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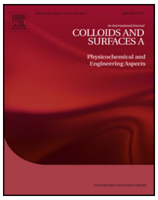

Subphase pH induced monolayer to multilayer collapse of fatty acid Salt Langmuir monolayer at lower surface pressure

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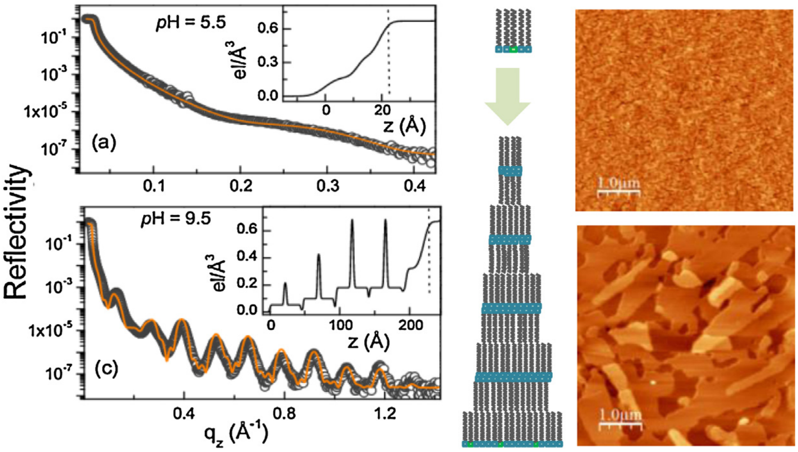
HIGHLIGHTS

- Barium stearate monolayer transforms into multilayer structure from very low surface pressure.
- Monolayer to multilayer collapse occurs at pH ≈9.5 of subphase water.
- Such lower pressure collapse for fatty acid salt Langmuir monolayer is unusual.
- Formation of bidentate chelate coordination in headgroups is responsible for this collapse.
- Monolayer of relatively longer chain barium arachidate or bariun behenate not collapses at that lower pressure.

GRAPHICAL ABSTRACT



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ABSTRACT

Subphase pH induced monolayer to multilayer collapse at very low surface pressure of barium stearate Langmuir monolayer has been confirmed from the surface pressure versus specific molecular area (π–A) isotherms, X-ray reflectivity (XRR) and atomic force microscopy (AFM) studies. From the π–A isotherms it is clear that stearic acid molecules form a monolayer on the water surface in the presence of Ba^{2+} ions at pH ≈ 5.5 (low) and ≈6.8 (moderate) and remain as a monolayer before collapse pressure ($\pi_c = 55$ mN/m). However, at high subphase pH (≈9.5), 2D–3D structural transition starts to occur from the very low surface pressure as indicated by the π–A isotherm and is verified by both XRR and AFM as the barium stearate multilayer structure deposits in the single up stroke of hydrophilic Si substrate at $\pi = 25$ mN/m. Subphase pH induced monolayer to multilayer formation at such lower surface pressure is unusual. Fourier transform infrared spectroscopy results confirm that the formation of bidentate chelate coordination in the metal containing headgroup is the reason for such monolayer to multilayer transition. Relatively longer chain fatty acid molecules like arachidic and behenic acids do not show such type of monolayer collapse.

1. Introduction

Langmuir monolayer is a thermodynamically metastable two-dimensional phase [1,2] and usually after passing through several two dimensional phases like liquid expanded, liquid condensed and

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solid [1–3], shows three dimensional phases [1] under over compression, where modified structures are formed in the direction perpendicular to the water surface [4–7]. Such two to three dimensional structural transformations occur at a particular surface pressure called collapse pressure (π_c). However, π_c for a particular monolayer depends upon the experimental parameters like barrier compression speed, temperature, subphase pH, dissolved ions in the water subphase etc [8]. and the structures formed after π_c also depend upon the relaxation time [9]. Structures of monolayer before and after π_c and the related mechanisms of 2D–3D transitions have been proposed [4,10–18]. In general, 2D–3D transition, i.e., collapse process and the corresponding structural modifications are irreversible [19], however, for certain monolayer [20] and mixed monolayers reversible collapse can also takes place [21–23]. Two dimensional crystalline order structures have also been observed from the collapsed films [24,25].

Long chain fatty acid molecules before π_c are in the typical asymmetric configuration [26–29] with all the hydrophilic headgroups touching the water surface and all the hydrophobic tails up in the air, and the layer can be called as asymmetric molecular layer or conventionally monolayer. After π_c, film generally takes two different configurations. In one configuration, only one symmetric molecular layer structure forms above the asymmetric molecular layer, where in the symmetric molecular layer all molecules take the symmetric configuration, i.e., tails are exist on the both sides of the headgroups [26–28]. This symmetric molecular layer is nearly same as conventional bilayer like structure where one monolayer touches the other inverted monolayer through the headgroups [2]. The total film, i.e., the sum of monolayer and bilayer structure is conventionally called as trilayer. In other configuration, more than one symmetric molecular layer or bilayer forms above the monolayer, i.e., multilayer structure forms. The former structure is usually observed for constant pressure collapse where surface pressure remains nearly constant after π_c [27,28], whereas the later structure is observed for constant area collapse where collapse occurs at a constant area per molecule [27] and the surface pressure drops just after π_c. Subphase pH and the types of dissolved ions modify the collapse nature of the monolayer and the corresponding collapsed structures [27,30]. Like external barrier compression, variation of chemical conditions also affects the monolayer collapse and collapsed structure. If fatty acid salt molecules are made chemically in bulk solution and then the pre-formed salt molecules are spread on the water surface then the film structure and the nature of collapse becomes different compared with that of the film formed by the fatty acid salt molecules at the air–water interface [29,31]. If the structural transition from monolayer to trilayer or multilayer is considered as the signature of monolayer collapse then for standard fatty acids and fatty acid salts, monolayer collapse occurs generally at higher surface pressure, i.e., above ≈50 mN/m [1,2,27,28,30]. On the other hand, preformed fatty acid salt molecules take trilayer or multilayer structures from the very low surface pressure [26,29]. Although structural modifications due to monolayer collapse for different systems for different physicochemical conditions have been observed and the corresponding mechanisms have been proposed, but a basic and thorough understanding of the structural transition from two to three dimensions at very low surface pressure is missing.

