Mol. Mat., 1996, Vol. 7, pp. 175–178
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Investigation of Langmuir Films of Fullerene Derivative Resulting by Addition of C_{60} to Tetracyanoethylene Oxide

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New fullerene-tetracyano-ethylene oxide derivative (C_{60}-TCNEO) was synthesized. The Langmuir layers of C_{60}-TCNEO on the water surface were investigated. The Langmuir-Blodgett films of C_{60}-TCNEO were prepared. The absorption spectra of obtained LB-films in UV and visible range (200 nm to 700 nm) and the dielectric constant at 1 kHz, 10 kHz, and 100 kHz were measured.

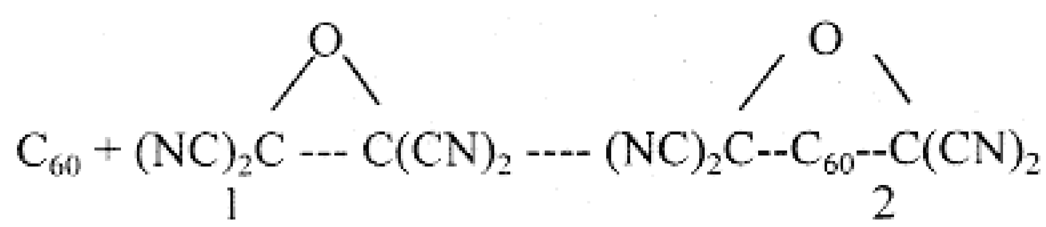
At present, the Langmuir-Blodgett (LB) films of fullerene C_{60} and its derivatives is a subject of extensive studies,[1-5] since fullerene is a molecular building block, which can be used to prepare new materials with interesting electronic properties.

In this paper we describe the synthesis of fullerene-tetracyano-ethylene oxide derivative (C_{60}-TCNEO) and the results of a study of its Langmuir monolayers on water surface and LB-films on solid substrates.

Synthesis of starting fullerene was carried out in our laboratory. An apparatus for production of carbon soot is analogous to that described in the literature[6] but modified for the purpose of high efficiency by construction of a rotating graphite rod holder. The method described in[7] was used for purification and separation.

NMR spectra were recorded on Varian XL-400 spectrometer at 400 MHz with tetramethylsilane as internal standard. IR spectra were determined in KBr by PYE UNICAM PU 9512 IR spectrometer. Mass-spectrum of compounds were recorded on Finnigan MAT 8430 mass-spectrometer. Samples were ionized by a xenon beam with energy of 8 kV from a matrix of m-nitrobenzyl alcohol.

Treatment of C_{60} with tetracyanoethylene oxide in dichloroethane under 2h reflux results in the formation of a new compound 2 (C_{60}-TCNEO) (Scheme). Evaporation of solvent and separation by column chromatography (silica gel, mixture of hexane/toluene) result in compound 2 with 90 % yield. 50-fold excess of tetracyanoethylene was used. New compound is characterized by their ^{13}C NMR, IR- and UV-spectra.



Scheme

The dependence of surface pressure versus area per molecule during compression of monolayer on water surface was investigated using a computer-controlled LB-trough "MDT-LB5" which had two compressing barriers. The surface pressure measurements were carried out with accuracy of ± 0.01 mN/m.

LB-films were deposited onto substrates by the Langmuir-Schaefer method. The substrates had dimensions $12 \times 24 \times 1\ mm^3$.

For study of dielectric properties we fabricated some samples in the form of thin-film capacitors with LB-films of C_{60}-TCNEO as dielectric layer. There were eight capacitors on a substrate. Each capacitor had area 1 mm^2. The sample capacitance was measured with an automatic capacitance bridge HP4270A.

