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Specific Features of Molecular Packing in Processes of Reorganization of Monomolecular Films of Amphiphilic Compounds on a Solid Surface

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Abstract—Properties of monomolecular films of behenic acid, beeswax, *N*-hexadecyl-3-oxobutanamide, *N*-hexadecyl-*N*'-(2-naphtyl)propanediamide, *N*,*N*'-dihexadecyl-, and *N*,*N*'-dioctadecylpropanediamide on the surface of water were characterized in terms of compression isotherms. The structure of films on mica and graphite was studied down to the molecular level by atomic-force microscopy. It was shown that the molecular packing in monomolecular films depends on the nature of the support. The self-organization of monolayers of amphiphilic amides into a multilayer supermolecular structure was found. It was established that monomolecular films of the amphiphilic amides are reorganized in storage to form multimolecular structures with a hexagonal packing of the hydrocarbon tails. The effect was attributed to the surface tension gradient appearing in the monolayer crystallization.

Since the early 1980s, scanning probe microscopy (SPM) has provided a means of obtaining information on the morphology, structure, and surface structure of soft films of organic compounds, in particular, highly organized Langmuir–Blodgett (LB) films. The scanning tunnel microscopy [1] and, subsequently, atomic-force microscopy (AFM) [2] techniques were used for studying the structure of such films down to the molecular level. At the present time, SPM data on the character of molecular packing in monolayers are available for higher fatty acids [3], phospholipids [4–6], acetylene derivatives [7], and other compounds [8]. In particular, it was established [3] that the rectangular centered two-dimensional lattice with the parameters $a = 0.482$ and $b = 0.748$ nm is typical of salts of fatty acids (for example, Cd arachidate).

Salts of fatty acids were selected as test samples because of the high quality of LB films formed by them. Unfortunately, the formation of films of other amphiphilic molecules on supports by the traditional vertical method [9] is frequently complicated by the disorientation of molecules and aggregation of the substance in the liquid meniscus and is also stopped by the action of some ions. Moreover, LB films on solid surfaces frequently exhibit spontaneous reorganization [10–15]. In particular, the phenomenon of reorganization was observed for films of salts of fatty acids under water [10–12], phospholipids films [14], etc.

The questions arise of how much the phenomenon of film reorganization is typical for different classes of amphiphilic compounds and what the factors destroying the films are. As a rule, it is difficult to distinguish between the instability of monolayers and the structural defects appearing in the film formation [14, 16]. Using the AFM method, it was shown [17, 18] that difficulties associated with the formation of films on supports by the vertical method can be avoided by using the “horizontal deposition” (HD) method, which provides a means of formation of high-performance, homogeneous monolayers on both hydrophilic (mica) and hydrophobic (graphite) supports. Our observations showed that, in some cases, homogeneous monomolecular films formed on supports are spontaneously reorganized on storage in air for 1–3 months to form monolayer structures.

The aim of this work is the study of the reorganization of monomolecular films of ketoamides down to the molecular level using the AFM method.

EXPERIMENTAL

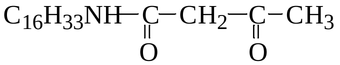
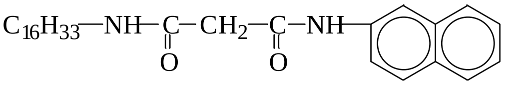
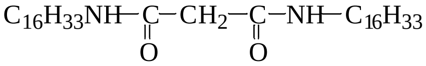
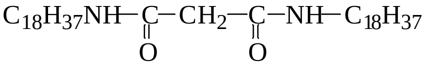
Monomolecular films were formed from *N*-hexadecyl-3-oxobutaneamide (**I**), *N*-hexadecyl-*N*'-(2-naphtyl)propanediamide (**II**), *N*,*N*'-dihexadecyl (**III**), and *N*,*N*'-dioctadecylpropanediamide (**IV**) and, for comparison, from behenic acid (Aldrich) and purified natural beeswax (melting temperature, 55–60°C). Beeswax (a mixture of higher fatty alcohols and esters of higher fatty acids [19]) was purified by fractional crystallization from chloroform solutions. β-Ketoamide (**I**) and β-diamides (**II**–**IV**) were synthesized by the procedure [20].

