ICMS 2017

Study of aggregation behavior of water insoluble metalloporphyrin (Zn) in LB film

Mitu Saha\textsuperscript{a*}, Soma Banik\textsuperscript{b}, S. A. Hussain\textsuperscript{a}, D. Bhattacharjee\textsuperscript{a}

\textsuperscript{a}Thin Film and Nanoscience Laboratory, Department of Physics, Tripura University, Suryamaninagar–799022, Tripura, India
\textsuperscript{b}Department of Physics, Women’s College, Agartala 799001, Tripura, India

Abstract

In the present communication, a water insoluble metalloporphyrin, 5,10,15,20-Tetraphenyl-21H,23H-porphine zinc (abbreviated as ZnTPP) has been used to prepare stable Langmuir monolayer at the air–water interface by allowing it to adsorb from the aqueous subphase, into the preformed Langmuir monolayer of stearic acid (SA). Surface pressure versus area per molecule (\(\pi-A\)) isotherm studies gave the thermodynamical behavior of the ZnTPP-SA mixed Langmuir monolayer formed at the air water interface. Access area per molecule (\(A_E\)) vs molefraction curve indicated the repulsive interaction between the two binary components in the mixed Langmuir monolayer. BAM images gave the visual evidence of the aggregation pattern of the mixed molecules at the air-water interface. UV-vis spectroscopic studies confirmed the formation of prominent J-band in the ultra-thin films.

Keywords: SA, ZnTPP, BAM, Isotherm studies, LB films, J-aggregates

1. Introduction

Metalloporphyrins are an important class of porphyrins as they can be used for mimicking many biological processes, catalysts in chemical and photochemical reactions, photosensitizers including the field of nonlinear optics,
molecular electronic devices, solar energy cells, artificial photosynthesis, photoinduced hydrogen production [1-7] etc. The molecular aggregation causes remarkable changes in the photophysical and electronic properties of the molecules. It is well known that J-aggregation (end-to-end) is characterized by strong, narrow, red shifted absorption bands (J-band), whereas H-aggregation (face-to-face) results in the blue shifted (H-band) band with respect to the monomeric absorption band [8-10]. According to Kasha et al. [11] strong intermolecular interactions between monomeric species and delocalized excitonic energy over the whole assembly of aggregates are the characteristics of such phenomena. Metalloporphyrins form J-aggregates under certain conditions due to hydrophobic π–π stacking and the electrostatic interactions between the anionic and cationic groups. In aqueous solution, aggregation of the porphyrin molecules depends on the structure of the molecule, concentration, pH, ionic strength, counter ions in inorganic salts in the aqueous medium [12–16]. They are used as a significant class of synthetic building blocks for different functional nano materials [17]. Apart from the excellent photophysical, photochemical, electrochemical and structural properties of the metalloporphyrins they have technological applications in the field of nonlinear optics [18,19] and for investigations of artificial light harvesting systems that mimic natural photosynthetic receptors [20].

5,10,15,20-Tetraphenyl-21H,23H-porphine zinc (ZnTPP) is a water insoluble metalloporphyrin which form stable Langmuir monolayer at the air-water interface. LB technique is a better way to prepare uniform and highly ordered thin films of ZnTPP. There are natural choices of using LB films of ZnTPP as sensing materials due to highly conjugated, high thermal stabilities, photovoltaic effect, redox activity, and strong absorbance in the UV-visible region [21–24]. ZnTPP molecules also form core dendrimers with a large number of chromophores at the branches or periphery and are used to mimic the antenna effect of light-harvesting photosynthetic complexes [25]. In dilute chloroform solution of ZnTPP, UV-Vis absorption spectrum shows intense monomeric band at 419 nm [25]. In mixed LB film it forms J-aggregates due to the regular stacking of the molecules onto the solid substrate, which has vast applications in the field of nonlinear optics [26,27] and also in optical switching devices [28].The different photophysical and photochemical properties of the Langmuir monolayer containing ZnTPP formed at the air-water interface have been studied due to their crucial roles in the construction of functional thin layer materials such as Langmuir-Blodgett (LB) films and self-assembled monolayers [29,30]. In the present work detailed investigations have been carried out to study aggregation behavior of a water insoluble metalloporphyrin ZnTPP at the air water interface and also in ultra-thin films. BAM images confirmed the aggregation of the ZnTPP-SA mixed molecules at the air water interface. UV-Vis absorption spectra confirm the aggregation of the mixed molecules onto the solid substrate.