In this article, we have shown the subphase pH induced structural modifications of the monolayers of long chain fatty acids in the presence of Ba^{2+} ions in the water subphase at lower surface pressure. Out-of-plane structures and the top surface morphologies are obtained from the X-ray reflectivity (XRR) and atomic force microscopy (AFM) studies after depositing the films on hydrophilic Si (001) substrates by using Langmuir–Blodgett (LB) method. In the presence of Ba^{2+} ions and at low (≈5.5) and moderate (≈6.8) subphase pH, and at lower surface pressure (25 mN/m), BaSt molecules form a monolayer on the water surface and are deposited as a monolayer on the Si substrate in single upstroke. However, at high (≈9.5) subphase pH, BaSt multilayer structure forms on the water surface and is deposited as a multilayer in the single upstroke of hydrophilic Si (001) substrate at 25 mN/m. Formation of monolayer and multilayer structures are verified by both the XRR and AFM analysis. The results obtained from the Fourier transform infrared (FTIR) spectroscopy confirm that the formation of bidentate chelate coordination in the metal-containing headgroup is the reason for such monolayer to multilayer transition. Monolayer to multilayer transition has not been observed for relatively longer chain fatty acid salt molecules like barium arachidate (BaAr) and barium behenate (BaBe) at that lower surface pressure and high subphase pH due to the presence of comparatively higher tail–tail hydrophobic interactions.

2. Materials and methods

Stearic acid [$CH_3(CH_2)_{16}COOH$, Sigma, 99%], arachidic acid [$CH_3(CH_2)_{18}COOH$, Sigma, 99%] and behenic acid [$CH_3(CH_2)_{20}COOH$, Sigma, 99%] molecules were spread from a 0.5 mg/ml chloroform (Aldrich, 99%) solution on Milli-Q water (resistivity 18.2 MΩ cm) containing barium chloride ($BaCl_2{\cdot}2H_2O$, Merck, 99%) in a Langmuir trough (Apex Instruments). pH of the water subphase containing 0.5 mM barium chloride was maintained at ≈5.5, 6.8 and 9.5 for different experimental conditions. No buffers were used to maintain the pH of the subphase. Nearly 3–4 h were spent for pH stabilization excluding initial magnetic stirring. π was measured with a paper Wilhelmy plate and the monolayer was compressed at a constant rate of 5 mm/min during all isotherm measurements and film depositions. All depositions were done by using LB method at 25 mN/m and at room temperature (24 °C). Depositions were carried out at a speed of 1.5 mm/min. Prior to the deposition, Si (001) substrates were made hydrophilic after keeping it in a mixed solution of ammonium hydroxide (NH_4OH, Merck, 30%), hydrogen peroxide (H_2O_2, Merck, 30%), and Milli-Q water ($H_2O{:}NH_4OH{:}H_2O_2 = 2{:}1{:}1$, by volume) for 5–10 min at100 °C. Immediately after cleaning, all the substrates were kept inside the Milli-Q water until LB deposition.

X-ray reflectivity (XRR) measurements were carried out using an X-ray diffractometer (XRD) setup. Diffractometer (D8 Advanced, Bruker AXS) consists of a Cu source (sealed tube) followed by a Göbel mirror to select and enhance Cu Kα radiation ($\lambda = 1.54$ Å). Scattered beam was detected using NaI scintillation (point) detector. Data were taken in specular condition, i.e., the incident angle (θ) is equal to the reflected angle (θ) and both are in a scattering plane. Under such condition, a nonvanishing wave-vector component, q_z, is given by $(4\pi/\lambda)\sin\theta$. Analysis of XRR data has been carried out using Parratt's formalism [32] where the film is considered as a stack of multiple homogeneous layers with sharp interfaces. To analyze the XRR data, surface and interfacial roughness has been included [33,34]. Electron-density variation, i.e., the electron-density profile (EDP) in a particular specimen is determined by assuming a model for the same and comparing the simulated profile with the experimental data. EDP is extracted from the fit [33,35] which gives in-plane (x–y) average electron density (ρ) as a function of depth (z) with high resolution [26,27,33–35].

Surface topography of all the deposited films were studied through an AFM (NTEGRA Prima, NT-MDT Technology) in semi-contact mode using silicon cantilever having spring constant 11.8 N/m. Scans were performed over several portions of the films for different scan areas. WSxM software [36] has been used for AFM image processing and analysis. Films formed on the silicon substrates by LB method were used to take attenuated total reflection-Fourier transform infrared (ATR-FTIR) spectroscopy