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Isotherm Behaviour of P3OT, P3HT and PCBM Langmuir Layer on Ionic Subphase

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ABSTRACT

Isotherms are generally curves that depict the phenomena that govern a substance's mobility at a constant temperature and pH. In this study, the Langmuir layer of P3OT, P3HT and PCBM were characterised by computing their surface pressure as a function of the surface area available to the molecules at the interface to obtain a curve called surface pressure – area (Π -A) isotherm. All three polymers were spread on two types of subphases - DI water and water containing bivalent metal ions, Pb²⁺. None of the Langmuir layers exhibits discrete gas-liquid-solid phase transitions on the water subphase. However, more stable Langmuir layers formed when lead ions were added to the water subphase. The stability enables the capping of lead ions between the polymer chain or within the balls, which can be implemented in flexible electronic devices.

1. Introduction

Thin films play a significant role in creating and exploring materials with novel and distinctive features. Thin films enable materials to be integrated into a multitude of devices, and they have directly or indirectly promoted many new fields of research in solid-state physics, chemistry and biology [1]. The properties of functional materials are significantly different when analysed in the form of thin films as compared to their bulk materials — the thickness of thin films ranges from tenths of nanometers to micrometres.

Thin films can be developed using one of three approaches: physical vapour deposition, chemical vapour deposition and wet chemical deposition [2]. Each technique has its advantages and downsides. The wet chemical deposition is a straightforward and economical alternative to chemical or physical vapour deposition. Among the most sophisticated technique in the wet chemical method is Langmuir film. Langmuir films are highly organised monolayers of organic molecules at a liquid/gas

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interface. It is a well-known method used to produce a monolayer or multilayer film using floating molecules and is highly dependent on the surface pressure [3]. The multilayer of Langmuir's film differs from multilayers produced by other techniques, such as the ion gelation technique [4].

Initially, the Langmuir film concentrated on tiny amphiphilic molecules such as stearic on a liquid (subphase) surface. Langmuir film production strongly depends on the film's surface pressure, determining whether the film is monolayer (2-dimensional) or multilayer. Although water is the most frequently used subphase in Langmuir film investigations, other substances such as mercury and glycerol have been used in their place.

The quality of Langmuir films is greatly dependent on the subphase's purity. Contaminants in the water, such as Na^+ or K^+ ions, can alter the subphase pH, influencing the dissociation of carboxylic fatty acidheads. Nonetheless, bivalent metal salt ions (e.g., Cd^{2+} , Cu^{2+}) contribute to the monolayer's stability. Dust contamination on the subphase surface can also degrade the film's quality. It may result in a spontaneous decrease in surface pressure, resulting in the monolayer collapsing.

Langmuir films can be used to investigate intermolecular interactions, monolayer/subphase interactions and as a model system for biological membranes [5]. Molecular recognition at the interface is crucial because biological systems operate primarily at interfaces between phases, such as the inside surfaces of enzyme pockets and the cell membrane surface. Additionally, the Langmuir monolayer provides an unparalleled environment for studying molecule interaction, a critical part of supramolecular chemistry [6]. The monolayer also has been utilised in the gas sensor [7] and solar cells [8] studies.

Langmuir monolayer can be transferred to a solid substrate using either the vertical dipping method, known as the Langmuir Blodgett technique or the horizontal dipping approach, known as the Langmuir Schaeffer technique. This approach has used low molecular weight chemicals such as stearic acid to make thin films. Recently, polymeric materials have been used to produce thin films with enhanced chemical, thermal, and mechanical stability.

This study investigated the isotherm behaviour of compressed conjugated polymers; P3OT and P3HT, as well as a fullerene derivative, PCBM, on water and ionic subphase. This experiment aims to examine the polymers' potential to entrap the ions so that they can be utilised either in flexible electronic devices or as the sensor.

2. Methodology

Regioregular Poly(3-octylthiophene-2,5-diyl) (P3OT) (MW: 34,000), regioregular Poly(3-octylthiophene-2,5-diyl) (P3HT) (MW: 87,000), and [6,6]-Phenyl C_{60} butyric acid methyl ester (PCBM) (MW: 910.9) were purchased from Sigma Aldrich. For the ionic subphase, lead (II) chloride PbCl_2 (Sigma Aldrich) was added into DI water (ultra-pure water supplied by Millipore-RO coupled to a Milli-Q system. Resistivity: 18.2 $\text{M}\Omega$ cm). Unless otherwise specified, all materials used were as-received. Chloroform (Mallinckrodt) was used as the solvent for the polymers because of its low volatility, relative inertness, and miscibility with most organic liquids.