2. Materials and Methods

The cationic chloroform soluble metalloporphyrin 5,10,15,20-Tetraphenyl-21H,23H-porphine zinc (ZnTPP) (MW = 678.11) (Formula = C_{44}H_{28}N_{4}Zn), purity >99%, Stearic Acid (SA) purity >99%, were purchased from Sigma-Aldrich chemical company and used as received. ZnTPP and SA, Working solutions were prepared by dissolving them in spectroscopic grade chloroform (SRL). A commercially available Langmuir–Blodgett (LB) film deposition instrument (Apex 2000C, Apex Instruments Co., India) was used for surface pressure–area isotherm measurements as well as for mono and multilayer film preparation. Ultrapure Milli-Q water of resistivity 18.2 MΩ·cm was used as subphase.

The concentration of the stock solutions for both ZnTPP and SA was 1mM. ZnTPP and SA were mixed at different mole fractions using the stock solutions. In order to measure the isotherm and film preparation, 100 μL of either pure or mixed solutions was spread onto the subphase with a microsyringe. After complete evaporation of volatile solvent, the barrier was compressed at a rate of 5 mm/min to record the surface pressure–area per molecule isotherms. The surface pressure (π) versus average area available for one molecule (A) was measured by a Wilhelmy plate arrangement. Smooth fluorescence grade quartz plates (for spectroscopy) were used as solid substrates. Y-type deposition at a particular surface pressure was followed to transfer Langmuir film onto solid substrates at a deposition speed of 5 mm/min.

UV–vis absorption of pure solution, microcrystal, as well as those of mixed LB films, was recorded using absorption spectrophotometer (PerkinElmer, Lambda 25). The absorption spectra were recorded at 90° incidence using a clean quartz slide as reference. For recording the BAM images of complex Langmuir monolayer, after
spreading of the mixed solutions sufficient time was allowed for the formation of domain structures at the air-water interface. Then the barrier of the Langmuir trough was slowly compressed and BAM images were taken.

3. Results and discussions

3.1. Molecular structures of SA and ZnTPP molecule

Fig. 1 shows the molecular structures of stearic acid (SA) and ZnTPP molecule. The thermodynamic behavior of ZnTPP monolayer and ZnTPP-SA mixed monolayer formed at the air-water interface was studied from the $\pi$-A isotherm. Chloroform solution of SA spread on the water subphase formed a stable Langmuir monolayer. ZnTPP molecules do not form any stable Langmuir monolayer at the air-water interface [31]. But when chloroform solution of ZnTPP mixed with SA and spread at the air-water interface, stable mixed Langmuir monolayer was formed and corresponding $\pi$-A isotherms were recorded.

![Molecular structure of ZnTPP molecules](image)

![Molecular structure of SA molecules](image)

3.2. Isotherm characteristic studies of pure SA, pure ZnTPP and ZnTPP-SA mixed Langmuir monolayer at the air-water interface

Fig. 2 (a) shows the $\pi$-A isotherms of Pure ZnTPP and ZnTPP mixed with SA at different molar fractions along with pure SA for comparison. With the compression of the isotherm SA, ZnTPP and mixed ZnTPP-SA monolayer shows a smooth rise of surface pressure. The initial lift-off area of SA was found to be 0.276 nm$^2$ determined by the method described by Ras et al.[32] In case of SA isotherm, at surface pressures 15mN/m and 25 mN/m the molecular areas are 0.23 nm$^2$ and 0.21 nm$^2$ which are in good agreement with the reported results [33]. When the porphyrin ring lies parallel to the interface the surface area occupied by a ZnTPP molecule is 1.9 nm$^2$ and at the corresponding molecular areas no significant changes in surface pressure were observed [30]. In ($\pi$-A) isotherms the surface pressure for pure ZnTPP curve rose steeply at a molecular area smaller than 1.1 nm$^2$. This smaller molecular area of ZnTPP may be due to the some tilted orientation of porphyrin ring to the solution surface in the monolayer.