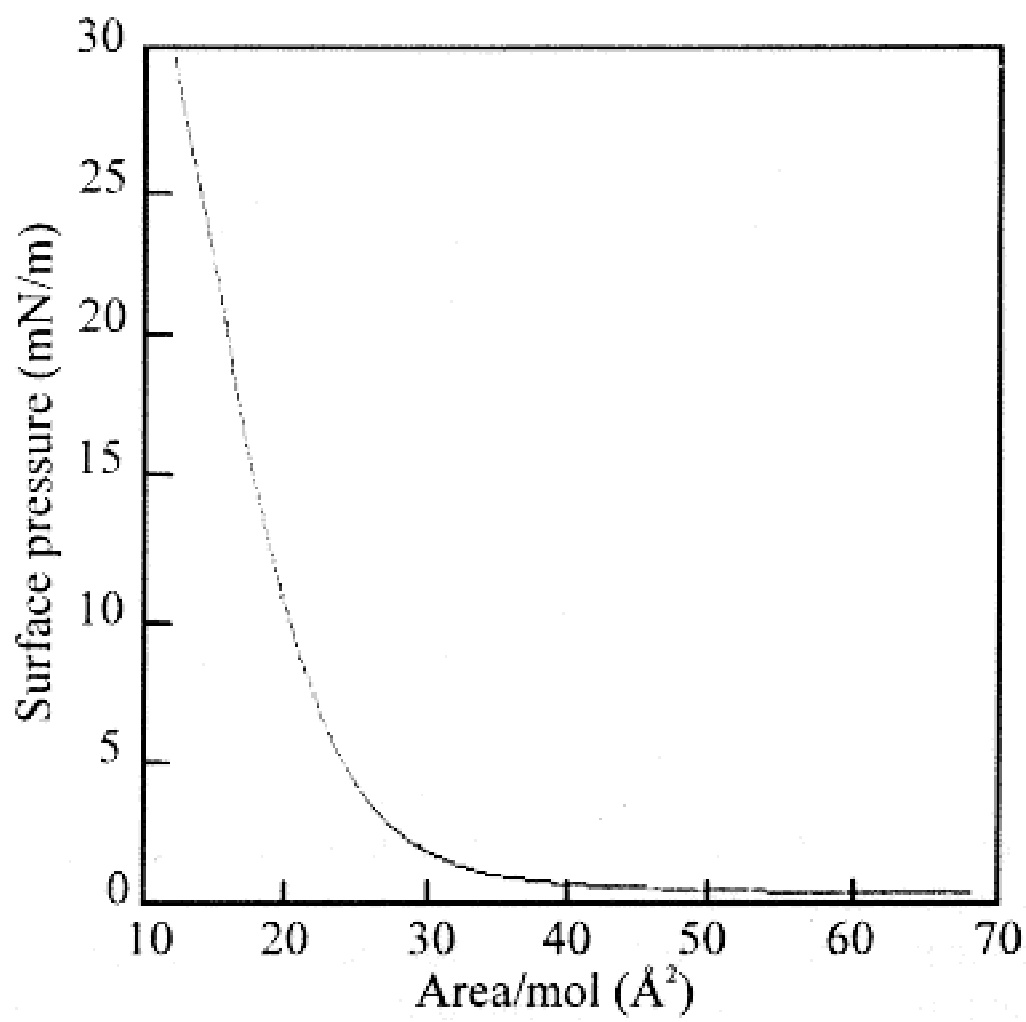


Figure 1 Dependence of surface pressure on area per molecule for the Langmuir layer of C_{60}-TCNEO on water surface.

The thickness of LB-films was measured with interference microscope "INTERFACE CARLZEISS".

Absorption spectra were recorded with LOMO CSVU-23 spectrophotometer.

A typical dependence of surface pressure versus area per molecule for C_{60}-TCNEO (π-A isotherm of compression) is presented in Figure 1 (dose of solution - 60 μl, concentration of C_{60}-TCNEO 0.56 mg/ml).

The limiting area per molecule of C_{60}-TCNEO in layer obtained from linear approximation of the part of π-A curve at large values of surface pressure gives the value close to 25 Å^2. This value, as in case of pure C_{60},[1-5] is much smaller than that predicted from the X-ray diffraction studies of C_{60} (about 87 Å^2).[4,5] It indicates the formation of aggregates in C_{60}-TCNEO layer as in the case of pure C_{60}.[3,5] It may be noted that π-A curves of C_{60}-TCNEO differ from the linear dependences of typical "condensed films",[8-10] and its form at a low surface pressure (Figure 2) reminds more the corresponding dependences for "expanded films".[8-10] In Figure 3 the surface pressure-area data are presented as surface pressure - molecular area product versus surface pressure. It may be seen that at low pressure ($\pi \approx 0.1 \div 1$ mN/m) this dependence is described by linear law:

$$\pi(A-A_o) = qkT \qquad (1)$$

which corresponds to the equation of state for two-dimensional gas.[8-11] In Equation 1 k is the Boltzmann constant, T is the absolute temperature, A_o is the effective area of one molecule and q is the parameter which characterizes the intensity of cohesive forces. Equation 1 may be given as:

$$\pi[(A/q)-(A_o/q)] = kT$$

were A/q is the area per one kinetic unit in a monolayer, A_o/q is the effective area of one kinetic unit and 1/q is the number of molecules in one kinetic unit. In our case the effective area per molecule in aggregate (A_o) is equal to 30 Å^2. This value is approximately three times smaller than the area of one molecule for C_{60} (87 Å^2).[4,5] Thus, the thickness of aggregates is approximately equal to three molecules of C_{60}-TCNEO. The average number of molecules in aggregate (1/q) is equal to 93. The average area of one aggregate is approximately 2790 Å^2 and the linear size is about 53 Å.