A Langmuir KSV 2002 System 2 (Helsinki, Finland) was used to create the Langmuir film, which contains a computer functioning as the controller, an interface unit, a moveable barrier, a trough, a pressure sensor, and a dipping mechanism (Figure 1). Before filling the LB trough with DI water, it was cleaned using chloroform, methanol, and copious amounts of deionised (DI) water. The subphase was then supplemented with anhydrous lead (II) chloride (PbCl_2) as a source of Pb^{2+} ions. The PbCl_2 concentration was 0.5 mM. P3HT, P3OT, and PCBM were dissolved in chloroform and dispersed onto the subphase at 0.2 mg/ml. Prior to barrier compression, the chloroform was allowed to evaporate for 15 minutes after the solutions were dispersed. Π -A isotherm graphs were obtained in this

investigation by gradually closing the LB barrier at a constant horizontal speed of 10 mm/min and a constant temperature of 25 °C. The barrier closure reduces the trough's area, causing the molecules on the subphase surface to reorganise.

A computer coupled to a sensor attached to chromatography paper monitored the changes in surface pressure during compression. Isotherm graphs were used to depict the Langmuir layer profiles.

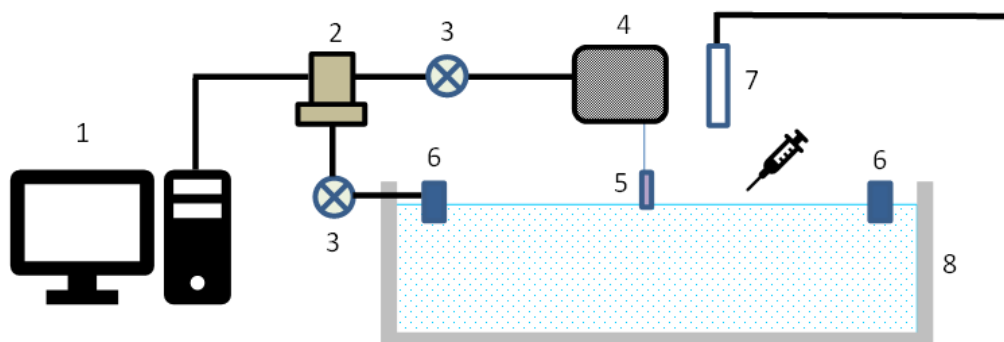


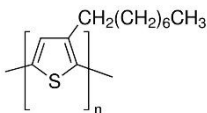
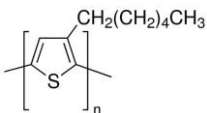
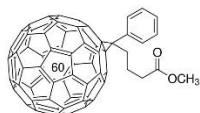
Fig. 1. Schematic diagram of the apparatus Langmuir KSV 2002 System 2: 1-computer 2-interface unit, 3-motor, 4 surface pressure sensor, 5-Wilhelmi plate, 6-movable horizontal barrier, 7-dipping mechanism, 8-trough

3. Results

The surface pressure-area ($\Pi - A$) isotherm graph elucidates the phase transformation of the Langmuir monolayer and quantifies the relationship between surface pressure (Π) and mean molecular area per molecule (A). Additionally, organic molecules' arrangement, structure, and properties at the air-water interface can be comprehended [9]. The isotherm graphs were obtained by gradually closing the LB barrier at a constant horizontal speed. The barrier's closure reduces the trough area, rearranging the molecules on the subphase surface.

The ($\Pi - A$) isotherms of P3OT, P3HT and PCBM on water and ionic subphase are shown in Figure 2. It can be seen that none of the polymers exhibits distinct phase transitions. Long polymer chains that form a two-dimensional lattice are responsible for the absence of a clear transition [10]. The fullerene derivate, PCBM on water, exhibits an isotherm comparable to that of fatty acids such as stearic acid, with a discernible gas-liquid-solid phase development. The similarities may be due to PCBM's diminutive size compared with the long chain polymers (Table 1).

Table 1
 Properties of the P3OT, P3HT and PCBM used in this study

	P3OT	P3HT	PCBM
Synonym	Poly(3-octylthiophene)	Poly(3-hexylthiophene)	[6,6]-Phenyl C ₆₁ butyric acid methyl ester
Structure			
Formula	(C ₁₂ H ₁₈ S) _n	(C ₁₀ H ₁₄ S) _n	C ₇₂ H ₁₄ O ₂
MW	~34,000	50,000-100,000	910.88

