AGGREGATION OF P-TERPHENYL ALONG WITH PMMA/SA AT THE LANGMUIR AND LANGMUIR–BLODGETT FILMS

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Molecular aggregation and monolayer characteristics of non-amphiphilic p-terphenyl (TP) mixed with either polymethyl methacrylate (PMMA) or stearic acid (SA) at the air–water interface were investigated. The miscibility of the two components was evaluated by measuring and analyzing surface pressure versus area per molecule (∙–A) isotherm. Both attractive and repulsive interactions between the sample (TP) and the matrix (PMMA or SA) were observed depending on the composition and microenvironment. TP and PMMA/SA were not completely miscible in the mixed monolayer. Aggregation and phase separation between sample TP and matrix molecule were revealed by UV–Vis absorption spectroscopic studies and confirmed by scanning electron micrograph of Langmuir–Blodgett films.

Keywords: Langmuir monolayer; ∙–A isotherm; miscibility; SEM.

1. Introduction

Langmuir–Blodgett (LB) deposition is a potential technique in fabrication of nanofilm of controlled structure.1–3 Langmuir monolayer at the air–water interface plays an important role in the application of Langmuir–Blodgett (LB) technique.4–6 The behavior of Langmuir monolayer at the air–water interface is of great importance for understanding the structure, stability, and deposition transfer ratio of the monolayer. By measuring and analyzing the pressure versus area isotherm, one would be able to understand the states of the monolayer and its changes, for example, molecular arrangement, phase structure, phase transition, etc.7,8

Although amphiphilic molecules are ideally suitable for LB technique, however, recent investigations suggest that nonamphiphilic molecules can also form good quality LB films, when they are mixed with suitable matrix materials.7–10 The spectroscopic and aggregating properties of these non-amphiphilic molecules in LB films are very similar to their amphiphilic counterpart. It is easy to synthesize the nonamphiphilic molecules, and also they are cost-effective with respect to their amphiphilic counterpart.
Recently mixed monolayers have brought more and more interest in the monolayer research due to the vast properties of the multicomponent system than that of pure ones.

For some cases, monolayer of one component may not be able to transfer onto solid substrate during film deposition and thus second component need to be incorporated into the monolayer to promote the transfer ratio. For a mixed monolayer, the miscibility of various components is important for stability and later application of LB films.

In this paper, we report an investigation of the monolayer characteristics and the miscibility of a well-known polyphenyl nonamphiphile: p-terphenyl along with stearic acid (SA) or polymethyl methacrylate (PMMA) at the air–water interface. The photophysical characteristics of polyphenyls have been extensively studied and continue to be an interesting area of research owing to the many subtle aspects exhibited by them. The extensive applications of polyphenyls as laser dyes and of their derivatives as excellent liquid crystalline materials make them potentially important for various technological applications. The electronic states of polyphenyls are the functions of the dihedral angles between the benzene rings. Parameters like temperature, pressure, electric and magnetic fields, which affect the dihedral angles between the benzene rings also affect their luminescence spectra. A thermodynamic analysis based on the study of the surface pressure versus molecular area isotherm as a function of the mixture composition allows us to probe the mixing behavior of the two components.

2. Experimental

2.1. Materials

p-terphenyl (98% pure) purchased from Aldrich Chemical Co, USA was purified under vacuum sublimation followed by repeated re-crystallization before use. SA (purity > 99%) purchased from Sigma Chemical Company and isotactic PMMA from Polyscience were used as received. Spectroscopic grade Chloroform (SRL, India) was used as a solvent, and its purity was checked by fluorescence spectroscopy before use. Solutions of TP, PMMA, SA as well as TP--PMMA and TP--SA mixture at different mole fractions were prepared in chloroform solvent and were spread on the water surface.

