Langmuir–Blodgett films of 9-phenyl anthracene molecules incorporated into different matrices

S.A. Hussain, S. Deb, S. Biswas, D. Bhattacharjee

Department of Physics, Tripura University, Suryamaninagar 799130, Tripura, India

Received 13 July 2004; accepted 13 September 2004

Abstract

This communication reports the surface pressure (π) versus area per molecule (A) isotherm characteristics of the mixed films of 9-phenyl anthracene (PA) in stearic acid (SA) and polymethyl methacrylate (PMMA) matrices, at the air–water interface. The mixed Langmuir films at the air–water interface have been observed to be easily transferred onto solid substrates to form uniform Langmuir–Blodgett films. By changing various parameters, namely mole fraction, surface pressure of lifting and number of layers, the mixed Langmuir–Blodgett (LB) films of various types have been fabricated successfully and their spectroscopic characteristics have been reported. From the isotherm characteristics and the area per molecule versus mole fraction plot, it is evident that the PA molecules are successfully incorporated into mixed Langmuir–Blodgett films. UV–vis absorption spectroscopic study of the mixed LB films at various mole fractions of PA in two different matrices reveal that formation of H-type aggregate in PMMA matrix whereas both I- and H-type aggregates are playing their dominant role in SA matrix. Moreover, fluorescence spectroscopic study reveals reabsorption effect. Molecular movement persists in the freshly prepared LB films, as is evident from the time dependent changes in both UV–vis absorption and fluorescence spectra of the mixed LB films in both matrices. From our observation it is evident that about 200 h is required to get the LB films in a stable condition. Dimers and higher order n-mers are formed at a higher surface pressure of 30 mN m⁻¹.

© 2004 Elsevier B.V. All rights reserved.

Keywords: Non-amphiphilic; Langmuir–Blodgett Films; UV–vis absorption spectroscopy; Fluorescence spectroscopy

1. Introduction

Organized molecular assemblies of Langmuir–Blodgett (LB) films of amphiphilic molecules containing specific photo-functional group or chromophores are considered to be extremely important for nanotechnology based optoelectronic and photonic devices and have been the subject of active research in recent years [1]. Perhaps the most interesting feature associated with LB films which makes them attractive for these photonic devices is the ability to control the spatial distribution and orientation of the molecules assembled in these films, to bring about desired changes in their optical properties [2–4]. Interestingly, LB supramolecular assemblies closely resemble natural biomembranes and provide a unique platform for mimicking energy and electron transfer reaction in real energy harvesting photo-synthetic reaction centers [5]. Moreover, the photo-physical properties of molecules incorporated in these supramolecular assemblies show enormous changes, which reflect the interaction of the molecules with their micro-environment providing an insight into the structure property co-relationship of these systems.

Polyatomic hydrocarbons (PAH) are of special interest as these molecules are deemed to be the active ingredient for future generation superfast optoelectronic devices and bio-computers [6–8]. Recently, several PAHs have been used to fabricate LB film-based light emitting diodes, optical switches and sensors [9,10]. Interest in anthracene and its derivatives stems from the fact that they have rigid molecular structure and interesting spectroscopic and photo-conducting properties as well as also have high fluorescence intensity. Moreover the properties of these derivatives are highly sensi-
tive to the micro-environment in which they are incorporated. LB films of amphiphilic anthracene derivatives have been extensively investigated [11]. Non-amphiphilic anthracene has also been incorporated into LB films mixed with stearic acid [12]. A preliminary report on one of the interesting derivatives namely 9-phenyl anthracene molecules incorporated into LB films mixed with SA has been reported [13]. However, detailed study in various matrices has never been done before. Here we report in detail the photo-physical characteristics of the mixed LB films of 9-phenyl anthracene in stearic acid (SA) as well as also in polymethyl methacrylate (PMMA) matrices. The most interesting thing in our observation is that both kinds of mixed films are sensitive to ageing effect. About 200 h is required to get the film in stable condition. Moreover the films lifted at higher surface pressure forms dimer and higher order n-mers of 9-phenyl anthracene.

2. Experimental

9-Phenyl anthracene (98% pure) purchased from Aldrich Chemical Co., USA was purified under vacuum sublimation followed by repeated re-crystallisation before use. SA (purity > 99%) purchased from Sigma Chemical Company and isotactic PMMA from Polyscience were used as received. Spectroscopic grade ethanol (E. Merck, Germany) and Chloroform (SRL, India) were used as solvent and also their purity were checked by fluorescence spectra before use. Langmuir–Blodgett (LB) film deposition instrument (Apex-2000C, India) have been used for the study of isotherm characteristics as well as also for multilayer film deposition. Surface pressure at the air–water interface was monitored using a Wilhelmy plate attached to a micro-computer which controls the movement of the barrier. Triple distilled deionised water was used as sub-phase and the temperature was maintained at 24 °C. Solutions of PA, PMMA, SA as well as PA–PMMA and PA–SA mixture at different molefractions are prepared in chloroform solvent and were spread on the water surface.

