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Fractal dimension and complexity in the long-term dynamics of a monomolecular layer

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ABSTRACT

The formation of three-dimensional domains in monomolecular layers (Nucleation Dynamics, ND) of four fatty acids, stearic, arachidic, behenic and lignoceric acids, containing the same carboxylic (–COOH) head and an alkyl chain with 18, 20, 22 and 24 carbon atoms, respectively, on water surface, has been studied through Specific Molecular Area (A) versus time (t) studies from Surface Pressure (π)-A isotherms and Brewster Angle Microscopy (BAM). To investigate the fractal nature, the gray-scale Brewster angle micrographs are converted to binary images containing only two pixel values – 0 for 2D phase and 255 for 3D phase before box-counting method is employed to compute the fractal dimension. The 3D phase in the background of 2D phase is found to be fractal in nature. In fact, 3D phase is an interpenetration of two fractal structures with two different fractal dimensions – one corresponding to smaller (intra-domain) structures and other corresponding to larger (inter-domain) structures. These fractal dimensions are seen to evolve with coverage as 3D phase grows. The two fractal dimensions and their evolution in ND dynamics are identical for the longest-tailed lignoceric acid which has a porous 3D phase.

1. Introduction

Langmuir Monolayer (LM), a two-dimensional (2D) system is a mono-molecular layer of insoluble molecules at the air/water interface. Complexity and tunability of interactions in this self-assembled monolayer make it a very interesting subject of research [1–3]. In addition to various applications in mimicking biological systems, electrical, electronic and optical device fabrication [4–9] etc, there has been focus on the stability and long-term dynamics [3,10–14] of this system since a Langmuir monolayer can be in various states of metastability above equilibrium spreading pressure (ESP), the surface pressure spontaneously generated when the bulk amphiphile is brought in contact with a water surface depending on the external parameters.

If a LM is allowed to relax at constant surface pressure above ESP it undergoes a 2D–3D transformation with time. This constant pressure collapse is visible in the decrease in monolayer area (A) with time (t). In the constant pressure collapse, 3D phase can grow inside water (Desorption Dynamics or DD) and/or in the air (Nucleation Dynamics or ND). DD and ND can be distinguished from the shape of A-t curves, which is exponential for DD and sigmoidal for ND. As 3D phase grows on water surface in ND it can be captured through Brewster Angle Microscopy (BAM). The ND of LM is dependent on various external parameters such as surface pressure (π), subphase pH, and temperature. The most important field parameter regarding the 2D–3D transformation is, however, the tail length of the molecules, an internal parameter. This is related to lipophilic interaction and determines the long-term dynamics of LMs [3]. Thus Brewster Angle Microscopy of LMs with varying tail lengths

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can lead to better understanding of long-term ND of these systems.

Fractal analysis is found to be very useful in understanding many natural objects and processes. Fractal geometries are in fact more prevalent in nature compared to the Euclidean geometry. Recently fractal analysis has been applied to a wide range of objects in various fields. Physical properties such as relative permittivity, specific capacitance etc, believed to be material specific, are shown to be dependent on the fractality of the structures, too [15]. The correlation between fractality and compressibility moduli of Langmuir monolayer structures provides an easy and unambiguous identification of the onset of percolation, a second-order phase transition [16]. There are many instances where the fractal natures of a system and its model have been compared to verify the reality of the model. Edler et al have compared the fractal parameters such as fractal dimension and lacunarity, together with other statistical descriptors of experimentally obtained Brewser Angle micrographs and simulated images, to show that the cluster-cluster aggregation (CCA) process is a good model for the growth of templated, mesoporous, silica thin films at the air/water interface [17]. Lydia et al have compared three different fractal analysis methods, Box-Counting Method, Sandbox Method and Minkowski Density Method for solid alkane monolayer domains at SiO_2/air interfaces and found out confidence limits for them by comparing the scaling behavior of various morphological measures such as area, boundary and curvature [18]. The domains of monolayers prepared with all the lipid and protein components of myelin at the air/water interface are reported to be highly self-similar and the fractality of the monolayers observed through epifluorescence, BAM and ellipsometry are found to span at least three orders of magnitudes, from the micrometer to the millimeter range with fractal dimension equal to 1.7 [19]. Although fractal analysis of various LM structures have been performed, the fractality of 2D–3D transformation dynamics has not been examined yet.

