorption of the film molecules.

From the constancy in the Γ–t relationship under atmospheric pressure it is concluded that the

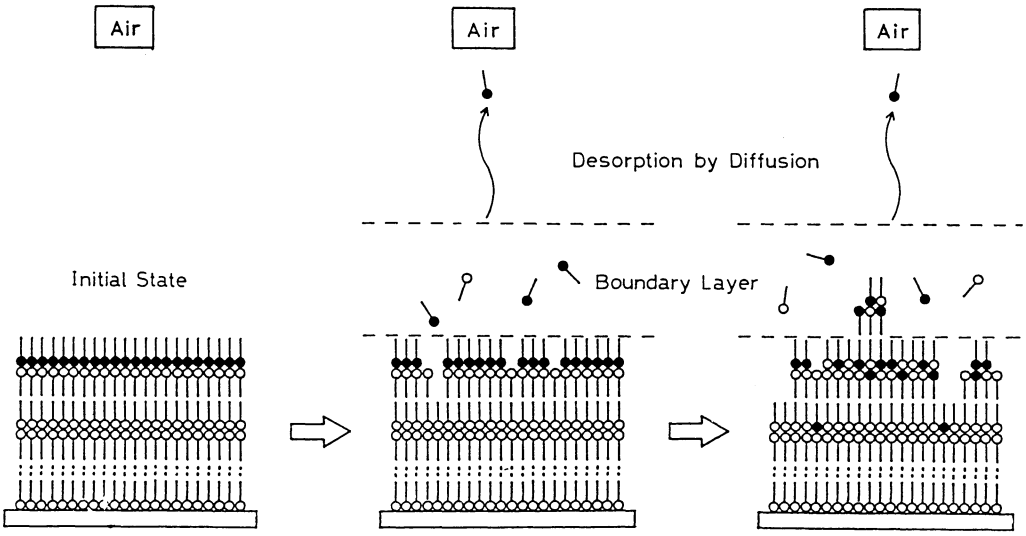

Fig. 7. Schematic drawing of molecular migration of the octadecanoic acid through the boundary (stagnant) layer near the surface of LB film.

adsorption and desorption rates are in balance with one another. Thus, we obtain

$$k_1 \Gamma = k_2 P S_o. \tag{3}$$

As Γ corresponds to the molecular density of octadecanoic acid at the outermost layer, S_o can be taken as equal to Γ, assuming that the adsorption occurs at any place in the outermost layer. According to the molecular kinetic theory, k_2 is proportional to the collision number of the molecules against the site having a definite area. Thus,

$$k_2 = N_a C \sigma_o \exp(-E_a^*/kT)/(2\pi MRT)^{1/2} \tag{4}$$

where N_a denotes the Avogadro number σ_o, the collision cross-section of octadecanoic acid molecule;[21] C, the sticking coefficient; M, the molar weight of octadecanoic acid and E_a^*, the apparent activation energy for the diffusion of the octadecanoic acid. Consequently, we obtain

$$P = k_1/k_2 = (2\pi MRT)^{1/2} k_1 / N_a C \sigma_o \exp(-E_a^*/RT). \tag{5}$$

The average time τ which the molecule remains on the surface is calculated to be of the order of 10^{21} s.[20] from the apparent activation energy, 191.2 kJ mol^{-1}, for the desorption of octadecanoic acid. The sticking coefficient can therefore be taken as unity. By putting the experimental k_1 value, 1.51×10^{-4} s^{-1}, at 298.2 K into Eq. 5, P is expressed as the function of E_a^*,

$$P = 6.66 \times 10^{-8} \exp(-E_a^*/RT). \tag{6}$$

Unfortunately as there are no data about the activation energy for the diffusion of the octadecanoic acid molecule in air, we substituted, as a rough approximation, the E_a^* value, 3.83 kJ mol^{-1}, for the octadecane into Eq. 6. This E_a^* value was obtained from the temperature dependence of its the diffusion coefficient[21] in air. Equation 6 gives 3.12×10^{-7} Pa at 298.2 K as the vapor pressure of octadecanoic acid. On the other hand, 10.6×10^{-7} Pa is obtained as the vapor pressure of octadecanoic acid at room temperature by the extrapolation of the reference value[2] of its vapor pressure near its melting point to room temperature. The former value is smaller than the latter. However, the molecular arrangement in the solid near its melting point is thought to be more disordered than at room temperature; the molecules in the former solid appear to evaporate more easily than at room temperature.

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