Table 1. Parameters of the two-dimensional packing of derivatives of higher fatty acids in monomolecular films (for comparison, theoretical data [21] on the packing of *n*-paraffin are included)

Compound	Support	*a*, nm	*b*, nm	*A*, nm^2 (AFM)
Behenic acid	Mica	0.53 ± 0.03	0.77 ± 0.04	0.203 ± 0.007 0.20 ± 0.005*
Beeswax	Graphite	0.50 ± 0.04	0.79 ± 0.07	0.195 ± 0.015
n-Paraffin, *R*[0, ±1] subcell		0.496	0.785	0.195
n-Paraffin, *H*[0, 0] subcell		0.48	–	0.196

* Determined from π–*A* isotherms.

Table 2. Parameters of the two-dimensional packing of monomolecular films of amide derivatives on mica obtained by the horizontal deposition method

Compound	*a*, nm	*b*, nm	*A*, nm^2	
			AFM	π–*A* isotherm
 $C_{16}H_{33}NH{-}\underset{\underset{O}{\|}}{C}{-}CH_2{-}\underset{\underset{O}{\|}}{C}{-}CH_3$ **(I)**	0.476 ± 0.018	0.80 ± 0.03	0.196 ± 0.008	0.27 ± 0.005
 **(II)**	0.566 ± 0.015		0.227 ± 0.011	0.325 ± 0.007
 $C_{16}H_{33}NH{-}\underset{\underset{O}{\|}}{C}{-}CH_2{-}\underset{\underset{O}{\|}}{C}{-}NH{-}C_{16}H_{33}$ **(III)**	0.477 ± 0.011		0.197 ± 0.006	0.265 ± 0.006
 $C_{18}H_{37}NH{-}\underset{\underset{O}{\|}}{C}{-}CH_2{-}\underset{\underset{O}{\|}}{C}{-}NH{-}C_{18}H_{37}$ **(IV)**	0.477 ± 0.014		0.197 ± 0.007	0.264 ± 0.006

Note: The unit cell of **II** is rectangular, and unit cells of other compounds are hexagonal.

Monolayers on the water surface were formed as follows: 0.5–0.8 mM solutions of amphiphilic compounds in chloroform were applied to the surface of twice distilled water (pH 5.5), and, after the evaporation of the solvent and stabilization of the applied molecules on the water surface (~10 min after the application), the obtained layers were compressed. Z-type monolayers were applied onto freshly cleaved surfaces of mica and highly oriented pyrolytic graphite (HOPG) by the HD method. In the formation of a monolayer, the surface pressure was maintained at 20 or 30 mN/m with a deviation in one cycle of less than 2–3 mN/m. Compression isotherms in the surface pressure–area per molecule coordinates (π–*A* isotherms) were recorded using an automated Langmuir setup [17] at a compression rate of 0.2–0.3 Å^2/(molecule min).

AFM images of the monolayers were obtained using a Nanoscope IIIa instrument (Digital Instruments, USA) equipped with a D-scanner. The images were obtained in the contact mode in air. 100- and 200-μm Nanoprobe cantilevers from Si_3N_4 with elastic constants of 0.12 and 0.36 N/m were used. The force exerted on the sample by the needle was of several nanonewtons. The horizontal-scanning frequency was varied from 5 to 60 Hz. The highest resolution was attained in the regime of frictional force measurement at the maximum scanning frequency. In the determination of the molecular packing parameters in the film, the measurement error due to the temperature drift was estimated by the results of the determination of the lattice parameters for a test object (mica). The unit cell parameters were determined by averaging the results of measurement of several AFM images, which allowed us to reduce the temperature-drift error to the error in the arithmetical mean. With this procedure, the error of determination of the desired parameters was equal to 3–5%. AFM data averaged over several tens of images are presented in Tables 1 and 2.