2.2. Isotherm measurement

A commercially available Langmuir–Blodgett (LB) film deposition instrument (Apex-2000C, India) was used for isotherm measurement. A surface pressure–area per molecule isotherm was obtained by a continuous compression of a monolayer at the air–water interface of the LB trough by a barrier system. The surface pressure at the air–water interface was measured using Wilhelmy plate arrangement attached to a microbalance, whose output was interfaced to a microcomputer, which control the barrier movement confining the monolayer at the air–water interface. Milli-Q water was used as a sub-phase, and the temperature was maintained at 24°C.

Before each isotherm measurement, the trough and barrier were cleaned with ethanol and then rinsed by Milli-Q water. In addition, the glassware was cleaned prior to the use. The surface pressure fluctuation was estimated to be less than 0.5 mN/m during the compression of the entire trough surface area. Then, the barrier was moved back to its initial position and the sample containing monolayer-forming material was spread on the sub-phase using a Hamilton microsyringe. After a delay of 30 min, to evaporate the solvent, the film at the air–water interface was compressed slowly at the rate of 5 mm/min to obtain a single surface pressure versus area per molecule (π–A) isotherm. All isotherms were run several times with freshly prepared solution.

2.3. UV–Vis absorption spectroscopy

UV–Vis absorption spectra were measured using a Parkin Elmer Lambda 25 spectrophotometer.

2.4. Scanning electron microscopy

A Hitachi model S-415A electron microscope was used for the SEM imaging of LB films. Accelerating voltage of the electron beam was maintained at 10 kV.

3. Results and Discussions

3.1. Monolayer characteristics of TP at the air–water interface

The measurement of the surface pressure versus area per molecule (π–A) isotherm is the basic technique
used for the characterization of floating monolayer at the air–water interface. The surface pressure ($\pi$) is a measure of the change in surface tension of the subphase covered with a monolayer with respect to pure sub-phase. The $\pi$–A isotherm represents the plot of the change of the $\pi$ value as a function of the average area available for one molecule on the sub-phase surface.

When a dilute solution of pure TP in chloroform solution was spread at the air–water interface and after sufficient time was allowed to evaporate the solvent, the barrier was compressed slowly, surface pressure rises more than 30 mN/m, however large patchy films of TP at the air–water interface was formed which was visible even to the naked eye. Upon relaxation of pressure, these large patchy films broke up into several small clusters, but did not disintegrate into the molecular level. This suggests that pure TP does not form stable Langmuir monolayer at the air–water interface, rather it forms multilayers or clusters of aggregates. Repeated attempt to transfer this floating layer onto solid substrate was failed.

However, when a building matrix such as stearic acid (SA) or polymethyl methacrylate (PMMA) was used, then the mixed film of TP and SA/PMMA form excellent and highly stable floating monolayer at the air–water interface and can be easily transferred onto a solid substrate.

Figures 1(a) and 1(b) show the surface pressure ($\pi$) versus area per molecule ($A$) isotherms of TP with PMMA and SA at different mole fractions of TP along with pure PMMA, pure SA, and pure TP, respectively.

The area per molecule of pure PMMA is 0.12 nm$^2$ at a surface pressure of 15 mN/m. In pure PMMA isotherm, there exists certain distinct part with two inflection points at about 8.2 and 18 mN/m, and collapse pressure occurs at about 48.6 mN/m. This is in good agreement with the reported result.$^{18,19}$ The transition observed at about 8.2 mN/m is characteristic of the isotherm of pure PMMA. The isotherm of PMMA also shows an inflection point at about 20 mN/m, but above this surface pressure, the monolayer remains no longer stable. From the isotherms

Fig. 1. Surface pressure ($\pi$) vs area per molecule ($A$) isotherms of TP in (a) PMMA (b) SA matrix at different mole fractions of TP along with pure TP and PMMA/SA isotherm. The numbers denote corresponding mole fractions of TP in PMMA/SA matrix. PM, SA, and TP correspond to the pure PMMA, SA, and TP isotherm, respectively. Inset shows the structure of TP.
of TP–PMMA mixed monolayer, it is observed that the inflection portion gradually loses its distinction with increasing mole fractions of TP, and at 0.7 M and above mole fractions of TP, the mixed isotherms show a sharp rise up to a surface pressure of 50 mN/m without any transition point.

