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The Role of Ammonium Sulfate in Regulation of the Structure and Properties of 2D Films of Fullerene C_{60}

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Abstract—The effect of ammonium sulfate on the parameters of surface pressure isotherms (surface pressure and area per fullerene molecule) of 2D films of fullerene C_{60} on the water/air interface has been studied by the Langmuir method. The possibility of regulation of the structure of 2D fullerene films has been shown. The maximal A_0 value is achieved at an ammonium sulfate concentration of 1×10^{-4} mol/L. Brewster angle microscopy shows that the presence of the electrolyte ensures the formation of a monomolecular 2D film with a lower content of defects.

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Fullerenes were discovered in 1985 by spectrometric analysis of interstellar dust [1]. The structure of the new carbon form was confirmed under laboratory conditions. The discovery of fullerene C_{60} and the identification of its structure were widely recognized by the world scientific community, and the authors of this discovery won the Nobel Prize in 1996 [2]. The use of the unique properties of fullerene in different fields is currently attracting attention worldwide [3–7]. One of the promising applications is the design of sensor systems and adsorbents based on transferred fullerene C_{60} films [8–10]. In most methods for producing ordered fullerene films on interfaces, some techniques are used for suppressing the high propensity of globules to form aggregates, which decrease the Hamaker constant or create steric factors stabilizing the monomolecular arrangement of the film [11, 12]. The drawback of these methods of modifying the fullerene globule surface is the fact that they change its physicochemical properties. The simplest and most economical method is production of fullerene films at the energetically homogeneous water/air interface. This method makes it possible to control the parameters of the nascent systems during film formation [13]. In the present work, we used the property of the fullerene molecule to become polarized, which allows ions to adsorb on the globule surface [14, 15]. As a factor that regulates the properties of 2D films, we studied the effect of the electrolyte composition on the structure and properties of fullerene C_{60} films.

EXPERIMENTAL

Chromatographically pure grade fullerene C_{60} was used. 2D films were produced and their parameters were controlled by the Langmuir–Blodgett trough method. A subphase containing different amounts of ammonium sulfate was used. The pH of the subphase was adjusted by adding an NH_4OH solution (pH 6.7). The morphology of the films on the subphase surface was studied by Brewster angle microscopy on BAM 2 and MiniBAM (at lower magnification) instruments. The structure of the 2D fullerene film transferred onto a silicon wafer was determined by atomic force microscopy (AFM). The images of the transferred 2D films were obtained on a Nanoscope III (USA) instrument in the tapping mode at a scan rate of 2.15 Hz. The scanner model was AS-12 E, with a horizontal scanning range of 10 × 10 μm and a vertical range of 2.5 μm. A TESP silicon cantilever (length, 225 μm; frequency, 300 kHz) was used. The samples for AFM studies were transferred by the Langmuir–Schaefer method.

RESULTS AND DISCUSSION

Systems obtained by deposition of different amounts of fullerene were studied. When 5.6×10^{-8} mol/L of fullerene was deposited on the water surface, the maximal area per fullerene molecule at a measurable surface pressure (A_0) was 54.5 Å^2/molecule, which corresponded to a two-layer film. The maximal film collapse pressure (π_{coll}) achieved in this system was 39.73 mN/m. The introduction of electrolytes into the aqueous phase increased the maximal area per fullerene molecule (Fig. 1). The largest change in this parameter, 94.2 Å^2, was observed for the system obtained on the subphase containing 0.2 mol/L of $(NH_4)_2SO_4$. With an increase in the electrolyte concentration from 1×10^{-4}

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Effect of the concentration of ammonium sulfate on the parameters of 2D films of fullerene C_{60} formed on the aqueous subphase when 5.6×10^{-8} or 8.3×10^{-8} moles of fullerene are deposited