RESULTS AND DISCUSSION

Typical π–*A* isotherms of the investigated compounds are presented in Fig. 1. Since beeswax is a mixture of higher fatty alcohols and esters of higher fatty acids, its molecular weight is unknown. In the recording of isotherms for beeswax, we used the molecular weight of behenic acid; therefore, only the behavior of the isotherms and the collapse point are realistic, not the area per molecule. From Fig. 1, it is seen that all of the investigated compounds form monomolecular films on the water surface in the phase state termed the “solid film,” which can be transferred onto a support.

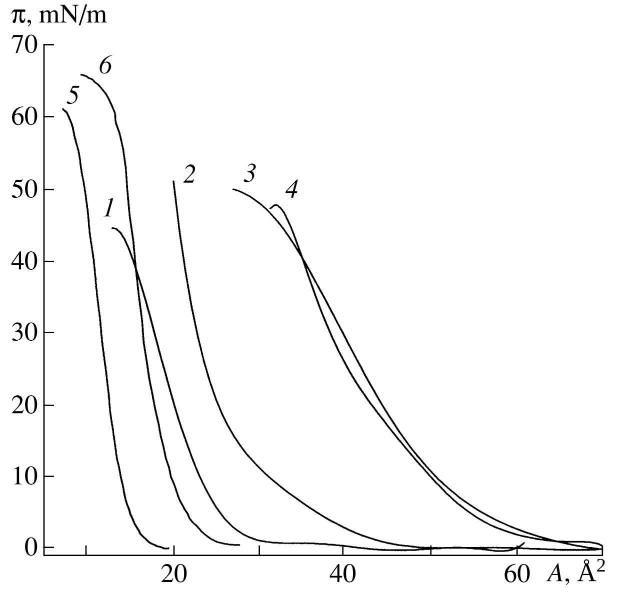


Fig. 1. Isotherms for monomolecular films on a pure water surface: amphiphilic amides (*1*) **I**, (*2*) **II**, (*3*) **III**, and (*4*) **IV**; (*5*) beeswax; and (*6*) behenic acid.

Films of higher fatty acids are usually transferred onto a solid surface by the vertical method; in this case, the acids are present as salts and transferred from the ionic subphase. With these films, molecular resolution can be attained only for multilayer samples. For example, it was noted [8] that molecular resolution can be obtained for multilayer films of cadmium arachidate but not for its monolayer films. However, the HD method allowed us to isolate monomolecular films of fatty acids from the water surface in the absence of counterions. In this case, the AFM method allowed us to observe the molecular structure in some regions of the behenic acid monomolecular film (Fig. 2). In the AFM image, we find the two coexisting phases: the closest-packed phase (regions with a greater height due to the vertical orientation of molecules) and the less compact phase (dark regions corresponding to domains of a lesser height probably due to a tilt of molecules with respect to the support). We failed to obtain such a film by the vertical method.

The area per molecule in the behenic acid monolayer on mica determined from the AFM data agrees very well with the value obtained from π–*A* isotherms (Table 1). However, the measured *a* value (0.53 nm) exceeds typical values (0.48–0.50 nm [3]). It is not improbable that the distortion of the unit cell parameters describing the molecular packing in the monolayer is due to the effect of the crystal structure of the support (mica).

We were able to obtain a uniform, homogeneous monomolecular film of beeswax only on HOPG. For this film, molecular resolution was also attained; it was established (Table 1) that the molecular packing corresponds to a centered rectangular unit cell (two molecules per unit cell). The area per molecule in the monolayer is of ~0.195 nm^2, which correlates well with the area per molecule in the closely packed monolayer of behenic acid on the water surface, i.e., with the cross-sectional area of the hydrocarbon tail of the molecule (Table 1). The obtained unit cell parameters are virtually in complete agreement with the theoretical data for *n*-paraffin [21] (Table 1).

