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Research paper

Structural and optical properties of two-dimensional gadolinium stearate Langmuir monolayer

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HIGHLIGHTS

- Langmuir-Blodgett (LB) films of rare-earth-ions are ideal to study 2D magnetic order.
- X-ray measurements on Gadolinium-Stearate Langmuir monolayer and LB films presented.
- Spectroscopy results show trivalent Gd-ion link to two COO groups and one OH group.

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ABSTRACT

Langmuir-Blodgett (LB) films having large stack of amphiphilic-fatty-acids bearing rare-earth-ions are ideal two-dimensional magnetic systems to study spin-vortex ordering as the distances of the magnetic-ions along the out-of-plane and in-plane directions differ by an order of magnitude. Here we present results of in-situ X-ray scattering measurements on Langmuir monolayer of the amphiphilic stearic acid on the water surface containing Gadolinium ions to understand the formation process of monolayer and multilayer LB films on the substrates. Infrared spectroscopy and microscopy measurements were also carried out to understand the growth and transfer mechanism of the LB films.

1. Introduction

A liquid surface provides us an ideal flat substrate to study the structure and phase behavior of two-dimensional (2D) assembly of amphiphilic molecules [1–5]. The molecules spread on a liquid surface assemble themselves into ordered superstructures through relative interaction between hydrophilic and hydrophobic parts [5–7]. Langmuir technique is a well-controlled and remarkably simple method to study structural organization of metallic ions just below the water surface with respect to the superlattice of hydrophobic 'tails' above it [7–8]. The 2D-ordering of these molecules can be changed simply by squeezing tails with sliding the surface barriers and it is known that sequential transfer of the Langmuir monolayer from water surface to solid-substrate forming multi-layer Langmuir-Blodgett (LB) films become easier in presence of metallic ions in sub-phase and above certain surface pressure [9–12].

Ordering and dynamics of the spin-vortices have remained an intriguing problem in low-dimensional physics as the understanding of this subject is important for both fundamental science and technological applications [13–17]. Multilayer stack of amphiphilic fatty-acids attached with ions of rare-earth elements provide excellent 2D system to study low-dimensional magnetic ordering and melting [18]; since the characteristic in-plane separations between metallic ions are an order of magnitude smaller than the out-of-plane layer-spacing decided by the hydrophobic tails [19–20]. By proper selection of rare-earth ions and amphiphilic anchoring molecules, one can effectively fabricate long-range ordered 2D systems [21–23]. Gadolinium is special among the rare-earth ions as it has high value of spin moment (7 Bohr magnetron) without having any orbital moment. The spin-vortex formation in Gadolinium Stearate (GdSt) LB films have been shown by a series of magnetization and polarized neutron reflectivity measurements [15,18,23]. The detailed structural analysis and bridging coordination of the Gd-ions with the carboxylate groups in GdSt films is thus of major importance.

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Here we present results on the structure, morphology and bonding of GdSt on the water surface and on solid substrates. We have primarily used X-ray reflectivity (XRR) and grazing incidence X-ray diffraction (GIXD) techniques in synchrotrons and Brewster angle microscopy (BAM) measurements to study the in-situ structure and morphology of the ML on water surface. XRR and Fourier transform Infrared (FTIR) spectroscopy were carried out on the LB films to elucidate information regarding the bonding of carboxyl and hydroxyl anions connected to the Gd-cations. We plan to extend these studies in other rare-earth ions like Erbium (Er) and Holmium (Ho) having non-zero orbital moments.

2. Experimental methods

The GdSt Langmuir monolayer was prepared by gently spreading stearic acid (SA; $CH_3(CH_2)_{16}COOH$) solution in chloroform (concentration ~0.2 mg/ml) on the surface of water (Millipore, resistivity ~18.2 MΩ cm) sub-phase containing 0.5 mM Gd^{3+} ions (dissolved gadolinium acetate) [19]. The trough was placed in a closed chamber under inert atmosphere on an anti-vibration table and the sub-phase temperature was fixed at 15 °C as we found through GIXD that the domain-size improves at lower temperature. The LB films were deposited on hydrophilic Si(0 0 1) substrate at a dipping speed of 2 cm/minute for decent transfer ratio and a constant pressure (30 mN/m) was maintained during transfer by an automated differential feedback arrangement. XRR measurements were performed at the Indian beamline in Photon Factory, KEK, Japan [24] with a focused beam of energy 11.38 keV and X-ray beam-size of 0.2 × 1.5 mm^2 (V × H). GIXD spectra were collected in an undulator-beamline (SIRUS) of SOLEIL, France [25] with a beam of energy 8 keV. BAM images were obtained using a monochromatic laser beam (658 nm) incident at the Brewster angle of water in a large Langmuir trough (Nima Technologies, UK). FTIR spectroscopy measurements were carried out in reflection mode at 4 cm^{-1} resolution using a Perkin-Elmer Spectrum 400 FTIR spectrometer [26].

