

ANALYSIS OF PHASE SEPARATION IN 2D MOLECULAR SYSTEMS

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1. Introduction

Monomolecular insoluble layers on the surface a liquid termed the Langmuir monolayers are formed as a result of a self-organized process. Organic molecules constituting the monolayer are amphiphilic and they spontaneously spread at the air/water interface. The Langmuir monolayer is a very suitable model for the study of self-organization in two dimensions. The water surface provides ideally planar and smooth (noncorugated) surface as a substrate. A pair of thermodynamic quantities, temperature and surface pressure, can be easily controlled; surface pressure by a moving barrier over the surface. Such mechanical compression, which is analogous to hydrostatic compression in 3D systems, is not available in other 2D systems and arrangements.

In this communication we describe aspects of monolayer technology by focusing on some particular properties of a binary system consisting of oligothiophene and fullerene: their mechanical properties in a monomolecular layer. In each part methodological importance is stressed and its specificity for studying molecular interactions in a mixed monolayer. This combination of materials is perspective in organic photovoltaic cells. The research involving polymer (donor) and fullerene (acceptor) heterojunctions became intense in the area of photophysics and device physics [1] after the evidence of photoinduced electron transfer from the excited state of a conducting polymer onto fullerene (C₆₀). As a single polymer layer device presents low efficiency due to the mechanism of charge generation and transport, the use of a C₆₀ molecule, which has a high electron affinity value, sublimed onto the polymer (donor) in a bilayer heterojunction or mixed in the polymer film (blend) in a bulk heterojunction increased dramatically the efficiency of the photovoltaic devices [2]. It was found that, besides tailoring electronic properties, the bulk film morphology of the blend is crucial for the photovoltaic performance. This needs to optimize the composition of a system of two segregated materials on a nanometer scale providing the spatially distributed interfaces necessary for exciton ionization and subsequent percolated charge transport. The intermolecular interactions play essential role in an intimate mixing of the components. These phenomena are studied here in a two-dimensional molecular structure, using the monolayer formed at the air/water interface as a model molecular system.

2. Materials and Methods

Chemicals

Fullerene (PCBO) - [6,6]-Phenyl C₆₁ butyric acid octyl ester, 99% - was purchased from Sigma-Aldrich Co. Oligothiophene hexamer (OTH) –

3,3''''-bis-decyl[2,2';5'.2'';5'';2'''';5'''';2'''';2''''']sexithiophene-5,5''''-didaroxilic acid was synthesized according to the procedure presented in [3].

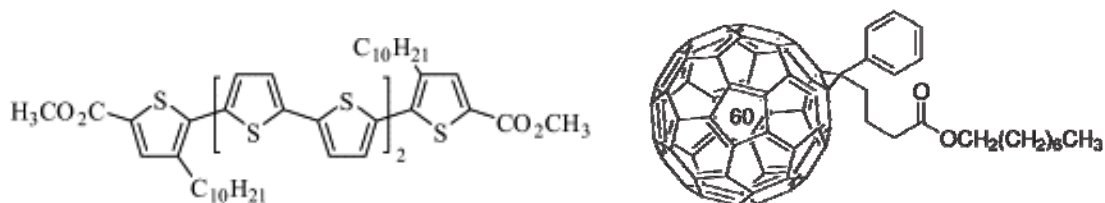


Fig. 1: Chemical structural formulae of oligothiophene hexamer (left) and fullerene (right).

For preparation of monolayers OTH and PCBO were dissolved in chloroform at a concentration of 0.5 mg/ml and at various molar ratios. As a subphase, bidistilled and deionised water (18 MΩ.cm, ELIX 5, Millipore, USA) was used. OTH, PCBO or mixed OTH/PCBO monolayers were formed by spreading a small amount of solutions (approx. 100 μl) on the water subphase of the Langmuir – Blodgett trough using a microsyringe (Hamilton, USA).