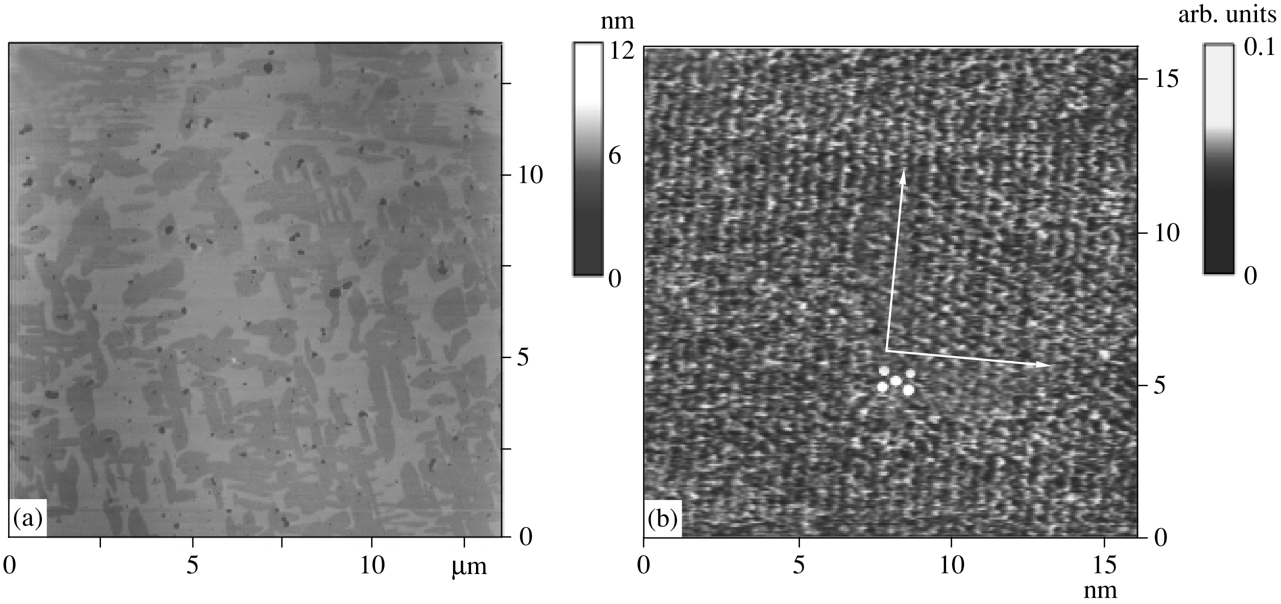


Fig. 2. (a) The large-scale and (b) molecular-scale AFM images of the monomolecular film of behenic acid formed on mica at a surface pressure of 20 mN/m

