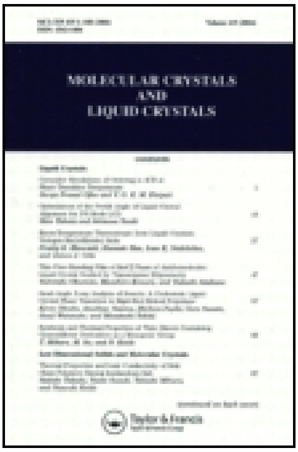

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Investigation of Miscibility and Aggregate Formation in the Mixed Langmuir–Blodgett Films of 2-Aminoanthracene by Surface Pressure and Spectroscopic Methods

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Nonamphiphilic 2-aminoanthracene has been incorporated within the Langmuir monolayer and Langmuir–Blodgett (LB) films when mixed with behenic acid (BA). Miscibility of 2-aminoanthracene and BA at the air—water (A–W) interface has been studied by using surface phase rule and excess area criterion. Our studies reveal that repulsive type interactions exist between the component molecules in mixed monolayer and this may facilitate the formation of aggregates. Spectroscopic as well as morphological studies of mixed LB films of 2-aminoanthracene and BA undoubtedly confirms the formation of aggregates.

Keywords 2-aminoanthracene; aggregates; behenic acid; Langmuir–Blodgett film; nonamphiphilic

1. Introduction

Two dimensional monolayer studies at the air—water (A–W) interface are now at the center of current research interests because of ability to obtain structural and morphological information from it. Langmuir monolayers at the A–W interface have attracted remarkable attention since 1891 when Fräoulines Agnes Pockels described a method for manipulating films formed by oils on water [1]. Since then numerous materials have been studied in the form of monomolecular films (Langmuir films) on the liquid surfaces at constant temperature [2]. The amphiphilic molecules, which exhibit a delicate balance between hydrophilic and hydrophobic contributions to overall polarities of the molecules, are capable of forming stable Langmuir monolayers at the (A–W) interface [3, 4]. Langmuir–Blodgett technique is a globally well-known method for transferring the monolayer films from a liquid surface to solid substrates to form Langmuir–Blodgett (LB) films. The advantage of the LB

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technique is that it offers simplest yet the most elegant method of obtaining highly organized molecular assemblies, which have their potential applications in sensors, optoelectronic devices and as models mimicking biological membranes [5–8]. Photoresponsive functional groups attached to long chain fatty acids and also inert polymers have been incorporated in LB films for various purposes, spectroscopic as well as morphological studies of these films have provided valuable insight into the spectra-property correlation in these systems. In addition, the remarkable similarity between the LB films and naturally occurring biomembranes makes LB films a unique platform for studying electron and energy transfer processes mimicking the photosynthetic reaction center or drug-protein interactions in biomembranes.

Although LB compatible materials are amphiphilic molecules, nonamphiphilic molecules when mixed with a suitable supporting matrix such as long-chain fatty acid (viz. stearic acid, behenic acid (BA), arachidic acid, etc.) or an inert polymer matrix (viz. poly methyl methacrylate, poly styrene, etc.) also form excellent organized LB films [9–11].

The polyaromatic hydrocarbons (PAHs) are deemed to be an important active ingredient for future generation superfast optoelectronic devices and biocomputers [12, 13]. Several PAHs have been used to fabricate LB film based light emitting diodes (LEDs), optical switches, and sensors [14–16]. Interest in an important PAH, namely 2-aminoanthracene stems from the fact that it can be used in molecular logic gate operations like molecular Half-subtractor based on the changes in Intermolecular Charge Transfer (ICT) or/and locally excited states (LE) using binary ionic inputs like H^+ and OH^- [17]. Such implementations of Boolean operations at the molecular level is deemed to be an alternative approach to silicon based processor technology as the nanodimensional discrete molecules could lead to the realization of miniaturation of computers.