Experimental methods

Computer – controlled Langmuir trough model 611M (NIMA Technology, Coventry, UK) was used for monolayer experiments. The maximum and minimum working areas of the trough were 600 cm² and 75 cm², respectively. The surface tension (π) of the monolayer was measured by the Wilhelmy method with an accuracy of ± 0.5 mN/m. The monolayer was allowed to equilibrate and the solvent to evaporate for 15 minutes. This time was found sufficient for evaporation of chloroform and stabilization of the monolayer. All monolayers were compressed at the constant speed of 5 cm²/min, which corresponds to 0.17 Å²/s per molecule. The trough was thermostated by a recirculating cooler FL 300 (Julabo Labortechnik, Germany) with an accuracy of 0.1 °C. The experiments were carried out at the temperatures 22 °C.

3. Results and Discussion

The fundamental characteristic description of a monolayer is usually in terms of its surface pressure – area curve, *i.e.* the relationship between the surface pressure observed and the area occupied on the water surface by the molecules of the film. This π – A dependence provides direct evidence on the phase transformations during the isothermal compression in 2D molecular system. Surface pressure – area isotherms of OTH and PCBO as well as of their binary mixtures are presented in Fig. 2.

The limiting areas of oligothiophene and fullerene derivative which is occupied by a molecule in pure monolayers are ca. 80 Å² and 35 Å², respectively. All the isotherm curves exhibit a monotonous increase during compression showing no visible phase transition from the liquid – expanded to the liquid - condensed phase, which is typical of long-chain hydrocarbons related to the chain alignment and ordering. Remarkable is a low value of π at which a pure oligothiophene monolayer collapses ($\pi \square 12$ mN/m). The area occupied by a thiophene monomer in a monolayer estimated from a space-filling model assuming that the ring lie parallel to the surface is approx 45 Å². If we compare the area calculated for a hexamer with the value obtained from the experiment it comes out that the thiophene hexamer backbone is tilted by ca. 35° from the normal.

The miscibility of two compounds in a mixed monolayer at the water-air interface can be deduced as a result of the behavior of molecular areas as a function of the mixture composition at constant surface pressure and temperature. Positive or negative deviations from an ideal dependence of the excess area as a function of OTH/PCBO ratio, characterize repulsive or attractive mutual interactions between the monolayer components: oligothiophene and fullerene molecules [4]. For this reason, monolayers in which

components are either immiscible or if they behave like an ideal mixture, the excess area of the mixture, ΔA , defined as

$$\Delta A = A_{12} - x_1 A_1 - x_2 A_2 \quad (1)$$

is equal to zero. A_{12} is the molecular area in the mixed monolayer at temperature T and surface pressure π , whereas A_1 and A_2 are molecular areas in the two single component monolayer and x_1 and x_2 are molar ratios of the pure components in the mixture ($x_1 + x_2 = 1$). Dependences of the excess areas on the mixture OTH/PCBO molar ratio are shown in Fig. 3. In all the mixtures the average area occupied by one molecule in a monolayer is higher than that given by the mixing rule, hence it unambiguously reveals decreased miscibility of the components in a binary mixture having its greatest effect at the PCBO molar ratio of 0.6 – 0.65, i.e. mixture of 2 fullerene molecules to 1 thiophene hexamer. It indicates that in a 2D system these molecules are not distributed homogeneously but molecular domains of different composition are formed. The separated domains may not mean pure components, this may suggest *e.g.* small 2D clusters of individual oligothiophene molecules being attached with a certain number of PCBO molecules in the prevailing pure PCBO phase.

Another parameter used for characterizing elasticity of the monolayer is elastic modulus and, in analogy with bulk material, is defined as

$$|E| = -A \left(\frac{\partial \pi}{\partial A} \right)_T \quad (2)$$

where π stands for surface pressure, A area per molecule and T is temperature. Evolution of elastic modulus as a function of area is sensitive to phase transitions, but the maximum value reached illustrates the rigidity of the monolayer [5].