It is also interesting to mention in this context that at higher surface pressure, in PMMA matrix, the isotherms of all mole fractions of TP almost coincide (Fig. 1(a)). This may be due to the fact that at higher surface pressure the mixed monolayer that consists of PMMA matrix remains no longer stable, and collapsing of monolayer occurs.10 Thus, at higher surface pressure, all the isotherms of TP–PMMA mixed monolayer lose their distinctness and almost overlap with each other.

Pure SA isotherm (Fig. 1(b)) is a smoothly increasing curve with lift-off area 0.26 nm², and collapsing of monolayer occurs at about 53.24 mN/m. The area per molecule of pure SA is 0.21 nm² at a surface pressure of 25 mN/m. These values as well as the shape of the isotherm are well consistent with those values reported in the literature.9,10

The most interesting feature of TP–SA mixed isotherm is that at lower mole fraction of TP up to 0.4 M, the area per molecule of TP is larger than that of pure SA. From 0.5 M and above mole fraction of TP, the area per molecule is lower than that of SA. The most plausible explanation seems to be that at lower mole fraction of TP in SA, there may be strong repulsive interaction between TP and SA. However, with increasing mole fraction of TP, phase separation between TP and SA moieties occurs, which may originate from the immiscibility of the components owing to their differences in molecular structures, physical and chemical properties. Unlike the TP–PMMA mixed isotherms, TP–SA mixed isotherms do not coincide at higher surface pressure and remained stable until the collapse of monolayer occurs. However, for both the matrices the area per molecule of the mixed monolayer gradually decreases with increase in the mole fraction of TP. This is indicative of the fact that the TP molecules are successfully incorporated into the matrix materials to form a mixed monolayer.

Table 1 shows the monolayer characteristics taken from the isotherms. Mean molecular area is the limiting area \(A_0\) occupied per repeating unit in the monolayer. This is estimated by extrapolating the steep rising part of the \(\pi - A\) isotherm to zero surface pressure.20

3.2. Apparent compressibility

To obtain more information from the \(\pi - A\) isotherms, the apparent compressibilities of the films are calculated by using Eq. (1) and listed in Table 1.

The apparent compressibility \(C\) is defined as \(^{21,22}\)

\[
C = - \frac{1}{A_0} \frac{A_{30} - A_{10}}{30 - 10}
\]

(1)

where \(A_{10}\) and \(A_{30}\) are the areas per molecule at 10 and 30 mN/m surface pressure, respectively.

The compressibility of pure PMMA film is 36.41 mN⁻¹. This is consistent with the distinct segment observed in PMMA isotherm (Fig. 1(a)).

Table 1. Monolayer characteristics taken from the \(\pi - A\) isotherms.

<table>
<thead>
<tr>
<th>Mole fraction of TP in PMMA/SA</th>
<th>(A_0) in PMMA (nm²)</th>
<th>(A_0) in SA (nm²)</th>
<th>(C) in PMMA (mN⁻¹)</th>
<th>(C) in SA (mN⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.127</td>
<td>0.236</td>
<td>36.41</td>
<td>4.35</td>
</tr>
<tr>
<td>0.1</td>
<td>0.087</td>
<td>1.061</td>
<td>29.81</td>
<td>8.17</td>
</tr>
<tr>
<td>0.2</td>
<td>0.07</td>
<td>0.452</td>
<td>27.1</td>
<td>12.05</td>
</tr>
<tr>
<td>0.3</td>
<td>0.069</td>
<td>0.313</td>
<td>26.7</td>
<td>7</td>
</tr>
<tr>
<td>0.4</td>
<td>0.07</td>
<td>0.211</td>
<td>26.78</td>
<td>7.27</td>
</tr>
<tr>
<td>0.5</td>
<td>0.05</td>
<td>0.145</td>
<td>26.01</td>
<td>13.9</td>
</tr>
<tr>
<td>0.6</td>
<td>0.048</td>
<td>0.107</td>
<td>26.1</td>
<td>8.73</td>
</tr>
<tr>
<td>0.7</td>
<td>0.045</td>
<td>0.056</td>
<td>24.97</td>
<td>8.13</td>
</tr>
<tr>
<td>0.8</td>
<td>0.042</td>
<td>0.049</td>
<td>21.67</td>
<td>7.67</td>
</tr>
<tr>
<td>0.9</td>
<td>0.033</td>
<td>0.034</td>
<td>18.27</td>
<td>16.4</td>
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</table>
Although with the increase in the mole fraction of TP in PMMA matrix, the C value decreases, interestingly the compressibility of the mixed monolayer of 0.3–0.6 M of TP in PMMA is almost the same. Interestingly, in SA matrix for 0.3, 0.4, 0.6–0.8 M of TP, the C value is also almost constant although the overall C value for TP–SA mixed films is lower. This may be the characteristic of the sample.