Electrolyte composition	Deposited amount			
	5.6×10^{-8} M		8.3×10^{-8} M	
	A_0, Å^2/molecule	π_{coll}, mN/m	A_0, Å^2/molecule	π_{coll}, mN/m
0	54.5	39.73	59.1	37.87
0.0001 $(NH_4)_2SO_4$	76.6	29.51	95.1	26.75
0.01 $(NH_4)_2SO_4$	85.0	29.52	94.3	31.25
0.2 $(NH_4)_2SO_4$	94.2	36.64	87.1	31.75
0.4 $(NH_4)_2SO_4$	90.7	35.75	87.1	30.11

to 0.4 mol/L, the area per molecule passed through a maximum: at the minimal measurable pressure, this area first increased from 76.6 to 94.2 Å^2 and then decreased to 90.7 Å^2 at the $(NH_4)_2SO_4$ concentration 0.4 mol/L. The introduction of an electrolyte into the subphase leads to a decrease in the film collapse pressure. Upon the introduction of ammonium sulfate into the subphase, a complicated dependence of π_{coll} on the electrolyte concentration was observed. The minimal π_{coll} value found in the system formed on the subphase containing 0.0001 mol/L of $(NH_4)_2SO_4$ was 29.51 mN/m. An increase in the electrolyte concentration to 0.01 mol/L had virtually no effect on this parameter. The change in the electrolyte concentration to 0.2 mol/L was accompanied by a sharp increase in π_{coll} to a maximum, 36.64 mN/m. A further increase in the electrolyte concentration for the system obtained by deposition of 5.6×10^{-8} mol/L of fullerene led to a decrease in the film collapse pressure. In the absence of the electrolyte, the increase in the amount of deposited fullerene from 5.6×10^{-8} to 8.3×10^{-8} mol/L led to an increase in A_0 from 54.5 to 59.1 Å^2/molecule. The maximal measurable surface pressure decreased by 1.86 mN/m as compared to the 2D film obtained by deposition of 5.6×10^{-8} mol/L of fullerene.

The films were studied by Brewster angle microscopy and AFM. Figure 2 shows images of the 2D films of fullerene on the surface of distilled water and a 0.01 M $(NH_4)_2SO_4$ solution. Figure 2a shows a microphotograph of the gaseous fullerene layer formed on the aqueous (distilled water) subphase with the area per molecule being ~2900 Å^2. It was shown that, under these conditions, there was a distribution between the monomer and separate aggregates of fullerene. To elucidate whether this distribution is thermodynamically stable, further studies are required. When this film was compressed to the area per molecule equal to 200 Å^2, structures with higher aggregation levels were formed (Fig. 2b). Under these conditions, the surface area free of fullerene molecules was calculated to be 10% of the total interface area. When the area per molecule became 96 Å^2, heterogeneous folded multilayers were observed. Further compression led to the formation of multilayer regions distributed uniformly over the subphase surface. These high-order structures were in equilibrium with less organized film regions that cover the rest of the interface (Fig. 2c).

Analogous studies were carried out for 2D films of fullerene C_{60} on the surface of the electrolyte. Figure 2d shows the microphotograph of the C_{60} film obtained on the surface of a 0.01 M $(NH_4)_2SO_4$ solution at the surface pressure 20 mN/m and the area per molecule 90 Å^2. The Brewster angle microscopy data were confirmed by the AFM study of fullerene C_{60} films transferred onto a silicon wafer.

When a fullerene solution is applied to the water/air interface, the toluene solution spreads over the surface of the aqueous subphase to form a thin film. Solvent molecules begin evaporating and penetrating into the subphase. A decrease in the number of solvent molecules leads to a buildup of the fullerene concentration

