Study of the possibility of using arachidic acid as a monocrystalline substrate for the formation of monolayers of aromatic hydrocarbons

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Abstract. The paper discusses one of the promising approaches for the synthesis of graphene formed at the interface in the Langmuir bath. The results of the investigation of the formation of pyrene monolayers (both initial elements of graphene) and a mixture of pyrene and arachidic acid are presented. It is shown how the mechanical characteristics of a monolayer change when pyrene is added to a mixture with arachidic acid: the rigidity of the monolayer increases and the compression modulus decreases. Also studied the hypothesis that arachidic acid can act as a single crystal substrate on which it is possible to form an ordered layer of pyrene.

1. Introduction
At the moment, among the most famous and studied materials is graphene, which has very attractive properties. It has an extremely high charge mobility, record conductivity, adjustable bandgap width, etc. The velocity of its electrons is about a hundred times higher than that of silicon. Already there are many directions where graphene could replace silicon. For example, a transistor based on it [1]. As its developers suggest, graphene taken as the basis, will allow working faster than its silicon analogs [2], which will significantly affect the performance of microprocessors and other devices. A large number of works are devoted to methods of obtaining graphene and they are very diverse. As the most promising, various modifications of the method of chemical vapor deposition from the gas phase [3,4], as well as methods based on the cross-linking of nanographene to obtain large-scale graphene sheets [5,6] can be distinguished.

But, despite the large number of publications in this field, there is no acceptable method for obtaining high-quality monolayers of a large area. In this regard, the development of new methods for the synthesis of graphene is interesting and relevant.

In this paper, we propose the following stage in the development of the method, which was described in [7-9]. Taking as a basis the reaction of Shole [10], a method of obtaining graphene by crosslinking molecules of polycyclic aromatic hydrocarbons (such as naphthalene, pyrene, coronene, etc.) is possible. The main factor in the implementation of this approach is the distance and orientation of the molecules that enter into the reaction. In the known methods for the production of graphene, solid
supports are used for these purposes, which are both catalysts and surfaces that orient the nanographene molecules. But at the same time for the realization of such methods of production, high vacuum conditions are required, the use of plasma and etc. as a stimulating effect.

In this connection, the "water-air interface" was used as a "substrate" in the work. Such an approach can be realized in Langmuir baths using the Langmuir-Blodgett method. Therefore, in this paper we investigated the possibility and effect of various conditions on the formation of monolayers of aromatic hydrocarbons on the surface of the water subphase using Langmuir-Blodgett technology.

2. Materials and methods

As a starting compound for the further formation of graphene, pyrene belonging to the class of aromatic hydrocarbons was selected (fig. 1 a). It is chosen because of its large structural similarity with graphene and the availability of the required physico-chemical characteristics.

![Figure 1(a, b). Molecules of (a) pyrene; (b) arachidic acid.](image)

A study of a mixture of pyrene and arachidic acid was carried out by studying the hypothesis, where arachidic acid can act as a single-crystal substrate that promotes the formation of an ordered pyrene layer above it. The study of this mixture was carried out by analogy with [8], where the formation of naphthalene molecules over the surface of arachidic acid was studied (fig. 2).

![Figure 2. Ordered structure of arachidic acid layer with a layer of naphthalene molecules applied to its surface [8].](image)

3. Results and discussion

To determine the possibility of formation of pyrene monolayers at the interface, solutions of arachidic acid, pyrene, and mixtures of arachidic acid and pyrene in various proportions were prepared. Then these solutions were spread on the surface of water and left for 5 minutes until the solvent completely
evaporated. After that, the monolayer was compressed by two movable barriers, the compression rate was 10 mm/min. The temperature of the aqueous phase was 23 °C. The surface tension measured during compression was used to obtain compression isotherms (fig.3).

![Figure 3(a, b). Compression isotherms of monolayers of (a) pyrene; (b) arachidic acid with pyrene.](image)

Analyzing the isotherm for pyrene (fig. 3a), it can be seen that the surface pressure reaches a value about 7 mN/m, this is due to the fact that pyrene molecules do not have pronounced surface-active properties, like aromatic hydrocarbon molecules. Comparing the obtained isotherm with the isotherms of a mixture of pyrene and arachidic acid (fig. 3b), it can be seen that arachidic acid exerts a major influence on the change in the surface energy of the system and an increase in the surface pressure. It is worth noting that the areas of the monolayers compression of the mixture were recalculated to the number of molecules of only arachidic acid. The monolayer of the mixture, unlike a monolayer of pure pyrene, is able to form a close-packed solid-crystalline state on the surface of the water subphase. It can be seen that the isotherms for different mix ratios are similar to each other. The main difference consists in the displacement of the graphs and the features of some sections in the liquid-condensed and solid-crystalline state.
The isotherms were used to determine areas occupied by monolayers in «close package state» by drawing a tangent line to the point of inflexion (corresponding to pressure range of 28-55 mN/m). The crossing point between the tangent line and horizontal axis was designated as the target area.