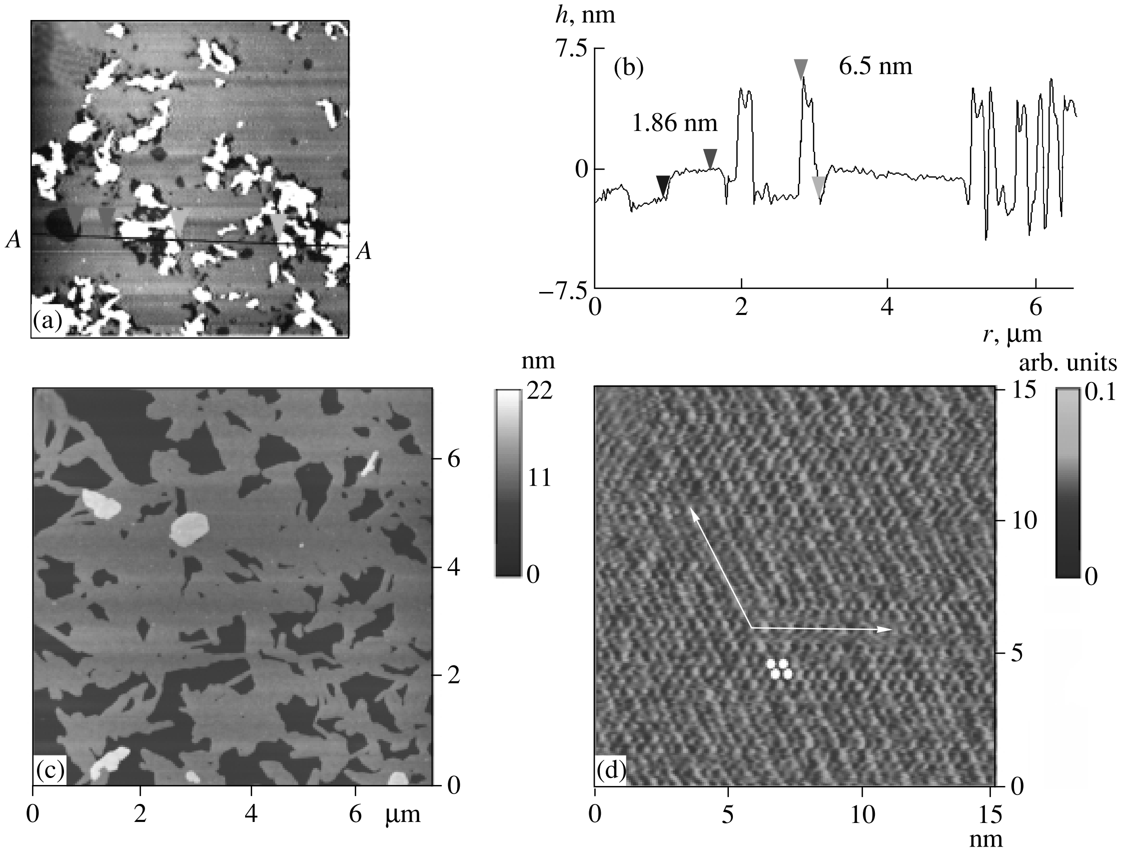


Fig. 3. AFM images: (a) the initial stage of crystallization of the monomolecular film of *N,N'*-dihexadecylpropanediamide formed on mica by the HD method at a surface pressure of 30 mN/m, (b) the surface relief of the film (*h* is the height, and *r* is the distance along the *A*–*A* section), (c) the final stage of the reorganization of the film of the amphiphilic amide derivative into three-layer aggregates, and (d) the molecular packing on the aggregate surface.

Thus, in the beeswax monolayer on graphite, the hydrocarbon tails of components of the film are closely packed. Unlike the monomolecular film of behenic acid on mica, graphite has no significant effect on the molecular packing in the beeswax monolayer. This result also supports the correctness of the estimation of the molecular packing in the investigated films using AFM data. On the whole, molecular resolution was attained due to the conservation of the molecular packing in the monomolecular films during the course of their isolation and also to the stability of molecules on the surface during scanning.

Unlike stable monomolecular films of derivatives of higher fatty acids, monolayers of derivatives of surface-active amides exhibit molecular reorganization, resulting in multilayer crystallites. Early in the film reorganization, neighboring molecules form small crystallites surrounded by vacancies (Fig. 3a). An analysis of the surface profile in such a region (Fig. 3b) shows that the height of the crystallites exceeds the monolayer thickness by a factor of ~3. This indicates that the crystals consist of three monomolecular layers. Note that the thickness of the monolayer (~2 nm) suggests the vertical orientation of both of the alkyl tails of the investigated diamide molecules in the monolayer (Fig. 4a). With time, monomolecular films of different amide derivatives are completely rearranged into multilayer structures (Fig. 3c).

From AFM images of the molecular structure of monomolecular films of compound **II**, it follows that, as in the foregoing cases, the two-dimensional molecular packing in the monolayer corresponds to the centered rectangular unit cell (Table 2). At the same time, we failed to resolve the molecular structure of monomolecular films of amides **I**, **III**, and **IV**. Molecular resolution was attained in only AFM images of the surfaces of reorganized three-layer structures of these compounds (Table 2). A Fourier analysis of these images established the following: (1) on the surface of reorganized crystalline structures, molecules of compounds **I**, **II,** and **IV** form a highly symmetrical hexagonal lattice (Table 2) and (2) the calculated area per building block of the hexagonal lattice (~0.195 nm^2) is very close to the cross-sectional area of the hydrocarbon tail of the molecule. The crystallographic parameters of the hexagonal unit cell (Table 2) are virtually identical to the translation parameters of the *H*[0,0] unit cell (Table 1) for the packing of hydrocarbon chains in