3. Results and discussion

3.1. Monolayers at the air-water interface

3.1.1. Isotherm studies

A schematic of the experimental set-up and a typical pressure-area (π-A) isotherm of the GdSt Langmuir monolayer at the air-water interface is presented in the Fig. 1. The region of flat plateau and high compressibility in the isotherm is the 'gaseous' phase. The phase of low compressibility is identified as 'liquid expanded' (LE) phase followed by the 'liquid condensed' (LC) phase. The 'kink' in the isotherm during transition (LE to LC) manifests the second order phase transition [5]. Beyond this phase the available area per molecule reaches to a limit and the monolayer goes into the 'collapsed' phase (C). The area per molecule of GdSt just before collapsed phase was obtained as ~22 Å^2.

3.1.2. BAM studies

BAM images of the GdSt Langmuir monolayer were collected at 15 °C, for π = 0.3 (G), 5 (LE), 30 (LC), 50 (collapsed) mN/m and representative data are shown in Fig. 2. At π = 0.3 mN/m, the film is made of discontinuous islands (Fig. 2a) as expected in the highly compressible gaseous state. The floated film forms a continuous monolayer starting from π = 5 mN m^{-1} (LE phase) to π = 30 mN m^{-1} (LC phase) as shown in Fig. 2b and c respectively. The presence of waviness/ripples in the image (Fig. 2d), obtained at collapsed phase suggests the formation of a buckled monolayer film due to excess compression. The difference in measured intensities from the monolayer and from the uncovered water in Fig. 2a is approximately proportional to the thickness of the monolayer and was defined as Φ. The patches in Fig. 2d produce an average intensity difference (ϕ) extracted from line profiles collected across different parts of the patches, which corresponds to a systematic small variation of thickness and ϕ was found to be an order of magnitude lower than Φ. This observation rules out any possibility of bilayer formation and the thickness variation could be understood through a periodic variation of molecular tilt, given by $\tau = \sin^{-1}(\phi/\Phi)^{1/2}$, and the values of τ were found to vary between 0° and 22°. This variation in tilt-angles give rise to additional roughness in tail-air interface even at lower pressure as observed in the XRR and GIXD results, presented below.

3.1.3. XRR studies

The collected reflectivity in an X-ray detector from the liquid surface can be written as [1,27]

$$R(q_z) = R_P(q_z)S(q_z, q_{xy}) \quad (1)$$

where, $R_P(q_z)$ is the reflectivity as considered in Parratt Formalism [28] and $S(q_z, q_{xy})$ is the contribution of diffuse scattering that depends primarily on the capillary wave fluctuations [1,27,29]. To avoid inclusion of diffuse scattering contribution $S(q_z, q_{xy})$ in the fitting of measured data [30], we have divided measured reflectivity ($R_M(q_z)$) by that of the pure water surface ($R_W(q_z)$). The obtained data was multiplied by theoretical Fresnel reflectivity ($R_f(q_z)$) of water surface to generate reflectivity profiles ($R(q_z)$) as given below.

$$R(q_z) \approx \frac{R_M(q_z)}{R_W(q_z)} R_f(q_z) \quad (2)$$

The electron densities (ρ), thicknesses (d) and interfacial roughness (σ) along the depth of the film are then extracted from the fitting of the corrected reflectivity data ($R(q_z)$) by Parratt Formalism [28].

The measured and fitted reflectivity profiles (R_P) are shown in Fig. 3a and the corresponding R/R_f profiles are shown in Fig. 3b for better clarity. The fitting was performed with a simple box model having two sub-layers of thickness d_1 and d_2 representing organic-tails

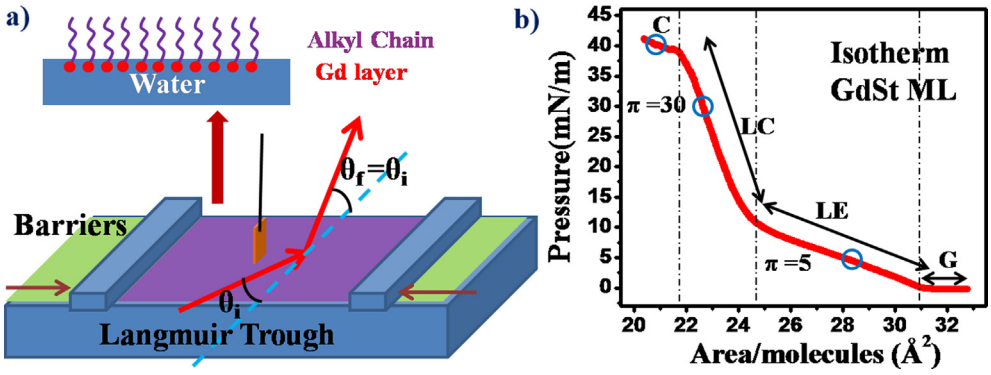

Fig. 1. (a) Schematic of the experimental set-up and the scattering geometry including incident and scattered X-ray beam directions are indicated. (b) Typical π-A isotherm of GdSt Langmuir monolayer at the air-water interface is presented (refer text for details).