After a delay of 15 min, to evaporate the solvent, the film at the air–water interface was compressed very slowly at a rate of $2 \times 10^{-3}$ nm$^2$ mol$^{-1}$ s$^{-1}$ to record the surface pressure versus area per molecule ($\pi$–$A$) isotherm. All isotherms were run several times with freshly prepared solution. Fluorescence grade quartz slide cleaned by standard procedure [2] is dipped with a speed of 5 mm min$^{-1}$ for the deposition of multilayer. A drying time of 15 min is allowed after each lift. For each molefraction of PA, 10 bi-layers LB films were deposited at a standard surface pressure 15 mN m$^{-1}$ for both the matrices. We have also studied the characteristics of LB film of PA at different pressure and varying the number of layers.

The transfer ratio of the mixed layer is found to be $0.98 \pm 0.02$. Fluorescence spectra and UV–vis absorption spectra of the LB films were studied by a Perkin-Elmer LS-55 spectrophotometer and Perkin-Elmer Lambda 25 spectrophotometer, respectively.

3. Results and discussions

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

When a very dilute solution ($2 \times 10^{-3}$ M) of pure PA in chloroform was spread at the air–water interface and after sufficient time was allowed to evaporate the solvent, compressed slowly at the rate of $2 \times 10^{-3}$ nm$^2$ mol$^{-1}$ s$^{-1}$, it was observed that surface pressure rises very little with negligible area per molecule. Addition of larger amount of solution resulted in the formation of large patchy films at the air–water interface which is visible even to the naked eye. On decompressing, this patchy film of micro-crystalline PA broke up into smaller clusters but did not disintegrate completely at the molecular level. All efforts to transfer this floating layer onto a solid substrate failed. These results clearly indicate that pure PA does not form a stable and self-supporting monolayer at the air–water interface. However when PA is mixed with a building matrix of either stearic acid (SA) or polymethyl methacrylate (PMMA) at various molefractions, the isotherms of these mixed monolayers are found to be highly stable with smooth surface pressure versus area per molecule isotherms. Fig. 1a and b show the surface pressure ($\pi$) versus area per molecule ($A$) isotherms of PA mixed with PMMA and SA respectively at different molefractions of PA along with pure PMMA and pure SA.

The area per molecule of pure PMMA is 0.12 nm$^2$ at a surface pressure of 15 mN m$^{-1}$ and the same for pure SA is 0.23 nm$^2$ at surface pressure 15 mN m$^{-1}$. From Fig. 1a and b it is observed that area per molecule decreases consistently with the increase in molefractions and they do not overlap. In case of PA–PMMA mixed isotherms, the surface pressure showed a sharp increase from an initial ‘zero’ value to about 12 mN m$^{-1}$, at which it remained constant for a large decrease in the area per molecule. Further compression of the barrier resulted in steep rise in the pressure with a very small change in area per molecule suggesting the attainment of a solid condensed phase [14].

It is interesting to note that the isotherm of pure PMMA shows an inflection point at about 20 mN m$^{-1}$. It is observed that the inflection portion gradually loses its distinctness with increasing the molefraction of PA. At about or above these inflection points, the collapse of the monolayer occurs. This is why a surface pressure of 15 mN m$^{-1}$ has been chosen for the film deposition. From the plot of area per molecule versus molefractions of PA (not given) it is quite evident that the PA molecules have been successfully incorporated in the mixed films which are consistent with the behavior of other non-amphiphiles.
3.2. UV–vis absorption and steady state fluorescence spectroscopic study

Once multilayered Langmuir–Blodgett films are deposited onto the quartz substrates, it would take several hours (some times more than 200 h) to get the film in a stable condition. Ageing effect of the LB films has been discussed later in the light of photo-physical characteristics. Here we first of all give our observations of the UV–vis absorption and steady state fluorescence characteristics of mixed LB films which attained their stability after ageing for more than 200 h. The UV–vis absorption and steady state fluorescence spectra of mixed LB films of PA (0.1–0.7 M) in PMMA and SA matrix along with the spectra in ethanol solution and micro-crystal are shown in Fig. 2a and b, respectively.

The solution absorption spectrum shows distinct and intense band systems in the 200–400 nm regions, with an intense and sharp band having peak at around 257 nm, owing due to $1\text{B} \leftarrow 1\text{A}$ transition. There are three other low intense but prominent vibrational bands in the spectral region 325–400 nm, with maxima at around 348, 368 and 387 nm, corresponding to $1\text{L} \leftarrow 1\text{A}$ transition [15]. The vibrational band system as observed in the micro-crystal spectrum of PA, are almost identical in position and shape, in comparison to the solution spectrum. However, unlike that of solution spectrum, the high energy band in the micro-crystal spectrum is observed to be much broadened and as if like diffuse overlapping of several bands.