From the mixed isotherms of ZnTPP-SA at various mole fractions it was observed that with increasing mole fraction of ZnTPP, the mixed isotherms of ZnTPP-SA increased systematically and do not coincide with the pure ZnTPP isotherms at higher mole fraction. The thermodynamic nature of mixing of two pure component systems was established by analyzing the $\pi$-A isotherms of the pure components as well as the binary mixtures [34]. The miscibility of mixed Langmuir monolayer was determined quantitatively by calculating the excess area $A_E$ of the mixed monolayer at the air–water interface. It is given by

$$A_E = A_{12} - A_{id}$$

with $A_{id} = A_1N_1 + A_2N_2$, where $A_{id}$ is the ideal area per molecule of the binary mixture, $A_1$ and $A_2$ are the areas occupied by the monomers of SA and ZnTPP, respectively, and $N_1$ and $N_2$ are the mole fractions of the components in the mixtures. $A_{12}$ is the experimentally observed area per molecule.
Fig. 2. (a) Surface pressure ($\pi$) vs area per molecule ($A$) isotherms of ZnTPP mixed with SA at different mole fractions along with pure ZnTPP and SA isotherm; (b) excess area per molecule ($A_E$) vs the mole fraction of ZnTPP in the ZnTPP-SA mixed monolayer at surface pressures of 10 and 20 mN/m.

Ideally the plot of $A_E$ versus $N_2$ should be a straight line. Any deviation from the ideal graph ($A_E = A_{12} - A_{id} \neq 0$) indicates partial miscibility and non-ideality of the binary mixtures [35,36]. If the value of $A_E$ is negative then the attractive intermolecular forces are dominant in the mixed Langmuir monolayer. On the other hand, positive value of $A_E$ ($A_E > 0$) indicates a repulsive interaction between the constituent components of the mixed monolayer.

Fig. 2b shows the plot of $A_E$ versus mole fractions of ZnTPP at surface pressures 10 and 20 mN/m. A positive deviation from the additivity rule was observed from the figure, indicating a predominance of repulsive interaction among the constituent molecules in the mixed Langmuir monolayer.

3.3. Studies of Compressibility at the air-water interface

From the $\pi$-$A$ isotherms, the compressibility data can be extracted. It is used to characterize the nature of monolayer phases and distinguish between different phases. Compressibility ($C$) can be calculated using the following standard thermodynamic relation in two dimensions;

$$C = - (1/A) \frac{dA}{d\pi}$$

where $A$ is the area per molecule at the indicated surface pressure ‘$\pi$’ [37,38].

Phase transition of Langmuir monolayer was reflected by a peak in the compressibility versus surface pressure ($C$-$\pi$) curve. Fig. 3 (a) shows the ($C$-$\pi$) curves of pure SA monolayer, pure ZnTPP monolayer and ZnTPP-SA mixed monolayer and calculated from the data of compression isotherms as shown in Fig. 3 (a). The asymmetry of the peaks in the different $C$-$\pi$ curves clearly indicates that phase transitions of different ZnTPP-SA mixed monolayers
are dependent on the extent of interaction among ZnTPP and SA. This depends on the mixing ratio of ZnTPP and SA. At 0.5:0.5 molefraction the maximum compressibility was obtained and compressibility of other molefractions is lower than the 0.5 molefraction but higher than the pure ones. So we can say that at 0.5 molefraction the mixed monolayer is more compressible in nature compared to the others. All the compressibility graphs also show the mixing of the ZnTPP molecules with the SA molecules and thus formed more compressible mixed monolayer at the air-water interface.

![Fig. 3](image)

**Fig. 3 (a)** Compressibility (Cs) as a function of surface pressure for pure SA, pure ZnTPP and mixed ZnTPP-SA (0.5:0.5) from (π−A) isotherm ; **(b)** In-situ Brewster Angle Microscopic (BAM) images of ZnTPP-SA (0.5:0.5) mixed Langmuir monolayer taken at different surface pressures namely (a) 5 mN/m; (b) 10 mN/m; (c) 15 mN/m and (d) 20 mN/m. Scale bar represents 20 µm.