The low values of compressibility make the TP–SA mixed films more harder with respect to TP–PMMA mixed films. This is reasonable that the SA mixed films more harder with respect to TP–PMMA mixed films. This is reasonable that the fatty acid monolayer on water surface has the closest molecular packing and can be considered as a two-dimensional crystal solid.\(^{21}\)

### 3.3. Miscibility of TP with the matrix molecules

The compression isotherm of a two-dimensional Langmuir film is a plot of surface pressure (\(\pi\)) versus area per molecule \((A)\) whose surface pressure is given by \(\pi = \gamma_0 + \gamma\), where \(\gamma_0\) and \(\gamma\) are the surface tension of the clean sub-phase and the sub-phase covered with film material, respectively.

An ideally mixed monolayer and a completely immiscible monolayer are absolutely opposite to each other. In an ideal mixed monolayer, the intermolecular attractive force \((F)\) between the constituent molecules 1 and 2 is given by \(F_{11} = F_{12} = F_{22}\), whereas for a completely immiscible monolayer, \(F_{11}/F_{12}/F_{22}\), where \(F_{ij}\) are the attractive forces between the molecules of the two components \(i\) and \(j\) \((i, j = 1, 2\) respectively).

In the terms of the molecular area of the mixed monolayer, the ideal value of the molecular area \((A_{id})\) is calculated from the molar ratio of the two components as

\[
A_{id} = A_1N_1 + A_2N_2,
\]

where \(N_1\) and \(N_2\) are the molar fractions of the pure components in the mixture; \(A_1\) and \(A_2\) are the areas occupied by the monomer of the pure components of the constituent molecules.

The excess area, \(A_E\), is the difference in molecular area between the ideal \((A_{id})\) and the experimentally observed molecular area \((A_{12})\), and is given by the following relation

\[
A_E = A_{12} - A_{id},
\]

\(A_E\) is the measure of the interaction between the constituent components in the mixed monolayer; when there is an interaction between the constituent molecules in the mixed monolayer the experimentally observed molecular area \((A_{12})\) deviates from the value supposed for ideally mixed monolayer. Once the two components form an ideally mixed monolayer or they are immiscible, the \(A_d\) will equalize \(A_{12}\), that is, if an ideally mixed monolayer is formed and the constituent components are completely immiscible, the excess area \((A_E)\) will be 0, i.e. \(A_E = A_{12} - A_{id} = 0\). The plot of \(A_{12}\) versus \(N_1\) will give a straight line. Any deviation from the straight line indicates miscibility and nonideality.\(^{21,22}\) Actually, there are always intermolecular forces between the constituent molecules in the mixed monolayer.

The magnitude of these forces determine \(A_E\). For a mixed monolayer, \(A_E\) will be negative if the intermolecular forces are attractive, i.e. greater cohesive forces between the unlike components exists; on the other hand, \(A_E\) will be positive for the repulsive interaction between the constituent molecules, i.e. greater cohesive forces between the like components.

Figures 2(a) and 2(b) show the plot of the data of the actual area \((A_{12})\) per molecule versus mole fraction of TP in the mixed monolayer with PMMA and SA, respectively at different fixed surface pressures of 5, 10, 15, 20, 25, and 30 mN/m.