In this communication, the long-term ND dynamics of fatty acid monolayers with varying tail-lengths has been studied through monolayer area versus time curves and BAM micrographs and also the evolution of fractal dimension of growing 3D structures in the 2D monolayer has been investigated.

2. Experimental details

Four fatty acids, stearic, arachidic, behenic and lignoceric acids, containing the same carboxylic (–COOH) head and an alkyl chain with 18, 20, 22 and 24 carbon atoms, respectively, with quoted purity > 99% were purchased from Sigma-Aldrich. Each fatty acid was dissolved in Chloroform (Merck) to prepare 3 mM solutions before spreading the solution on Milli-Q water (resistivity 18.2 MΩ -cm) in a KSV-NIMA Langmuir trough at room temperature (25°C). The monolayer was compressed with a speed of 5 cm^2/min after solvent evaporation and equilibration and the surface pressure was measured by a Pt Wilhelmy plate.

Relaxation curves (A-t) of each monolayer were obtained by maintaining the monolayer at $\pi = 30$ mN/m, measuring the monolayer area as a function of time (t) and normalizing the area values with the initial area. The subphase temperature was maintained at 25°C using Julabo Recirculating Cooler (FL300).

The long-term dynamics of the monolayers was captured using an Imaging Ellipsometer (Accurion GmbH) in the BAM mode with laser intensity set high. Time for a monolayer to transform entirely into multilayers was obtained from BAM movie filmed at 8 frames per second (fps) during destabilization.

3. Results and discussions

3.1. Nucleation dynamics with tail length

Fig. 1(a) shows the area fraction (A_n) versus time (t) curves for monolayers of the four different fatty acids. For fatty acids with tail containing more than 16 carbon atoms, the dominant destabilization mechanism is nucleation. Thus all the fatty acids used in our experiment destabilize via nucleation dynamics as seen in in this figure. In ND, multilayer centers form (slow transformation), grow and overlap, with new multilayer centers forming in the intermediate period (fast transformation) and finally only a small portion of monolayer is left to be transformed into multilayers (slow transformation). Although the shape of the $A_n - t$ curves is sigmoidal for all the four fatty acids yet the dynamics becomes slower for longer tailed fatty acids.

The time taken by a monolayer to transform entirely into multilayers can be obtained from the asymptotic lines of the $A_n - t$ curves and also from BAM movies. The transformation time obtained from the two techniques is the same. The transformation times are higher for the longer tailed fatty acids indicating slow destabilization dynamics and high stability. In ND the monolayer forms multilayers, hence the minimum upward displacement of a molecule is the length of the molecule. Fig. 1(b) shows the plot of the squares of nominal chain lengths of the four molecules against their transformation times. From the plot it is clear that the upward displacement varies linearly with the square root of the times indicating out-of-plane diffusion of the molecules. The linear fit of the plot gives the slope of 0.011 nm^2/s which corresponds to the value of the average upward diffusivity. This value is larger than the upward diffusivity of arachidic acid molecules obtained from ellipsometric measurements [3] most probably due to the larger Surface Pressure at which these measurements are carried out here.

BAM images of stearic, arachidic, behenic and lignoceric acid monolayers are captured during 2D–3D transformation and are shown in Fig. 2(a–h) for the same fractional area coverage. Each of the BAM images has the dimensions of 336.00 μm × 430.89 μm (740 px × 949 px). Fig. 2(a–d) shows the BAM images of the four fatty acid monolayers around the fractional area coverage of 4.0%. It is clear from the images that the total number of 3D domains decrease and the size of the 3D domains increase for shorter tailed fatty acids. The total number of 3D domains is maximum for lignoceric monolayers. Fig. 2(e–h) shows the BAM images of the same four monolayers around the fractional coverage area of 31.0%. Both the number of 3D domains and the porous character of the monolayers increase with the tail length probably due to the high degree of lipophilic attraction of these