3.4. In-situ Brewster Angle Microscopic (BAM) images of ZnTPP-SA mixed monolayer at the air-water interface

The microstructure of the mixed monolayer at the air-water interface can be directly visualized by in-situ BAM images. Domains of different sizes and shapes in the BAM images of Langmuir monolayer indicate phase transition and formation of micro-domains. In the present investigation in-situ BAM images of ZnTPP-SA (0.5:0.5) mixed Langmuir monolayer were taken at different surface pressures namely (a) 5 mN/m, (b) 10 mN/m, (c) 15 mN/m and 20 mN/m as shown in Fig. 3(b). Image (a) shows the monolayer film containing large number of big circular holes. These dark holes represented the absence of film and showed only the aqueous surface. The white illuminated region covering the circular holes represented the mixed film. At gaseous phase, molecules in the Langmuir monolayer tried to move away from each other resulting in the formation of large circular holes in the mixed Langmuir monolayer film. With increasing surface pressure the large dimensional circular holes reduced to small holes as shown in the images (b) and (c) and at 20 mN/m surface pressure, a uniform monolayer surface was observed with the presence of very little small dimensional circular holes (d). It indicated a uniform film structure. Thus BAM images gave visual evidence of different phases of the mixed Langmuir monolayer as observed from the isotherm studies.
3.5. UV-vis absorption spectroscopic studies

Fig. 4 shows the UV-vis absorption spectra of ZnTPP in (i) chloroform solution (10^{-7} \text{ mol L}^{-1}), (ii) thin cast microcrystal film and (iii) monolayer LB film. The absorption spectrum of chloroform solution of ZnTPP consists of two distinct bands. One is higher energy band with higher oscillator strength called Soret Band or B band and the other is lower energy band with lower oscillator strength called Q band. This absorption bands of porphyrins have been ascribed to the in-plane $\pi-\pi^*$ transitions [39].

In the UV-vis absorption spectrum of chloroform solution of ZnTPP, intense Soret band is observed in the range 400-435 nm with a sharp peak at 419 nm [25]. Other Q band is observed in the range 520-630 nm with a weak peak at 547 nm. These two bands are mostly affected by the changing in the microenvironment. Thin cast microcrystal absorption spectrum also shows a broad absorption band with a small red shifted Soret peak at 428 nm. This shifting of the Soret band is due to the closer association of the ZnTPP molecules onto the solid substrate. Due to the changes in the micro environment small shifting in the peak position of the Q band was observed. In SA-ZnTPP mixed LB film more red shifting of the Soret band was observed at 442 nm with a weak hump at 428 nm. This longer wavelength band has been assigned as the J-band originating due to the regular molecular arrangement of the SA-ZnTPP mixed molecules onto the solid substrate. Thus the aggregation in this case was highly induced by the attachment of the ZnTPP molecules with the SA molecules which influenced the arrangement of the mixed molecules onto the solid substrate.

Fig.4(a) Normalised UV-vis absorption spectra of ZnTPP (a) in pure aqueous solution (10^{-7} \text{ mol L}^{-1}); (b) Microcrystal; (c) mixed monolayer LB film.
4. Conclusions

The interfacial behavior of ZnTPP monolayer and ZnTPP-SA mixed monolayer formed at the air-water interface was studied by using the Surface pressure-Area per molecular isotherms. Deviation from the ideality graph indicated the repulsive interaction between the constituent components in the mixed Langmuir monolayer. C-π curves gave the compressible nature of the mixed monolayer at the air-water interface. Domain structure formation at the air-water interface has been studied by employing in situ Brewster Angle Microscopy (BAM). UV–vis absorption study confirmed the formation of the prominent J-aggregated band in the mixed LB film.

Acknowledgement

The authors are grateful to FIST- DST Program Govt. of India (Ref. NO. SR/FST/PSI-191/2014, Dated 21.11.2014) for financial grant to the department. The author Mitu Saha is grateful to DST Govt. of India for financial support to carry out this research work through Women Scientist Project (Ref. No. SR/WOS-A/PM-1034/2014). The author S.A.H is obliged to DST and CSIR for financial support to carry out this work through DST Fast-Track Project Ref. No. SE/FTP/PS-54/2007, CSIR project Ref. 03(1146)/09/EMR-II.

References: