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Adsorption of a water soluble cationic dye into a cationic Langmuir monolayer

Ashis Shil, S.A. Hussain, D. Bhattacharjee *

Department of Physics, Tripura University, Suryamaninagar 799022, Tripura, India

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ABSTRACT

This communication reports the successful adsorption of a water soluble cationic fluorescent dye Rhodamine B (RhB) into a cationic Langmuir monolayer of Octadecylamine (ODA). Anionic nano clay platelets Hectorite played an important role in the process of adsorption. Surface pressure vs. area per molecule (π–A) isotherms were studied to monitor the adsorption process. In-situ fluorescence Imaging Microscopic (FIM) technique was employed to visualize the domain structures formed at the air–water interface. Atomic Force Microscopic (AFM) image of the monolayer Langmuir–Blodgett (LB) films were taken to study the morphology and ultrastructure of the film. Detailed spectroscopic investigations were carried out on the mono- and multilayer Langmuir–Blodgett (LB) films.

1. Introduction

Langmuir monolayer is a well defined two dimensional monolayer where molecular orientation, packing order, phase behavior and other properties can be controlled precisely by changing various parameters [1]. There are various experimental techniques to analyze the monolayer at the air–water interface, namely surface pressure vs. area per molecule isotherm (π–A), in-situ Florescence Imaging Microscope (FIM) and in-situ Brewster Angle Microscope (BAM) techniques etc. Mono- and multi- layered Langmuir–Blodgett (LB) films are obtained when the Langmuir monolayers at the air–water interface are transferred onto solid substrates. Studies of Langmuir monolayer at the air–water interface and LB films on the solid substrates are important to understand the molecular interactions and especially for biomembranes [1]. Recently works are now going on to study the effect of incorporation of various water soluble organic dyes, proteins, DNA and other biologically important molecules into preformed Langmuir monolayer of surfactants and lipids [2,6]. It may be mentioned in this context that various lipids are the important constituents of biomembrane or biological membranes. Most of the lipids and other surfactants are ionic in nature.

Proteins, enzymes and bioactive fluorescent dyes are mostly water soluble. They are cationic or anionic in nature. For immobilization of these molecules by Langmuir–Blodgett (LB) technique, first of all they are allowed to be dissolved into the aqueous subphase of the Langmuir trough and subsequently adsorbed onto a preformed Langmuir monolayer of opposite charge at the air–water interface. The template monolayer plays the role to adsorb these molecules from the aqueous solution and also immobilizes the molecules into the corresponding LB film. Electrostatics interaction plays a significant role in the process of adsorption.

A large number of works have been done previously to study the adsorption and immobilization of anionic/cationic types of water soluble materials into the Langmuir monolayer of oppositely charged lipids and various other surfactants. In such studies anionic surfactants used for the preparation of Langmuir monolayer were stearic acid (SA) and arachidic acid (AA). Octadecylamine (ODA) forms cationic Langmuir monolayer. The well known phospholipid 1, 2-dipalmitoyl-sn-glycero-3-phosphocholine (DPPC) is a zwitterionic lipid and has the capability to form the stable Langmuir monolayer at the air–water interface. Both anionic and cationic types of molecules are adsorbed into the DPPC monolayer.

Adsorptions of cationic molecules into the anionic stearic acid (SA) monolayers have been investigated by several authors. Interaction between cationic protein ovalbumin (OVA) and stearic acid monolayer (SA) was investigated under different conditions [2]. Interaction of stearic acid (SA) with various metal ions present in the sea water has been investigated in detail [7].

Adsorption and immobilization of several water soluble anionic

* Corresponding author. Fax: +91 3812374802.
E-mail addresses: ashisphy.tu@gmail.com (A. Shil), sa_h153@hotmail.com (S.A. Hussain), debu_bhat@hotmail.com (D. Bhattacharjee).

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molecules have been done into the cationic ODA monolayer. Adsorption of anionic merocyanine dye (MC540) into the cationic ODA monolayer was investigated to understand the photophysical properties of MC540 in LB film [8]. DNA-surfactant complexation is a non-viral method of gene delivery into the cell. In a recent work the adsorption of DNA into the preformed Langmuir monolayer of cationic surfactant ODA at the air–water interface has been studied [3]. The incorporation of water soluble anionic surface active enzyme Pepsin (PEP) within an insoluble cationic ODA Langmuir monolayer was investigated by changing various parameters [9].

The most important works in this respect are the adsorption of various anionic and cationic molecules into the zwitterionic lipid monolayer of DPPC. DPPC is a major constituent of cell membrane [10]. It can form stable Langmuir monolayer at the air–water interface [11]. Being zwitterionic, it can interact electrostatically with both cationic and anionic types of molecules. Cationic biological macromolecules Chitosan imposes disruption on cell membrane and can interact strongly with a modal membrane bilayer of DPPC under a slight acidic solution [4]. A lipid layer composed of a binary mixture of cholesterol myristate (CM) and DPPC form a modal tear film [5]. Adsorption of Lysozyme in this model tear film increased the compressibility and resulting in a more expanded film. Interaction between DPPC phospholipid Langmuir monolayer and the cationic protein hemoglobin was studied by Langmuir–Blodgett technique under different conditions [6]. Interaction of Langmuir monolayer of DPPC with a tetramaric enzyme Bovine testicular hyaluronidase (BT-HAase) was studied [12]. Enzymatic activity was found to increase in the mixed medium of lipid film compared to homogeneous medium. In a recent work effect of submicrometer particles such as negatively charged polystyrene particles on the interfacial property of DPPC monolayer has been studied [13].

Several charged nanoparticles (NP) from aqueous dispersions were adsorbed into the preformed charged (anionic, cationic or zwitterionic) Langmuir monolayer. Formation of Iron–oxide nano particles (IONP) by the adsorption of Fe^{+3} ions from subphase containing $FeCl_3$ into a preformed zwitterionic DPPC Langmuir monolayer was investigated by Langmuir and Langmuir–Blodgett technique [14]. In another recent work the adsorption of negatively charged nanoparticles of Prussian Blue Analogues (PBA) into a zwitterionic phospholipid DPPC under various conditions has been investigated [15]. The adsorption of gold nanoparticles (Au NPs) dispersed in the subphase by floating ODA Langmuir monolayer was investigated [16].

Adsorption mechanisms of water soluble cationic RhB molecules onto anionic stearic acid (SA) monolayer [17] and zwitterionic DPPC monolayer [18] have been reported previously. In-situ Fluorescence Imaging Microscopic (FIM) studies revealed the formation of distinct circularly shaped domains at the air–water interface.

Thus it is clearly evident that a number of works have been reported on the adsorption of water soluble ionic molecules onto the oppositely charged preformed Langmuir monolayer of surfactants and lipids. However the main drawback of this process is that during the process of adsorption, molecular aggregation may occur to a larger extent.

Unlike in the previous works here in the present investigation, water soluble cationic fluorescent dye Rhodamine B (RhB) molecules were allowed to be tagged and organized onto the surface of the anionic nano-clay platelets dispersed in the aqueous subphase of the Langmuir trough. Subsequently the RhB tagged nano clay platelets were adsorbed onto the preformed Langmuir monolayer of cationic surfactant Octadecylamine (ODA). The purpose of the present work was to establish the following things: First one was to demonstrate the feasibility of adsorption of water soluble cationic molecules onto the preformed Langmuir monolayer of same kinds of cationic amphiphilic molecules ODA. During the process of adsorption, oppositely charged nano clay platelets were used as mediators. Thus we need not have to be concerned about the oppositely charged monolayer while adsorbing an ionic molecular dye onto the preformed Langmuir monolayer. Depending on the ionic nature we may use an oppositely charged mediator. The ionic nano clay platelets are excellent mediator in this respect due to their particular shape, rigidity, non hazardous nature, non-toxicity and large charge concentration on the surface. Also once the water soluble molecules were organized onto the nano clay platelets and subsequently adsorbed onto the preformed Langmuir monolayer, chances of aggregation might be reduced. This is our second purpose of investigation.

UV–vis absorption and fluorescence spectroscopic studies have been employed to study the nature of aggregation.

Clay minerals such as smectites are well known for their ability to adsorb organic materials and thus have shown great promise for the construction of hybrid organic–inorganic nanomaterials due to their unique material properties, colloidal size, layered structure and nano scale platelet dimensions. They have high mechanical strength, mechanical stability and provide unique conducting, semi-conducting and dielectric properties. Organo clay hybrid film is an important area of research in recent time and has applications in sensors, electrode modifiers, non-linear optical devices and pyroelectric materials [19–22]. Smectites clay minerals exhibit high affinity for metachromic cationic dyes because the negative charges of the smectites are compensated by the positive charges of cationic organic materials by cation exchange reaction [23].

Rhodamine B (RhB) is a xanthene molecular dye with outstanding spectral luminescence properties and has vast applications in the field of biological systems, sensors and marker based on thin films [24], in studies of nano objects [25] etc. In biological device application RhB is required to be embedded in a solid matrix. Therefore, studies for the immobilization of fluorescent dyes into a template monolayer are important. In the present investigation surface pressure vs. area per molecule (π–A) isotherms and in-situ fluorescence imaging microscopic (FIM) technique have been employed to study the adsorption mechanism at the air–water interface. Mono- and multi-layered LB films of this hybrid monolayer have been studied in the light of UV–vis absorption and fluorescence spectroscopy.

2. Experimental

2.1. Materials

Rhodamine B (RhB) and Octadecylamine (ODA), purity $>99\%$, were purchased from Sigma chemical company and used as received. The purity of the samples was checked by UV–vis absorption and fluorescence spectroscopy. Solvent chloroform (SLR, India) was of spectroscopic grade and its purity was checked by fluorescence spectroscopy before use. The Clay mineral Hectorite used in this study was obtained from the Source Clays Repository of the Clay Minerals Society.

2.2. Instruments

Surface pressure vs. area per molecule (π–A) isotherms and LB films preparation were done by using LB film deposition instrument (APEX-2000 C). Fluorescence Imaging Microscopic (FIM) studies were done by using in-situ Fluorescence Imaging microscope (Motic AE 31) attached with the LB instrument. Aqueous clay dispersion was prepared by using ultra pure Milli-Q (resistivity 18.2 MΩ cm) water. Concentration of clay dispersion was 10 ppm. It was stirred for 24 h and then sonicated for 30 min prior