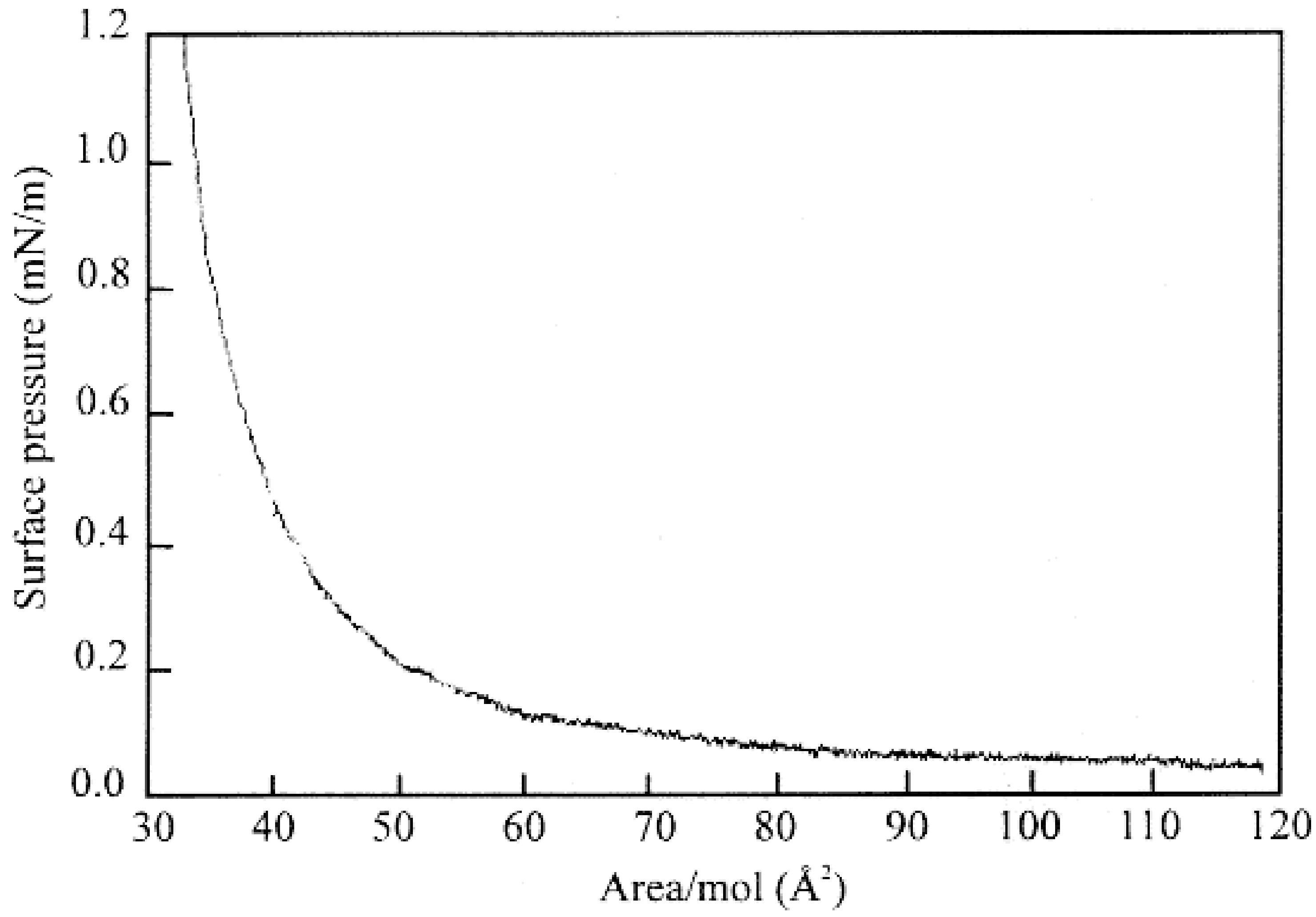


Figure 2 Dependence of surface pressure on area per molecule for the Langmuir layer of C_{60}-TCNEO on water surface at low surface pressure.