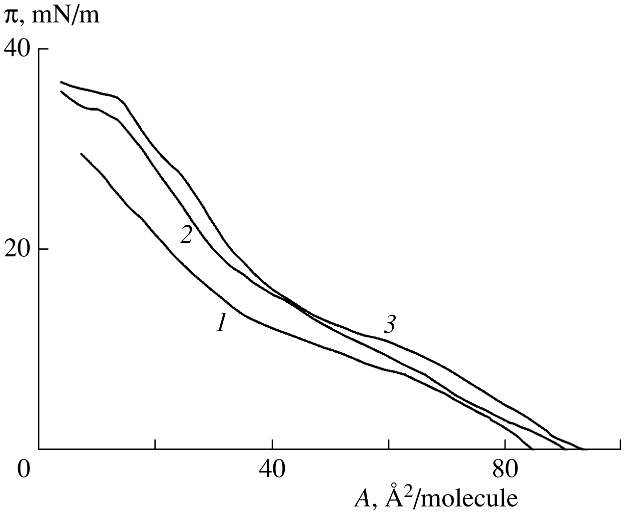

Fig. 1. Isotherms of the surface pressure of 2D films of fullerene C_{60} formed upon the deposition of a toluene solution containing 5.6×10^{-8} mol/L of fullerene on the an aqueous solution containing (*1*) 0.01, (*2*) 0.2, and (*3*) 0.4 mol/L of $(NH_4)_2SO_4$ (T = 294 K; pH 6.7; compression speed, 0.01309 m^2/min).

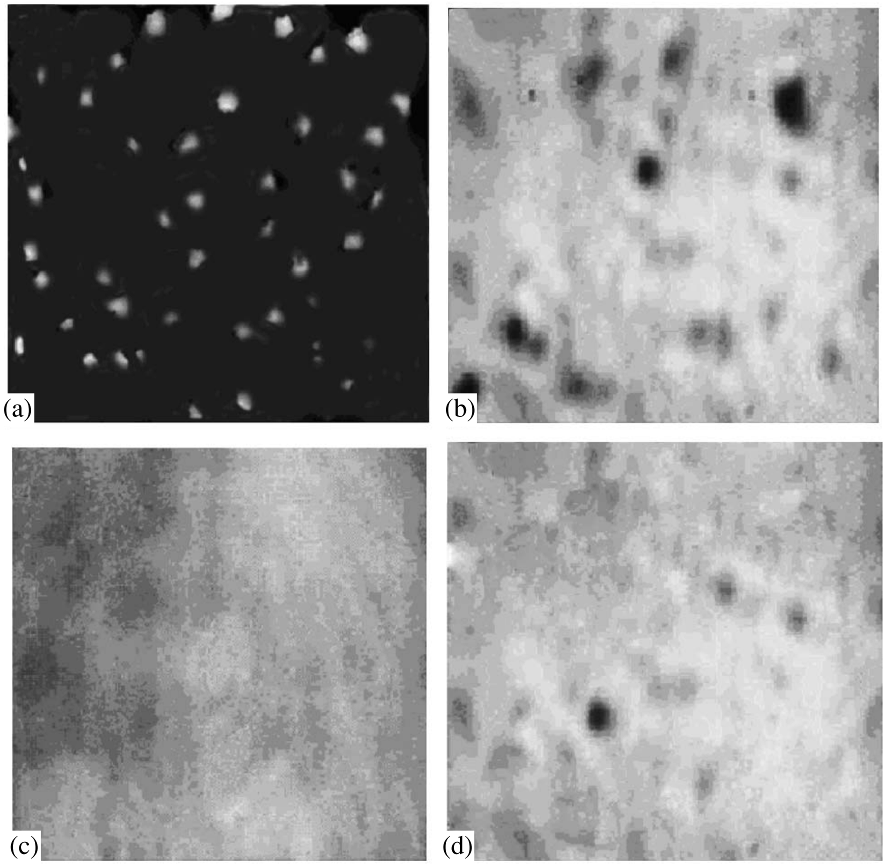

Fig. 2. Brewster angle microscopy images of 2D films of fullerene C_{60} on the surface of the water subphase (T = 294 K, pH 6.7), the surface per molecule (Å^2) is (a) 2900 (gaseous layer), (b) 90, and (c) 30; (d) films of the surface of a 0.01 M $(NH_4)_2SO_4$ aqueous solution with the surface per molecule 90 Å^2.

and to the formation of a system almost completely consisting of fullerene globules. Due to different ratios between the spreading rate and evaporation/dissolution rate of the toluene phase on the subphase surface, molecular dispersions or aggregates of a certain size can form.

To characterize the state of the 2D film of fullerene at the water/air interface, Langmuir isotherms were examined. Although fullerene is not a classical surfactant, the presence of its molecules at the interface reduces unbalanced intermolecular interactions in the interface layer due to dispersion interactions arising between C_{60} molecules and subphase molecules. The efficiency of these interactions can be observed upon an increase in the surface pressure that accompanies a decrease in the area per fullerene molecule.