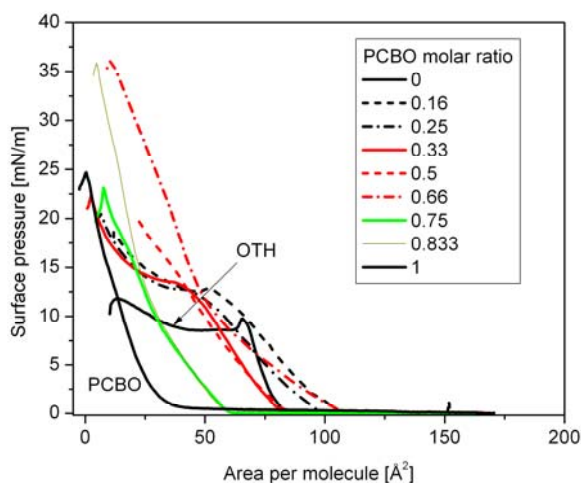


Fig. 2: Pressure-area compression isotherms of OTH/PCBO mixed monolayers and pure components at the air-water interface. Curves correspond to various molar fraction of PCBO (see insets in the figures). 0 means pure OTH and 1 is pure PCBO. The isotherms shown were recorded at 22 °C.

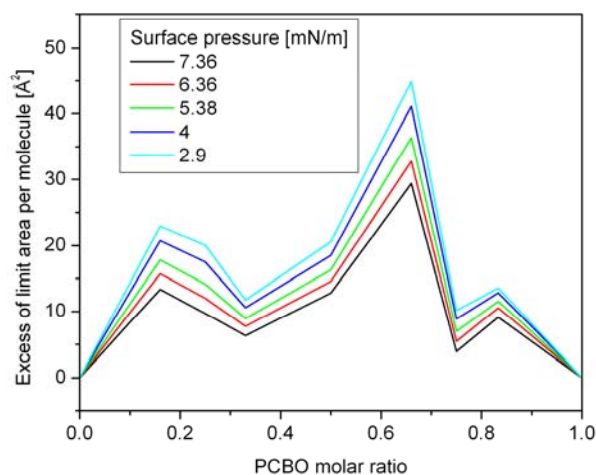


Fig. 3: Plot of the excess area as a function of molar ratio of PCBO/OTH at temperature 22 °C, and at different levels of surface pressures (see the inserts in the figure).

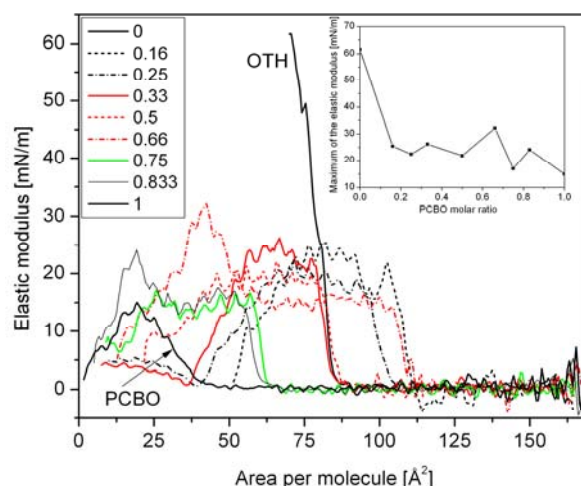


Fig. 4: *Elastic modulus as a function of area per molecule. Maximum elastic modulus vs. PCBO molar ratio is shown in the insert.*

The experimental findings for the maximum values of elastic modulus as a function of the PCBO/OTH ratio are presented in Fig. 4. In a low PCBO fraction until 0.2 molar ratio this parameter decreases dramatically to the value which further remains constant as far as the pure fullerene monolayer.

The deeper insight into the interactions in 2D molecular systems can be found from the application of the ordinary phase rule on this system [6]. If temperature and external pressure are constant, assuming 2 surface phases (PCBO and OTH) the number of degrees of freedom $F=3-q$, where q is the number of surface phases which are in equilibrium with each other.

We will use the phase rule in the region of critical collapse, but it is also applicable for 2D phase transitions (L-S or LE-LC transition). If the two components are miscible, then two phases are in equilibrium. Therefore, $q=2$ and system has still one degree of freedom. If the two components are immiscible then $q=3$ and the system has no degree of freedom. Therefore, when two components are immiscible, mixed monolayers will possess the unvaried mechanical properties (be in equilibrium with bulk phase) at the same surface pressure, regardless of composition. If components are miscible, elastic modulus will vary with the composition. In this binary mixture this PCBO phase is “more fragile” which determines elastic modulus of a monolayer as a whole.

This finding is in good agreement with the results on the excess area and provides convincing evidence on phase separation in these molecular systems which are of fundamental relevance for the performance of organic photovoltaic devices.

Acknowledgement

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