If we assume that the change in the surface tension is due only to the presence of the amphiphilic component of the mixture (arachidic acid) on the water surface, and the presence of pyrene does not contribute to this change and is not integrated into the monolayer, then the isotherms should not shift. However, the opposite was observed experimentally: the area values for the ratio 0:1 (pure arachidic acid) 1:1, 1:2 and 2:1 were 21, 22.1, 19 and 21.2 Å, respectively. Thus, it can be assumed that some of the pyrene molecules are present in the monolayer of arachidic acid. This can also be evidenced by several transitions in the solid-crystalline state of the monolayer, which may be associated with the reorientation and incorporation of pyrene molecules in the composition of arachidic acid. This is most noticeable for the ratio 1:1.

In addition, to compare the obtained curves, the \( \frac{A}{A_0} \) ratio for the solid-crystalline and liquid-condensed states was analyzed. This isotherm is shown in Fig. 4. The tangents on the sections of the liquid-condensed or solid-crystalline phases crossed the abscissa axis at one point.

The physical meaning of such a normalization is as follows. For a liquid-condensed phase, the onset of linear growth of surface pressure (or a decrease in surface energy) indicates the initiation of the interaction of surfactant molecules and a significant change in the orientation of the hydrocarbon chains of these molecules with respect to the interface. With a common starting point, it becomes possible to compare the rate of flow of such changes, or the relative compressibility of the monolayer in this state. For the solid-crystalline phase, the linear growth of the surface pressure is more closely related to the optimization of the mutual arrangement of the hydrocarbon chains of the surfactant molecules relative to each other without a significant change in the orientation of the hydrocarbon chains. In this case, it is also possible to compare the slope of the isotherms in this section or the relative compressibility of the monolayer in the solid-crystalline state.

For the presented data, the compressibility of the monolayer (K) and the compression modulus (\( \chi \)) for each state of the mixtures was also calculated, the results of the calculations are presented in Table 1. These parameters were calculated by the following formulas:

\[
K = -\frac{1}{A_0} \left( \frac{dA}{d\pi} \right)_{\pi=\text{const}}
\]

and

\[
\chi = \frac{1}{K}
\]

Figure 4. Compression isotherms of monolayers of arachidic acid with pyrene.
Table 1. Characteristics of monolayers of a mixture of arachidic acid and pyrene.

| Ratio | Solid-crystalline states | Liquid-condensed states |
|-------|-------------------------|-------------------------|
|       | $K_S$, m/mN | $\chi_S$, mN/m | $A_0$, Å² | $K_L$, m/mN | $\chi_L$, mN/m |
| 0:1   | 0,0009     | 1060       | 21           | 0,0062     | 160          |
| 1:2   | 0,0010     | 980        | 19           | 0,0064     | 157          |
| 1:1   | 0,0013     | 746        | 22.1         | 0,0079     | 127          |
| 2:1   | 0,0018     | 552        | 21.2         | 0,0100     | 100          |

Analyzing the mechanical characteristics of the monolayer (K and $\chi$) for various ratios of a mixture of pyrene and arachidic acid, it can be noted that when it is added to arachidic acid, the mechanical properties of the monolayer change noticeably. In the solid-crystalline state, the rigidity of the monolayer increases, indicating an increase in compressibility from 0.009 to 0.0013 m/mN, with the compression modulus correspondingly decreasing. The rigidity of the monolayer also changes in the liquid-condensed state, which is confirmed by a change in the compressibility from 0.0062 to 0.0079 m/mN.

4. Conclusion

The study of mechanical characteristics suggests that the addition of polycyclic aromatic hydrocarbons to arachidic acid leads to an increase in the compressibility of the monolayer, and a decrease in the modulus of compression. Analysis of graphs allowed to conclude that some of the molecules of aromatic hydrocarbons are embedded in the space of hydrocarbon chains of arachidic acid and have a significant effect on the formation of the solid-crystalline state of the monolayer of the mixture. In addition, it can be assumed that some of the pyrene molecules go over the surface of the monolayer of arachidic acid.

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