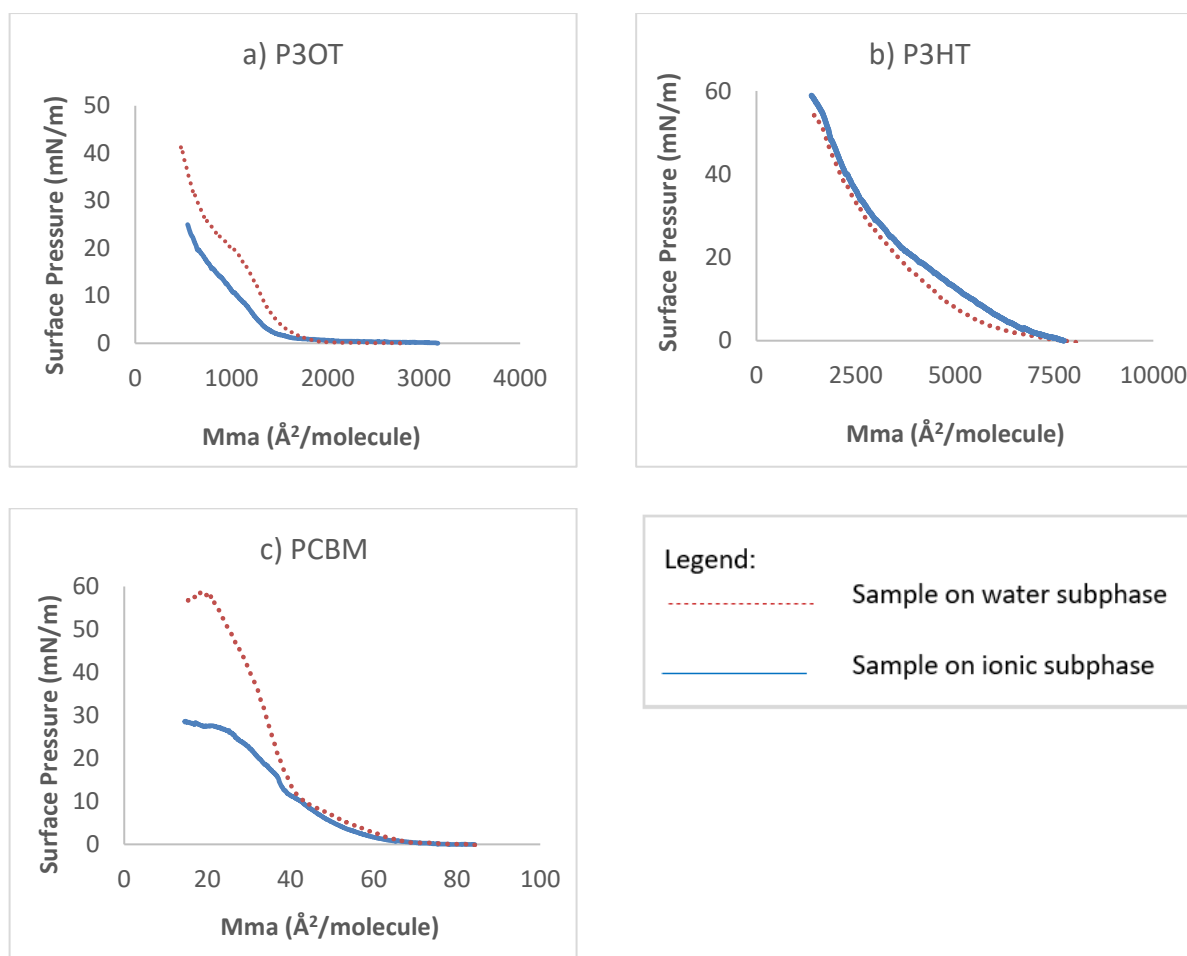


Fig. 2. (II – A) isotherms of (a) P3OT, (b) P3HT, and (c) PCBM on water and ionic subphase

Figure 3 displays the $\Pi - A$ isotherm graph for PCBM on water subphase only. The plots are denoted with the roman number, where (i) is gas phase, (ii) is liquid phase, (iii) is solid phase and (iv) is collapse phase. The liquid-solid phase transition occurred at a surface pressure of 42 mN/m and collapsed at 58 mN/m. By extrapolating the solid phase linear section of the graph, it was found that a PCBM molecule occupied at a molecular area (A_o) of approximately 52 $\text{\AA}^2/\text{molecule}$.

At the beginning of the compression process, the monolayer is considered to be in a “gaseous phase” because the molecules are still far apart and not interacting with one another; hence, the surface pressure approaches zero as the compression continues. The extremely low surface vapour pressure of the molecules complicates the experimental examination of the gaseous phase. As the compression continues, the molecules become more pack and exert a repulsive force. The surface pressure increases as the area per molecule decreases. At this time, the monolayer is regarded as being in “liquid phase” and is still compressible. When the compression reaches a critical point, however, the monolayer transforms into a “solid phase” in which the molecules are packed as closely as possible. Extrapolating the steepest portion of the graph to intersect the x-axis yields the area occupancy value, A_o , of a molecule in its condensed state. This value would be assumed to remain unchanged once the monolayer has been transferred to a solid substrate [11]. The collapse phase occurs due to mechanical instability at very high surface pressures.