Systems in which fullerene is applied to the subphase surface are characterized by low A values at which the surface pressure begins to be detected. This minimal area is smaller than the cross section area of the fullerene globule. These data can be explained by the fact that, due to the high propensity of fullerene molecules to form aggregates, aggregates consisting of several fullerene globules form in the gaseous layer. Differences in areas per molecule observed upon the deposition of different amounts of fullerene are due to the formation of larger amounts of aggregates when a solution containing 8.3×10^{-8} mol/L of fullerene is applied. This dependence is a result of a definite ratio between the spreading rate and evaporation/dissolution rate of the organic solvent in the aqueous phase.

The introduction of the electrolyte in all cases changes the parameters of the 2D films under consideration. This points to a tendency of formation of monomolecular films. Due to electrostatic repulsion, the propensity of fullerene to form aggregates is suppressed, which is favorable for a more uniform distribution of the substance over the subphase surface. The extreme values of the surface pressure isotherm parameters when 5.6×10^{-8} or 8.3×10^{-8} mol/L of fullerene was deposited are presumably associated with the compression of the double electric layer that occurs upon the increase in the electrolyte concentration in the subphase.

The microphotographs in Fig. 2 show that, after the deposition of the solution on the water subphase, objects with a complicated structure are formed. This is due to the high propensity of fullerene molecules to form aggregates. Such structures can be detected by Brewster angle microscopy, which allows one to determine the surface morphology. This method of studying thin films at interfaces is based on measuring the intensity of light reflected from different areas of the interface film. Our findings allow us to conclude that, after deposition of the system on the water subphase, aggregates of fullerene globules are formed.

Our study show that, even in the case of the gaseous state of the 2D film of fullerene, most fullerene molecules are incorporated in surface clusters. A decrease in the area per fullerene molecule leads to the formation of structures with a definite amount of defects. In this case, the defect is a region of the interface not covered with fullerene molecules. The introduction of an electrolyte, namely, ammonium sulfate, into the system leads to a decrease in the total area of defects of the 2D fullerene film at the interface.

The detailed three-dimensional structure of the 2D fullerene film transferred onto a silicon wafer can be studied by AFM. The AFM study shows the system is composed of 2D clusters of packed fullerene molecules. Compression of this system leads to the formation of a film consisting of 3D structures and regions at the subphase surface free of fullerene molecules. This result confirms the high propensity of fullerene to form aggregates, which prevents the formation of a uniform monomolecular film at the water/air interface. AFM shows that the resulting structures are formed due to aggregation of initial clusters. The microphotographs of films with $A_0 = 30$ Å^2 show that they are multilayer systems spread over the subphase surface.

In this work, we showed that the use of an electrolyte solution that creates the electrostatic barrier is, in principle, able to regulate the structure of the 2D film of fullerene formed on the surface of the water subphase. The charge on the surface of the hydrophobic fullerene molecule appears when it adsorbs cations from the aqueous subphase. The possibility of using adsoption of transition metal cations on the surface of fullerene globules for their separation was shown in [16]. Adsorbed cations interact with the π electrons of the fullerene molecule. In our opinion, the water/air interface can affect the interaction of cations dissolved in the subphase. At the water/air interface, water dipoles are oriented creating a potential jump of ~25 mV [17]. When fullerene molecules, exhibiting considerable polarizability [18], find themselves in the electrostatic field of the interface, they can acquire enhanced electron density at the surface presented to the subphase. This redistribution of π electrons creates conditions for electrostatic interactions of the initially nonpolar molecule with the cations in the aqueous phase. The cations immobilized on the fullerene globule surface create an electrostatic barrier that prevents their aggregation in the 2D film. Only the use of an electrolyte solution as the subphase makes it possible to obtain $A_0 = 90$ Å^2 corresponding to the theoretically calculated area per molecule in the monolayer. Comparative analysis of the microphotographs of the films obtained on water and an electrolyte solution in a given range of surface pressures shows the decrease in the area free of fullerene molecules in the latter case. Adsorption of cations on the fullerene surface generates electrostatic repulsion between the globules, which leads to the formation of a 2D film with a more uniform distribution of fullerene over the subphase surface.

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