In this work, miscibility behavior of a nonamphiphilic molecule 2-aminoanthracene (structure shown in Fig. 1) and a long chain fatty acid, viz. BA in the mixed monolayer is first investigated by analyzing the surface pressure versus mean molecular area isotherms with surface phase rule and excess area criterion and then the aggregation by absorption spectroscopy complemented with scanning electron microscopy.

2. Experimental

2-aminoanthracene (Purity $>$ 96%), abbreviated as 2-AA was purchased from Aldrich Chemical Company, USA and was used without further purification. Purity of the 2-AA sample was checked by absorption and emission spectroscopy. Behenic acid (BA), purchased from Aldrich Chemical Company, USA was also used as received. A commercially available automated Langmuir–Blodgett deposition unit (Apex, India, Model 2007 DC) was used for studying the behavior of the mixed films of 2-AA and BA at the (A–W) interface and for the deposition of the mono- and multilayers on quartz slides. Triple distilled water was deionized by a Milli-Q plus water purification system and used as a subphase. The

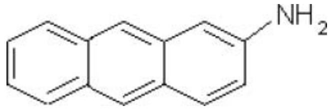

Figure 1. Molecular structure of 2-AA.

resistivity of the deionized water being 18.2 MΩ-cm indicating a high order of purity. The temperature of the subphase was maintained constant at 24°C .The pH of the subphase was 6.8. Quartz slides cleaned by leaving them overnight in chromic acid were subsequently boiled in concentrated nitric acid to remove all the traces of organic material and then washed with deionized water, dried and stored in a vacuum oven till use. Surface pressure isotherms were obtained by spreading the chloroform solution of BA and 2-AA mixed in a predetermined ration. After evaporation of the solvent, the film at the (A–W) interface was compressed very slowly at a rate of about 5×10^{-3} nm^2 mol^{-1} sec^{-1} and a Wilhemy plate was used for measuring the surface pressure at (A–W) interface. Data was acquired by a DELL computer interfaced to Wilhemy balance that also controlled the compressing barrier maintaining the constant pressure of subphase with an accuracy of 0.1 mN m^{-1}. Y-type deposition of the LB films of 2-AA mixed with BA on quartz slides have been obtained at dipping speed of 5 mm min^{-1} at the surface pressure of 15 mN m^{-1}. A drying time of 15 minutes were allowed after each lift. For each mole-fraction of 2-AA, LB films of 10 bi-layers were deposited. The transfer ratios were found to be 0.97 ± 0.01. A Hitachi model S-415A electron microscope was used for recording of Scanning Electron Micrographs (SEMs) of the films. The accelerating voltage of the electron beam was maintained at 10 kV. All the measurements were carried out at 24°C.

3. Results and Discussion

3.1. Behavior of Langmuir Film of BA and 2-AA at the Air-Water Interface

A small amount of chloroform solution of 2-AA (1×10^{-3} M) was slowly spread at the A–W interface and then compressed at a rate of 5×10^{-3} nm^{-2} mol^{-1} s^{-1}, after allowing sufficient time (20 minutes) for the volatile solvent chloroform to have evaporated. It was observed that the Langmuir film of pure 2-AA collapsed at a low surface pressure. Addition of large amount of 2-AA solution to the water surface lead to the formation of microcrystals, which are visible to the naked eye. This clearly indicates that pure 2-AA does not form stable films at the A–W interface. However, mixing 2-AA with BA resulted in highly stable and compressible monolayers that could be easily transferred onto quartz substrates.