The mixing behavior of TP in PMMA matrix (Fig. 2(a)) is quite interesting. At the surface pressure of 5, 10, and 15 mN/m, there is a negative deviation from the ideality curve for lower mole fraction (0.1–0.5 M of TP), whereas, for higher mole fraction the experimentally observed values almost coincide with the ideality. This is an indication of certain miscibility or nonideality, and the cohesive force between TP and PMMA predominates at lower mole fractions of TP in PMMA, whereas, with an increase in the mole fraction, the TP and PMMA are completely immiscible resulting in an ideal mixed monolayer at the air–water interface.

At higher surface pressures of 20, 25, and 30 mN/m, ideal mixing of TP and PMMA occurs for lower mole fraction of TP, and at higher mole fraction slight positive deviation from the ideal behavior is observed. The repulsive interaction between TP and PMMA and cohesive force between TP–TP and PMMA–PMMA may be responsible for this positive
deviation at higher mole fraction of TP at higher surface pressures.

In SA matrix the experimental data show positive deviations from the ideality curve for lower mole fraction up to 0.5 M. The positive excess areas in the case of SA matrix as discussed previously is an indication of more favorable cohesive interactions between the like molecules (TP–TP and SA–SA) than the unlike components (TP–SA), which can lead to partial or total phase separation and formation of clusters or microcrystalline aggregates of TP molecules in the SA-mixed LB films. However, for higher mole fraction of TP, the sample and matrix molecules are immiscible, and ideally mixed monolayer is formed.

Figure 3 shows the plot of the collapse pressure versus mole fraction of TP in PMMA and SA matrix. According to the phase rule, the two components in the mixed monolayers are miscible at the interfaces when the collapse pressure varies with the compositions of the mixed monolayer. In the present case, the collapse pressures are almost independent of the mole fractions except a small variation. The appearance of the phase transition points similar to that of pure components in the mixed monolayer also suggests the existence of a pure SA/PMMA phase in the mixed monolayer. That is, the two components TP and PMMA/SA are not completely miscible in the mixed monolayer.

3.4. UV–Vis absorption spectroscopy

Figure 4 shows the UV–Vis absorption spectra of LB films of TP along with the solution and microcrystal spectrum.
Aggregation of $P$-Terphenyl Along with PMMA/SA at the Langmuir and Langmuir–Blodgett Films

Fig. 3. Collapse pressures versus mole fraction plot for (a) TP–PMMA and (b) TP–SA mixed films.

TP solution absorption spectrum possess a distinct broad and structureless band in the 200–325 nm region with the peak at around 280 nm. This is consistent with the literature reported elsewhere.24 This band has been assigned to $^{1}L_{a}$ state.24 Also, there is an almost indistinguishable weak hump observed at about 240 nm in the solution absorption spectrum. The microcrystal absorption spectrum is quite different with respect to TP solution absorption spectrum. Unlike that of the solution spectrum, microcrystal spectrum possesses distinct band systems within the 200–300 nm region with specific structural features. The high-energy band is located at 229 nm along with a broad low-intense band in the longer wavelength region with diffused but prominent vibrational bands with peaks at 261, 275, and 285 nm, respectively, which are almost indistinguishable in the absorption spectra of LB films. The absorption spectra of mixed LB films for both matrices show almost similar band profile and have distinct similarity with the microcrystal absorption spectrum with high-energy band at around 233 nm and a broad low-intense band in the longer wavelength region with peak at around 290 nm. In LB film spectra, the vibrational peaks are not so prominent. The weak hump at 240 nm in solution absorption spectrum gives rise to the intense prominent high-energy band at around 233 nm in the LB films. Moreover, all the absorption bands in the LB films are overall broadened. This may be due to the change of planarity of TP molecules due to the organization in the mixed LB films when it goes from solution to films/solid states.