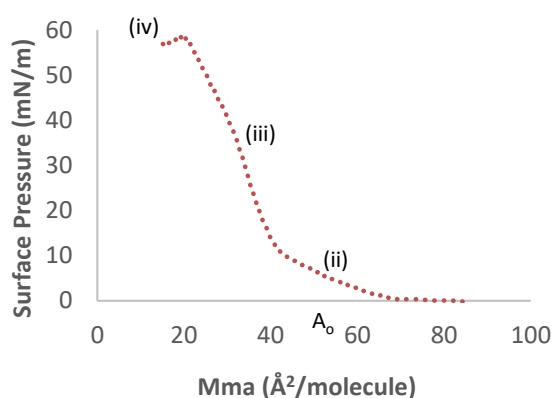


Fig. 3 ($\Pi - A$) isotherms PCBM on water subphase only and its solid phase extrapolation

In contrast, the isotherms of the polymer layers, either on water or ionic subphase, are simpler - gas phase, liquid-like phase, or solid-like phase. The polymer molecules either adopt a three-dimensional conformation or are capable of assuming a random two-dimensional shape. The 2D structure results from maximum material interaction with water, forming a very thin polymeric monolayer, as seen in Figure 4. The phase of polymeric Langmuir film can be divided into extended and condensed stages [12]. An expanded monolayer is a 2D “dissolved” state dependent upon hydration forces with the subphase, whereas a condensed monolayer is a 2D “collapsed” state. Comparable to the graph of small-molecule isotherms [11], the surface pressure of expanded polymer monolayers rises slowly, whereas the ($\Pi - A$) isotherm has a steeper slope in the condensed state.

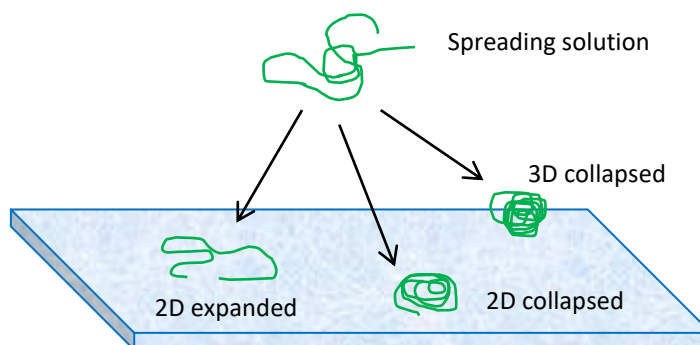


Fig. 4. Spreading of polymeric solution on subphase (adapted from [13])

The addition of PbCl_2 into the water subphase did not change much of the isotherm profile, except for PCBM. While the long-chain polymers exhibit smoother graphs, the PCBM graph was pretty uneven. The ionic substance reduced the solid phase of P3OT and PCBM relative to the aqueous subphase. When bivalent metal ions, such as Pb^{2+} or Cd^{2+} are introduced to the water subphase, more ordered Langmuir layers are generated. The ordering is because most solid surfaces assume a limited surface charge in water and interact with polar or charged organic molecules. The strong electrostatic interaction of bivalent ions adheres or immobilises organic molecules to the substrate. Higher multivalent ions exhibit identical feature [14]. Contrarily, monovalent ions do not show the same characteristic. In the presence of Pb^{2+} ions, the aberrations in the isotherm graph are caused by the

structural rearrangement of Langmuir layer molecules. According to studies, molecules can expose polar head groups to substrate and subphase [15, 16].

The research can be expanded by utilising different ions, such as Cu, Zn, and Cd. The ability of conjugated polymers to encapsulate these ions can be used in either organic electronic devices or water purification sensors. This is due to the fact that these ions are considered heavy metals and are frequently associated with environmental issues, particularly water pollution [17].

4. Conclusions

The surface pressure-area ($\Pi - A$) isotherms of two types of conjugated polymer, P3OT and P3HT, as well as fullerene derivative, PCBM was investigated. On the water subphase, the long-chain polymers portray a simple isotherm profile, while the PCBM display a distinct characteristic of the gas-liquid-solid phase. PCBM has a graph profile comparable to fatty acids due to its tiny size. The introduction of impurities, Pb^{2+} ions, into the water did not change the behaviour of P3OT and P3HT. On the other hand, the PCBM plot started to behave like a polymer with a less distinct gas-liquid-solid phase transition. Again, the size of PCBM may be why the ions disrupt the structural rearrangement of PCBM molecules' Langmuir layer. Extending the study to include other bivalent ions is possible. Conjugated polymers' unique capacity to enclose these ions has wide application in organic electronics and sensors for water purification.

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