

Yu. M. L'vov and L. A. Feĭgin. *Production and structure of Langmuir films.* 1. Production of films. Amphiphilic molecules placed on a water-air interface arrange themselves in such a way that their hydrophilic parts are in water and their hydrophobic parts are in air. If the area (σ) of the water surface along which the molecules are situated is decreased with the surface pressure (π) being controlled in the process, then three characteristic regions can be distinguished on the ($\pi - \sigma$) diagram: "Two-dimensional gas",

when the amphiphilic molecules interact weakly, "two-dimensional liquid" and "two-dimensional solid" when a two-dimensional crystalline lattice is formed on the surface of the water.

If a substrate is slowly moved through the surface with the formed "two-dimensional liquid" (Fig. 1) a monolayer of amphiphilic molecules will be formed on it. Then the substrate is moved in the opposite direction and the next monolayer is formed in which the molecules are oriented towards

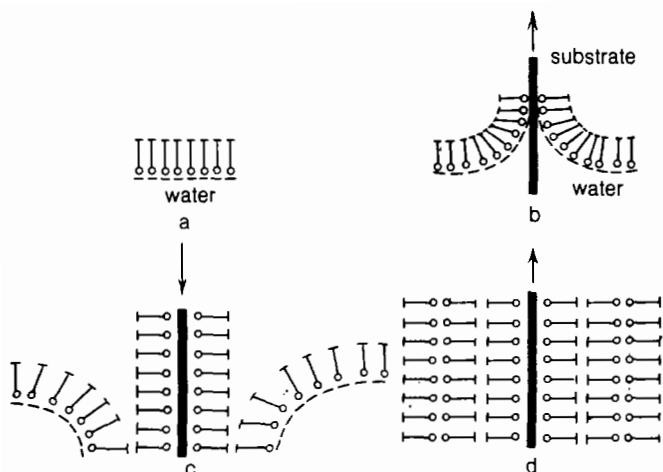


FIG. 1. Sequence of deposition of L-B films of Y type (a-d). The arrows indicate the direction of motion of the solid substrate.

the substrate with their other ends. Such central-symmetric films are called films of the Y type, but if the deposition is obtained by moving the substrate in one direction then polar films of the X or Z type are formed.^{1,2}

A big contribution to the study of such films on the surface of water was made by the American physicist I. Langmuir, while his pupil K. Blodgett developed methods of transferring the films to substrata and therefore the films on substrata obtained in this manner are called Langmuir-Blodgett films or L-B films. In its essence the L-B method is a method of controlled layered crystallization of amphiphilic molecules which enables one to obtain on substrata exactly 1, 2, 3, 4, 5, ... 25, etc., monomolecular layers.

L-B films have been made from fatty acids and their salts, from lipids, from perfluorinated compounds, and also from a wide class of molecules which have donor-acceptor

properties, and from dyes with hydrocarbon chains "attached" to them. At the present time dielectric, semiconducting and conducting L-B films have been made.^{3,4}

2. Structural analysis of L-B films. The principal methods of investigating the structure of L-B films are small-angle x-ray analysis and electron diffraction.^{5,6} X-ray analysis enables one to obtain information concerning the total thickness of the film on the substrate, the number in it of molecular layers, the repetition period, and to calculate the profile of the electron density across the layer, to localize the position of the heavy atoms and the characteristic groups of molecules, to determine the magnitude of the inclination of the hydrocarbon chains in the layers and the type of packing of the molecules into a two dimensional lattice. Electron diffraction is used to obtain the parameters of the packing of the molecules into a lattice, even in the case of analyzing samples