It is interesting to note that the absorption spectra of the stable LB films of PA in PMMA matrix at all molefractions show almost similar band pattern irrespective of the change in molefraction and have distinct similarity and identical band position with that of the solution spectrum. Although the high energy band at around 257 nm is broadened than that of the solution spectrum.

The absorption spectra of stable LB films of PA in SA matrix at different molefraction show the most interesting thing, that their vibrational bands are too weak to distinguish and the high energy band is also quite low intense, and broadened and in case of some lower molefraction it is blue shifted. The broadening of the high energy band may arise due to aggregation.

It may be worthwhile to mention in this context that according to the intermediate strength exciton coupling theory [16,17], dipole–dipole interaction results in the raising or lowering of the exciton band to a position either energetically higher or lower than the monomer band. Such a change in energy is given by,

$$\Delta E = \frac{2M^2(1 - 3\cos^2\theta)[1 - (1/N)]}{r^3}$$

where, $M$ is the transition dipole moment vector, $N$ the number of monomers in the aggregate, $\theta$ the angle made by the dipole with the vector $r$ and $r$ the length of the vector joining the centers of two dipoles. For $0 < \theta < 54.7^\circ$. 
Fig. 2. (a) UV–vis absorption and steady state fluorescence spectra of PA in ethanol solution (EtOH), in micro-crystal (MC) and in PA/PMMA mixed LB films. The numbers denote corresponding molefraction of PA in PMMA matrix. (b) UV–vis absorption and steady state fluorescence spectra of PA in ethanol solution (EtOH), in micro-crystal (MC) and in PA/SA mixed LB films. The numbers denote corresponding molefraction of PA in SA matrix.

The exciton band is located below the monomeric band, that causes a red shift and the corresponding aggregate are known as I-aggregates, while for $54.7^\circ < \theta < 90^\circ$, the exciton band is located above the monomeric band and this gives rise to a blue shift in the absorption spectrum known as H-aggregates. Corresponding to the magic angle $\theta = 54.7^\circ$, the shift observed is almost zero and independent of $N$ and $r$ and such aggregates are referred to as I-aggregates.

The almost identical peak position in case of PMMA matrix may well be concluded as due to the formation of I-type of aggregate of PA in the mixed LB films. However in case of SA matrix simultaneous observation of blue shifting as well as no shifting of the high energy band depending on molefractions may lead to the conclusion that there is a competition between two different types of aggregation, namely, I- and H-type playing their dominant role in the mixed LB films of PA in SA matrix.

Steady state fluorescence spectrum in ethanol solution (as shown in Fig. 2a and b) shows distinct vibrational bands in 375–425 nm region with 0–0 band at 399 nm and another intense band at 418 nm. A shifting of the 0–0 band at around 11 nm in fluorescence spectrum in comparison to absorption spectrum may be due to slight deformation of electronic state owing to the closer association of the molecules. This spectrum also shows a weak hump at around 450 nm. Micro-crystal fluorescence spectrum shows a broad band in the region 400–550 nm, a weak hump at around 450 nm and a peak at about 465 nm. Fluorescence spectra of the mixed LB films of PA in PMMA and SA matrix at different molefraction of PA (0.1–0.7 M) are also shown in Fig. 2a and b, respectively. All these spectra have distinct similarity with solution spectrum, although the high-energy band at 399 nm is considerably reduced in intensity and the band at 417 nm becomes considerably intense. This may be due to reabsorption effect owing to the closer association of the molecules. Also at higher molefraction of 0.6 and 0.7 M, a weak hump is developed at 465 nm may originate due to the formation of low dimensional micro-crystal in the LB films at higher molefraction of PA.

### 3.3. Ageing effect

Stability of LB film is important from the point of view of various technological aspects. Once the LB film is formed it is observed that some molecular movements are continued even after several hours of LB film formation [18]. Stability of the mixed LB films of PA in PMMA and SA matrices has been studied in the light of absorption and fluorescence spectroscopy. Fig. 3a and b, respectively shows the absorption and fluorescence characteristics of PA in PMMA and SA matrix at two different molefraction 0.1 and 0.5 M. Although we have studied the time evolution of these characteristics, however, in the figure we have given the spectra observed recently lifted (00 h) LB films and stable (>200 h) LB films. From Fig. 3a it is observed that, absorption spectra are almost same although comparatively reduced in intensity after stability is achieved. However, fluorescence spectra of 0.5 M recent
LB film show a broad band whereas stable LB film shows a well-structured vibrational band system. Ageing effect of PA in SA is also somewhat interesting. In the absorption spectra of recent film, although all the bands are present and have distinct similarities with the solution spectrum, however, the absorption spectra of stable LB film shows the disappearance or indistinguishably low intense vibrational bands and also blue shifted high-energy band. Although, the fluorescence spectra of both recent and stable films have distinct similarities with the fluorescence spectra, however, some changes in intensity distribution of various vibrational bands are observed in recent and stable film. All these investigations may be summarized to the fact that in the recent LB films, molecules are not in stable position rather there are some movements of the molecules until the final stable condition is achieved.