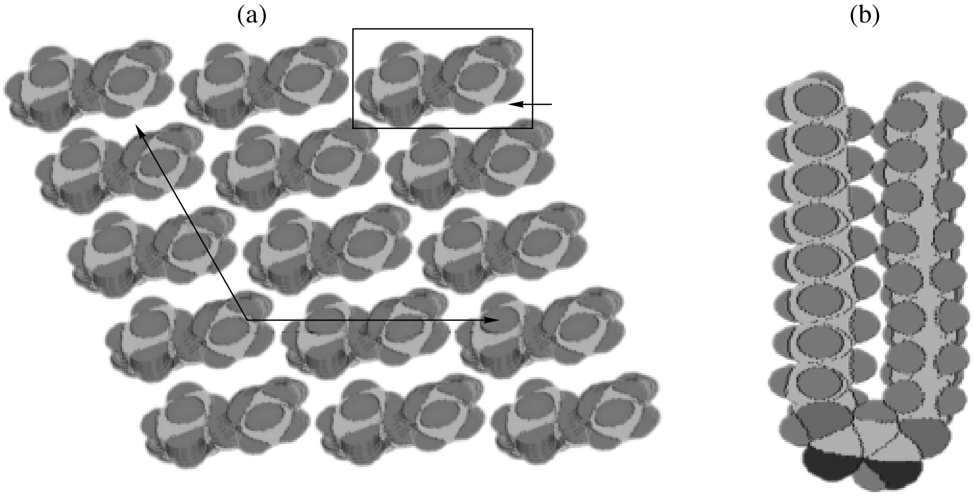


Fig. 4. (a) The top view of the supermolecular structure of *N*,*N*'-dihexadecylpropanediamide molecules (an individual molecule is confined in a frame) and (b) the side view of an individual molecule (dark atoms in the lower part of the molecule are involved in the keto-enol ring).

the "gas-crystal" state of the Kitaigorodskii model [21] (the deviation is less than 1%). This allows us to conclude that the obtained images correspond to the packing of the hydrocarbon tails of molecules. Consequently, we can suggest that polar fragments are absent from the surface of the reorganized structures.

Note that the ultimate area per molecule determined from π–A isotherms far exceeds the value obtained by the AFM method for the surface of reorganized crystallites (Table 2). The decrease in the area per molecule on the transformation of a monolayer into a supermolecular structure indicates that the polar fragments of molecules also change their orientation. The hexagonal molecular packing in the monolayer can be explained under the assumption that the polar fragments of molecules do not affect the packing of hydrocarbon tails. This is possible in the case of formation of planar, hexagonal enolic rings [20] in polar fragments of the amide derivatives.

Indeed, the rigid fixation of such rings in arrays is no hindrance to the formation of the hexagonal packing of hydrocarbon tails, which have some rotational–translational degree of freedom. Based on these assumptions, we can interpret, say, the AFM image of the superstructure in the film of compound **III** (Fig. 3d). In accordance with the model shown in Fig. 4, the molecules are arranged in arrays. Molecules in adjacent arrays are displaced relative to each other to form the hexagonal packing of their hydrocarbon tails. Enolic rings are parallel to each other and perpendicular to the support. One of the tails of a molecule in an array corresponds to a peak in the image, and the other tail, to a valley.

It is possible that the cohesion of hydrophobic moieties of molecules is precisely the factor that does much for the self-organization of molecules into supermolecular structures. It is likely that the molecular structure is responsible for the reorganization of the film as a whole and the shape of reorganized crystallites. Sometimes, we can find needle-shaped, three-layer crystals and, at other times, crystals growing in a direction perpendicular to the support. For the considered amides, we usually find planar, three-layer structures whose shape is far from the perfect crystal shape. These observations suggest that the molecular structure is an essential factor determining the reorganization of monolayer films on supports. At the same time, the balance of van der Waals forces, adhesion between the hydrophilic and hydrophobic moieties of molecules, and the interaction of molecules with the support determine the mobility of molecules on the surface [22].

Thus, for an understanding of the complex process of reorganization of films on a surface, it is necessary to take into consideration effects of the support, the adsorbed water, steric hindrances, and also electrostatic and other effects. However, the surface tension gradient is the main motive force of the process of reorganization of films on a surface with a change in the character of the molecular packing.

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