

Short Communication

Features in Formation and Properties of Langmuir-Blodgett Monolayers

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Features in formation of Langmuir-Blodgett films and possible control and study of their properties directly in depositing them onto sub-strates are studied. Linearity of the dependence of polarization on the slope angle of the static dipole moment for $C_{18}H_{36}O_2$ and $C_{18}H_{34}O_2$ has been checked.

Keywords: Langmuir-Blodgett monolayers, phase transitions, electrical polarization, Stark effect, second harmonics.

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1. INTRODUCTION

Synthesis of monolayered materials of organic, inorganic, and mixed nature is undoubtedly of great interest, which is due to the necessity of obtaining unique set of properties required in electronics, optics, photovoltaics, micromechanics, membrane technologies, applied chemistry, biophysics, and other domains [1-3]. Such materials are formed by direct synthesis, crystallization, self-organization or Langmuir-Blodgett (LB) method. The present paper considers features in working installations for the implementation of LB method and physical characteristics of obtained monolayers.

2. HARDWARE AND ANALYSIS OF MONO- AND MULTILAYERED LB FILMS

Installation KSV NIMA makes it possible to form and study properties of LB films, measure characteristics of mono- and multilayers of organic substances on the surface of water subphase, make layerwise deposition of films onto solid substrates. Basic units and functional interrelations are schematically shown in Fig. 1. The installation affords conditions for the stationary mode of monolayer formation from multiphase system "liquid medium-monolayer-air-condensed substrate". Solution of liquid subphase (water) with surface at which monolayer from amphiphilic compounds sits is working medium.

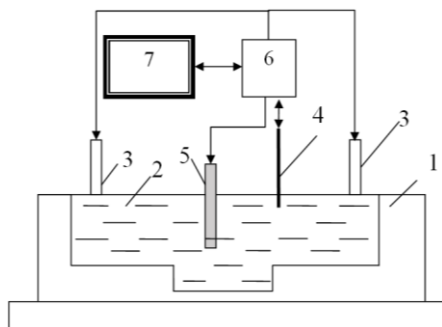


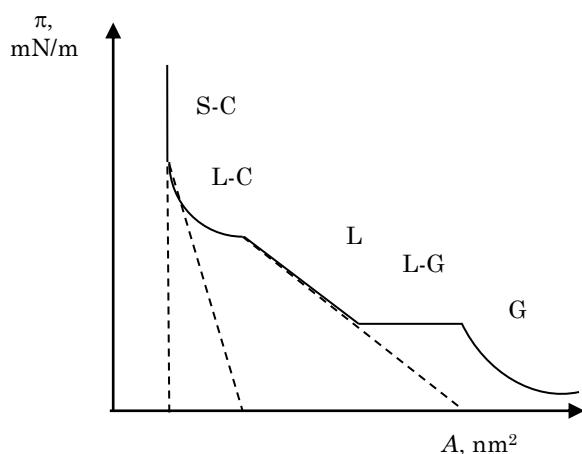
Fig. 1 – Functional block diagram of installation KSV NIMA Langmuir-Blodgett

The installation affords a uniform (0.1-270 mm/min velocity) compression (symmetrical or one-sided) of monolayer with moving barriers (3). Adjusting the extent of barrier compression causes phase transitions in monolayer among the following states: gaseous – liquid crystal – solid crystal (Fig. 2). The monolayer deposition velocity is dictated by an immersion mechanism (5) and varies in the range 0.1-100 mm/min. Quality of a substance being monolayered is secured by programmable control with PC (7) by both of the immersion mechanism with a substrate (5) and the extent of the barrier compression (3). A sensor (4) of surface pressure (Wilhelm's scale), which is in the feedback circuit (6), affords parameter control. The magnitude of surface pressure is determined with an accuracy of 4 N/m within the range of 0 to 150 mN/m. Pressure on the water surface (2), as monolayers are transferred to the substrate (5), is reduced in proportion to the substance content that forms the monolayer. To compensate for this substance reduction the moving barriers (3) automatically drift, supporting the surface pressure constant. Uniqueness of the LB method consists in the fact that the monolayer, with the help of barriers (3), is compressed until continuous film is formed with a dense packing of molecules. Specific molecular area A in this film is virtually coincides with the cross-section of a molecule. In this case, available, for instance, hydrocarbon radicals prove to be oriented virtually perpendicularly to the substrate surface.