In this context it is interesting to mention that molecular exciton coupling theory25 predicts that in the simplest case of a two-molecule system, the dipole–dipole interactions result in splitting the energy level of the excited state into two levels with higher and lower energies relative to the undisturbed excited state. The change in energies of these two
levels is Davydov splitting, and can be calculated from the equation:
\[ \Delta E = E'\prime - E'\prime' = 2 \left( \frac{M_i M_j}{R_{ij}^3} - \frac{3}{2} \left( \frac{R_i}{R_{ij}} \right) \left( \frac{R_j}{R_{ij}} \right) R_{ij}^3 \right). \]

Here, \( M_i \) and \( M_j \) are the electric dipole transition moments in molecules \( i \) and \( j \), respectively, and \( R_{ij} \) is the center to the distance between these molecules. In the case of the co-planar alignment of the dipole transition moments of two molecules, the transition to one of the excited states, corresponding to the antiparallel arrangement of dipole moments is forbidden. The energy difference between the excited monomer level and the exciton level, \( \Delta \varepsilon \), is given by:
\[ \Delta \varepsilon = \frac{1}{2} \Delta E = \frac{M_i^2}{R_{ij}^3} (1 - 3 \cos^2 \theta). \]

Here, \( \theta \) is the angle between the transition moment direction and the line connecting the molecules’ centers. When \( 0^\circ \leq \theta < 54.7^\circ \), the exciton level is energetically located below the monomer level causing a red shift in the electronic absorption spectrum, creating aggregates termed J-aggregates.\(^{26}\) For \( 54.7^\circ < \theta \leq 90^\circ \), the exciton level is located energetically above the monomer level, causing a blue shift. Corresponding aggregates are called H-aggregates.\(^{26}\) When \( \theta = 54.7^\circ \), no shift in the absorption spectrum is observed. The aggregates are then termed I-aggregates.\(^{27}\)

So, in the present case, the observed blue shift accompanied by the broadening of the band profile in LB films with respect to the solution spectrum may be due to the aggregation of TP molecules in the films. In the light of the molecular excitation theory this aggregation is identified as H-aggregates. Our SEM studies also support the aggregation of the TP molecules due to the phase separation between the samples and the matrix molecules.

### 3.5. Scanning electron micrograph

In Fig. 5 we have shown the SEM picture of the 10 bilayer LB film (TP:SA = 1:1). Under an optical microscope the LB film appeared homogeneous, but the SEM picture reveals a clear heterogeneous morphology. The SEM image of TP–PMMA mixed LB films also shows similar morphology (figure not shown). The homogeneous dark background is due to that of the SA forming larger region compared to TP, and TP molecules seem to be in the islands above that. Strong repulsive interaction between TP and matrix molecules may squeeze out the TP molecules in the matrix. This is expected since the nature of TP and the matrix molecules are quite different, which is reflected in the SEM morphology. The formation of aggregates due to the phase separation and demixing of binary components in LB film is thus confirmed.

### 4. Conclusion

Although non-amphiphilic TP molecules are not ideally suited for LB technique, however, our investigation showed that stable self-supporting Langmuir monolayer of TP can be formed when they are mixed with either PMMA or SA. TP–PMMA mixed films may not be stable at higher pressure, but the TP–SA mixed films were stable until collapse pressure was reached. The compressibility of TP–SA mixed films was observed to be lower than the TP–PMMA mixed films. The interaction between sample (TP) and matrix (PMMA/SA) molecules largely depends on the mole fraction of mixing and the surface pressures. At lower surface pressure and lower mole fraction, there exist an attractive interaction between TP and PMMA, whereas, repulsive interaction predominates at higher surface pressure and higher mole fractions. In SA matrix, strong repulsive interaction between TP and SA and strong cohesive interaction between the TP–TP and SA–SA were observed at all surface pressures for lower mole fraction of TP, whereas, at higher mole fraction...
of TP the sample and matrix molecules are immiscible and form ideal mixed monolayer. H-type of aggregation of TP molecules in the mixed LB films was revealed by UV–Vis absorption spectroscopy. SEM studies confirmed the phase separation and demixing between the sample TP and the matrix molecules.

References