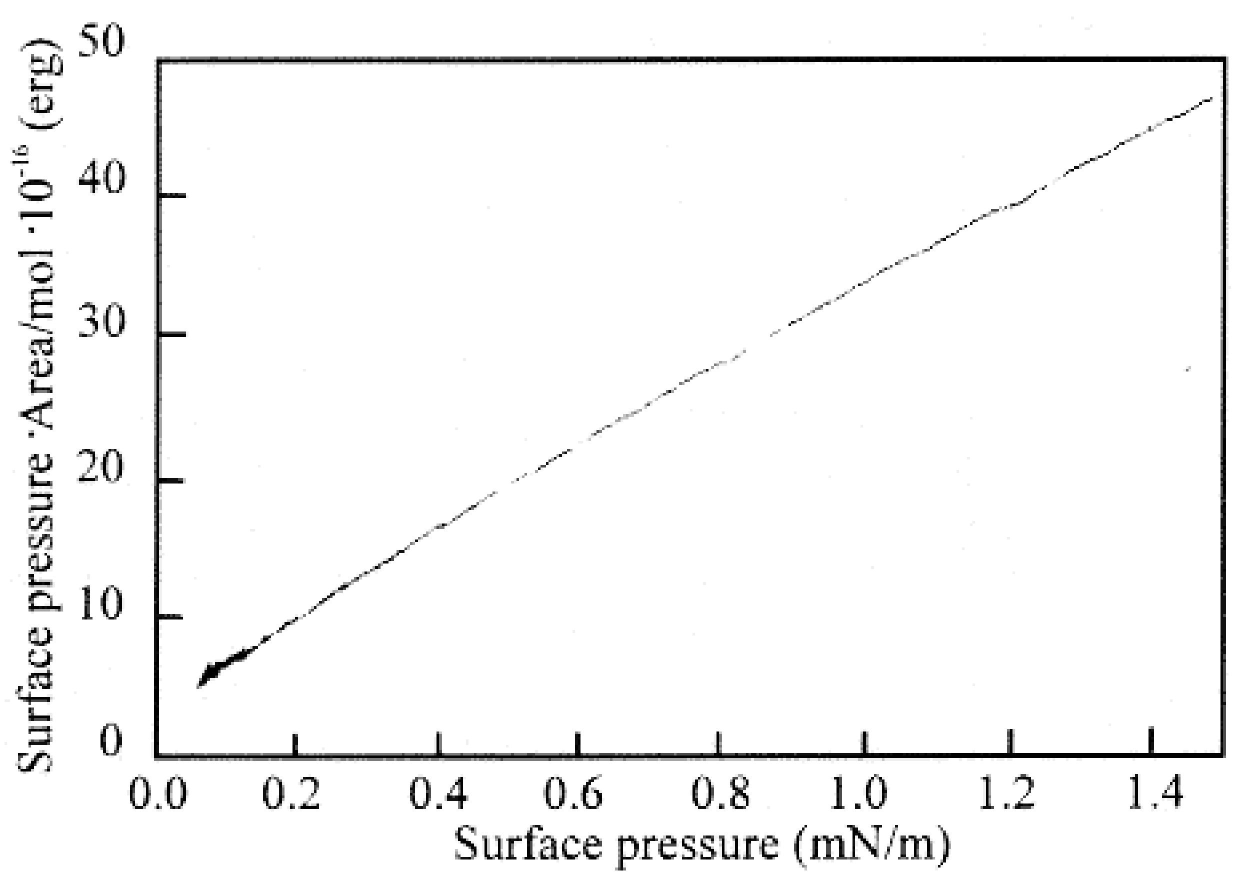


Figure 3 Surface pressure - molecular area product versus surface pressure for the Langmuir layer of C_{60}-TCNEO on water surface at low surface pressure.

The Langmuir layers were deposited onto a substrate from water surface at area per molecule $A = A_o$, where $A_o = 30$ Å^2 is an affective area per molecule in an aggregate obtained from the surface pressure-area isotherm.

The electronic absorption spectra of LB-films of C_{60}-TCNEO on fused quartz were measured in UV and visible range (200 nm to 700 nm). The investigated films have absorption bands at $\lambda_1 = 215$ nm, $\lambda_2 = 265$ nm, and $\lambda_3 = 335$ nm.

The values of the dielectric constant of C_{60}-TCNEO are 3.29 ± 0.05 at 1 kHz, 3.08 ± 0.05 at 10 kHz and 2.96 ± 0.05 at 100 kHz.

The effective thickness of one layer deposited on a substrate was determined by dividing the LB-film thickness into number of deposited layers. The resulting value for C_{60}-TCNEO is 27.7 Å ± 0.2 Å. Thus, the effective thickness of one layer of C_{60}-TCNEO equals approximately three molecules. This result is in agreement with the data obtained from the surface pressure-area experiment.

The authors are grateful to Dr. V.K. Ivanov for supplying carbon soot. This work was supported by Russian Research Program "Fullerenes and Atomic Clusters".

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