3.4. Layer effect

For various technical applications sometimes it is required to have thick films. We also studied the dependence of photophysical characteristics of multilayered LB films with different number of layers. We have studied 5, 10, 15, 20, 25 and 30 multilayers in both matrices of PMMA and SA. However, we do not observe any appreciable change in band position except only increase in intensity (figure not shown here).

3.5. Pressure effect

Pressure effect of PA in SA matrix has also been studied using 15, 20, 25 and 30 mN m$^{-1}$ pressure. All the films are 10 bilayered. Although at low molefractions of 0.1 and 0.2 M of PA in SA matrix, no appreciable change is observed, however, at a higher molefraction of 0.5 M we observe some interesting change in both absorption and fluorescence spectra with increasing pressure as shown in the Fig. 4a. From the fluorescence spectra it is observed that when the LB film is lifted at 25 mN m$^{-1}$ pressure a weak hump is developed at about 480 nm along with a prominent peak at around 450 nm and other vibrational bands at 420 and 397 nm. Although the high energy band at 397 nm is considerably reduced in intensity. At the higher surface pressure of 30 mN m$^{-1}$, 482 nm band is more prominent along with 450 nm band. Other vibrational energy bands are considerably reduced.

Excitation spectra of PA-SA mixed films at 15 mN m$^{-1}$ and high surface pressure of 30 mN m$^{-1}$ are shown in the Fig. 4b. The monitoring wavelengths are 420, 448 and 480 nm, respectively, while monitoring at 420 and 448 nm, the excitation spectra in the 300–420 nm region show prominent and distinct vibrational bands system with identical peak position, prototype of absorption spectra. Therefore we may definitely conclude that these bands arise due to the monomeric/excimeric sites present in the LB films. However, while monitoring the band position at 480 nm, the excitation spectra are somewhat different as also shown in the Fig. 4b. The vibrational bands are diffused and only a broadened band appears at longer wavelength sides. Especially at higher sur-
face pressure of 30 mN m\(^{-1}\) the broadened band is shifted to 400 nm, a shift of about 11 nm in comparison to longer wavelength vibrational band at 389 nm. Moreover this band is sufficiently broadened and other vibrational bands are totally absent. This totally different nature of excitation spectra while monitoring at 480 nm definitely brings us to the conclusion that some higher order \(n\)-mers (dimer, trimer, tetramer, etc.) species may exist in the LB films.

It must be mentioned in this context that the excitation spectra of the mixed LB films of very low molefractions of PA (0.1 and 0.2 M), lifting at high surface pressure of 30 mN m\(^{-1}\) do not support the existence of any higher order \(n\)-mers. Only the LB films of higher molefractions of PA (0.5 M and above) and higher surface pressure of lifting gave the evidence of the existence of higher order \(n\)-mers. Fluorescence decay characteristics of these LB films have been studied corresponding to the emission at 480 nm with excitation at 380 nm. The decay curves are found to fit well with a biexponential equation. This indicates that a large number of slightly different traps exist. From the results, we may conclude that mixed LB films of higher molefractions and higher surface pressure are found to form aggregated dimer or some higher order \(n\)-mers.

4. Conclusion

In conclusion, our results suggest that non-amphiphilic 9-phenyl anthracene molecule when mixed with stearic acid as well as also with polymethyl methacrylate forms stable Langmuir films at air-water interface and can be easily transferred onto solid substrate to form uniform Langmuir–Blodgett films. UV–vis absorption and fluorescence spectroscopic study of the mixed LB films at various molefractions of PA in two different matrices reveal that I-type aggregate is formed in PMMA matrix where as both I- and H-type aggregate forms in SA matrix. It is also observed that molecular movement exist in the freshly prepared LB films and it takes about 200 h to age the LB films in a stable condition. Another interesting thing observed is that dimers and \(n\)-mers are formed in the mixed LB films of higher mole fraction of PA in SA matrix and which is lifted at higher surface pressure of 30 mN m\(^{-1}\).

Acknowledgement

The authors are grateful to DST, Government of India for providing financial assistance through SERC-DST Project No. SR/FTP/PS-05/2001.

References