Interphase transitions are illustrated in Fig. 2 in which provided are isothermal dependencies (π - A isotherms) of surface pressure (π) on specific molecular area (A) at constant temperature. The isothermal dependence carries the information both of intermolecular interactions and reorientation, conformation, rearrangements, and other processes that describe the behavior of a complex molecule at the water surface. Extrapolation of linear portions on the dependence π - A that correspond to the monolayer compression in various phase states provides the value of A_0 , namely, the area taken by one molecule. For example, according to π - A isotherm obtained at room temperature stable layers for the subphase surface C_{60} appear at a compression of $\pi = 25$ mN/ms by forming crystal islets with an area per one molecule $A = 0.85$ nm² [4].

Table 1 – Check for linearity of polarizability dependence on the slope angle of the static dipole momentum for C₁₈H₃₆O₂ и C₁₈H₃₄O₂

Surfactant	Density, g/cm ³	Molecular mass, g/mole	Momentum, D	cosψ			Coefficient, k	Magnitude, R ²
				5	45	60		
Stearine acid	0.847	284.48	4.84	0.99	0.7	0.5	0.032	1
Oleic acid	0.895	282.46	1.69				0.012	0.99

**Fig. 2** – Isothermal states in LB method: G – gaseous, LG – liquid-gaseous, L – liquid, LC – liquid-crystal, S – solid-crystal

Structural study of formed monolayered films with thicknesses of greater than 20 nm by X-ray and neutron diffractometry reveals information on the film thickness on the substrate, the number of molecular layers in it, repetition period, electronic density profile, localization of heavy atoms and typical molecular groups, the slope of carbon chains in layers, and the type of molecule packing into two-dimensional lattice. Thinner layers that are studied by slow electron diffraction technique and transmission electron microscopy provide averaged data on the focused area of the radiation beam, and may cause defects and film destruction. A special place is taken by small-angle scattering techniques, among other things, X-ray scattering, which is applied to examine entities the size of 0.1 to 100 nm. Scanning tunneling microscopy and atomic-force microscopy being nondestructive methods feature high spatial resolution, making them much needed techniques for studying monolayered LB films [5-7].

LB films have various physical properties among which of special importance are the following ones: mechanical (structural transformations), optical (parameters of orientation order of molecular fragments), and electrical (orientation of molecular dipoles and charge distribution across the monolayer cross-section).

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For example, electrical polarization determined as $p = (N_A \rho \mu_0 \cos \psi) / M$ is inversely proportional to the molecular mass M . Here N_A is the Avogadro number, ρ is the monolayer density, μ_0 is a static molecular dipole moment, ψ is the angle between the molecular dipole and normal to the film. Using expression for p , one can check if the condition of its linearity on the angle slope of the static dipole moment for most used in the LB method surfactants C₁₈H₃₆O₂ и C₁₈H₃₄O₂ is fulfilled.

The calculation of this dependence has revealed that the highest reliability on linearity is characteristic for stearine acid, which is intensively used at monolayer deposition.

Optical methods for studying generation of the second optical harmonic provide data on inversion centers in monolayer; establish correlations between the relevant nonlinear susceptibility and the magnitude of polar ordering parameter. Generation of the second harmonic in polar multilayers in the absence of an external field is feature of LB films. The intensity of the second harmonic is determined by expression

$$I^{2\omega} \approx \left\{ \frac{\sin[(n_1 - n_2)2\pi l / \lambda]}{(n_1 - n_2)2\pi / \lambda} \right\}^2, \text{ where } \lambda \text{ is the wavelength, } n_1$$

and n_2 are the medium refractive indexes at the prime and double frequencies, respectively, l is the monolayer thickness, according to which the second harmonics intensity is linearly proportional to the number of minelayers. One more way with which formed LB monolayeres are characterized is the Stark effect. It has sensitivity that is enough for measuring on one monomolecular layer. In this case the absorption of quantum of light is linearly dependent on the rotation angle μ_0 : $h\Delta v_{\text{line}} = (\Delta \mu E)$, whereas on the applied electric field – quadratically dependent $h\Delta v_{\text{line}} = \frac{1}{2} \Delta \alpha E^2$ with the shift of the straight (terms). Here h is the Plank constant, v is linear frequency, E is the electric field intensity, $\Delta \mu$, $\Delta \alpha$ are changes in the dipole momentum and polarization, respectively [8, 9].

3. CONCLUSION

It is shown that in forming LB films one can determine their polarization and mono- and multilayeredness, which makes it possible to create structures with preset properties that meet the practical demands.