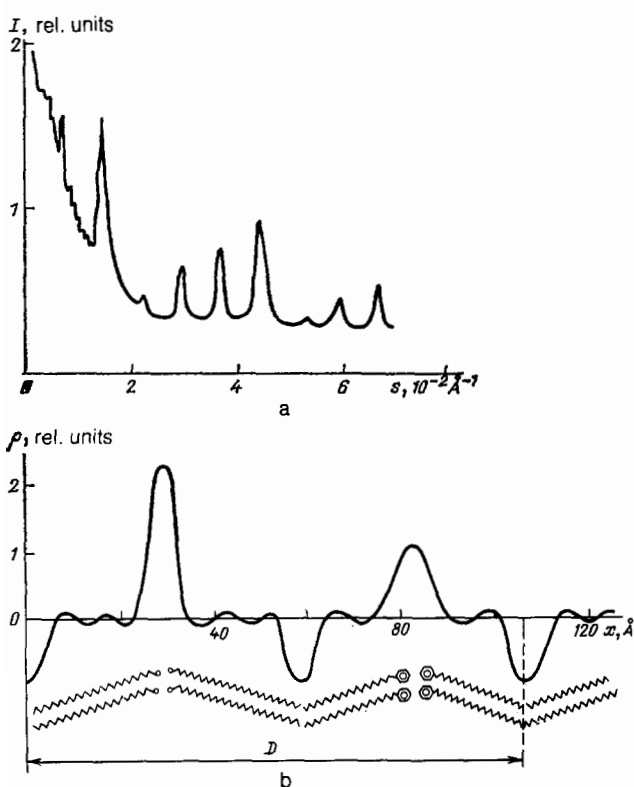


FIG. 2. Intensity of small-angle x-ray scattering in the meridional direction from a L-B superlattice: (bilayer of octadecylphenol + bilayer of Ba behenate)₁₀ (a), profile of its electron density and a schematic arrangement of molecules (b)

containing only a single monomolecular layer.

For L-B films of the *Y* type of salts of the fatty acids $\text{CH}_3[(\text{CH}_2)^n\text{COO}^-]_2\text{Me}^{2+}$ the repetition period of the bilayers (*D*) lie in the range from 44.1 Å [for palmitates (*n* = 14) to 64.0 Å for lignocerates (*n* = 22) with the period increasing by 5.0 Å as the length of the hydrocarbon chain increases by 2 links. Between bilayers of the residues of fatty acids metal ions are situated, and films with the following interlayers have been obtained: Mg, Ca, Mn, Cd, Ba, Pb, Tl.

The intensity curves for small-angle x-ray scattering by L-B films contain 10–20 reflections of the 00*l* type and also oscillations between reflections—secondary maxima of the Laue function the possibility of recording which is determined by the presence of a small number of elementary cells in the samples (Fig. 2). From the period of the oscillations (ΔS) one can calculate the total thickness of the film: $L = 1/\Delta S$, $S = 2 \sin \theta / \lambda$, while an analysis of the set of integrated intensities of the reflection $I(h)$ enables one to calculate the profile of the electron density:

$$\rho(x) \approx \bar{\rho} + \frac{2}{D} \sum_{h=1}^{h_{\max}} \pm (I(h)h)^{1/2} \cos \frac{2\pi hx}{D}.$$

3. Molecular architecture. One can obtain not only one-component L-B films; they can be synthesized from alternating layers of different molecules, and this enables one to realize the ideas of molecular architecture, i.e., of the construction of different arrangements of molecular elements. Such films are called L-B superlattices.

If there are two types of amphiphilic molecules: \vec{A} and \vec{B} (the arrows indicate their polarity), then the following alternations of their layers in the L-B films are possible: $\vec{A} \vec{A} \vec{A} \vec{A} \vec{A}$, $\vec{B} \vec{B} \vec{B} \vec{B} \vec{B}$, $\vec{A} \vec{A} \vec{A} \vec{A}$, $\vec{B} \vec{B} \vec{B} \vec{B}$, $\vec{A} \vec{B} \vec{A} \vec{B}$, $\vec{A} \vec{B} \vec{B} \vec{A} \vec{B} \vec{B}$, $\vec{A} \vec{A} \vec{B} \vec{B} \vec{A} \vec{A} \vec{B} \vec{B}$. An elementary cell across such films includes 1, 2, 3, an 4 layers of molecules and the repetition period lies in the range between 25 and 110

Å. All the indicated variants of alternation of molecular layers have been realized^{5,7,8} (in positions which we have denoted by \vec{A} and \vec{B} different amphiphilic molecules have been utilized with properties of importance for applications). Fig. 2 shows the curve of small-angle x-ray scattering by a L-B superlattice with an elementary cell including a bilayer of octadecylphenol + a bilayer of Ba behenate, its profile of electron density and the arrangement of molecules.

A further step in the development of molecular architecture was the development of the methods of selective action on a particular type of molecules in L-B superlattices. Thus, in Ref. 8 the method has been developed of layer by layer polymerization in superlattices with x-ray and electron-defraction control over the process. A bilayer of octadecylphenol was polymerized by irradiation with electrons of 100 eV energy, then this was covered by a bilayer of molecules of Ba behenate, then again a bilayer of octadecylphenol was deposited and polymerized, and then again a bilayer of Ba behenate, etc. In this manner it was possible to obtain superlattices with polymer interlayers, which nevertheless preserved long-range order in the packing of layers (the correlation radius amounted to approximately 1000 Å and this corresponds to 40 molecular layers).

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