The surface pressure versus area per molecule (π-A) isotherms of 2-AA mixed with BA at different mole fractions of 2-AA along with pure BA and pure 2-AA isotherms are shown in Fig. 2 (for clarity, not all concentrations recorded are shown). The area per molecule of pure BA is 0.22 nm^2 at a surface pressure of 15 mN m^{-1}. This value is in good agreement with the result reported in the literature [18]. From the close inspection of the Fig. 2, it has been observed that with increasing mole fraction of 2-AA in the mixture the area per molecule of the mixed film initially increases, reaches maximum and then decreases. The isotherm for the mole fraction 0.1 is quite interesting, because the area per molecule increases remarkably here. This type of behavior is also exhibited by some other nonamphilphic molecules, such as carbazole [19], p-Terphenyl [20], and bathophenanthroline [21]. Initial increase of area per molecule with the increase of mole fraction suggests that 2-AA moieties are accommodated within the chains of BA and the repulsive interaction between the molecules may be strong. However, decrease of area per molecule with the further increase of mole fraction may be due either to the submerging of 2-AA moieties in the water or accommodation of 2-AA moieties between the fatty acid chains not in contact with the water surface. To check the possibility of 2-AA moieties being

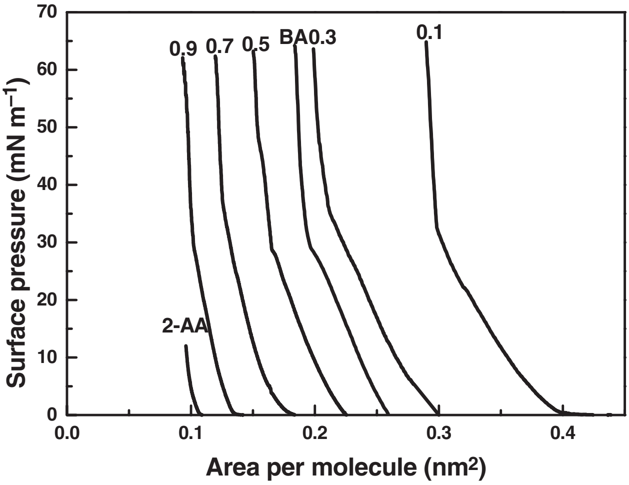

Figure 2. Surface pressure (π) versus area per molecule (A) isotherms of 2-AA mixed with BA at different mole fractions of 2-AA. The numbers 0.1, 0.3, 0.5, 0.7, and 0.9 denote the corresponding mole fractions of 2-AA in BA.

precipitated into the bulk of water subphase, we checked the emission of a small aliquot collected from below the water surface by a bent pipe [22], and no emission corresponding to the characteristics of 2-AA was found. This clearly indicates that the observed decrease in molecular area is not due to submerging of 2-AA molecules. At higher mole fractions, 2-AA molecules are squeezed out on the surface of fatty acid layers. Similar results have been obtained for other nonamphiphilic molecules [10, 11].

3.2. Miscibility of 2-AA and BA in the Mixed Langmuir Films

In general, an understanding of the miscibility for two components is provided by comparing the molecular areas of mixing, which are calculated through the additivity rule with experimental molecular areas [3, 23]. For an ideal mixing behavior (complete miscibility or complete phase separation), molecular areas of mixture show a linear dependence on the molar equation [(Eq. (1)] [3].

$$A_{12} = f_1 A_1 + f_2 A_2 \tag{1}$$

where f_1, A_1 and f_2, A_2 are the mole fractions and area per molecule of the first and second components, respectively at a specific surface pressure. A_{12} is the mean area per molecule of the mixed monolayer of the two components. A positive or a negative deviation of the observed curve from the ideality relation signifies a repulsive or an attractive type of interaction between the constituent components of the mixture. Figure 3 shows the plot of area per molecule versus mole fraction of 2-AA at different surface pressures, namely, 5, 10, 15, 25, 35, and 45 mN m^{-1}. The dotted lines in the figures correspond to an ideal curve dictated by the Eq. (1). In our investigated mixed system, a positive deviation has been observed indicating repulsive type of interaction between the component molecules that is manifested as a phase separation of the components. This phase separation may facilitate the formation of aggregates at the A–W interface. This result is consistent with behavior of other nonamphiphiles [10, 11].

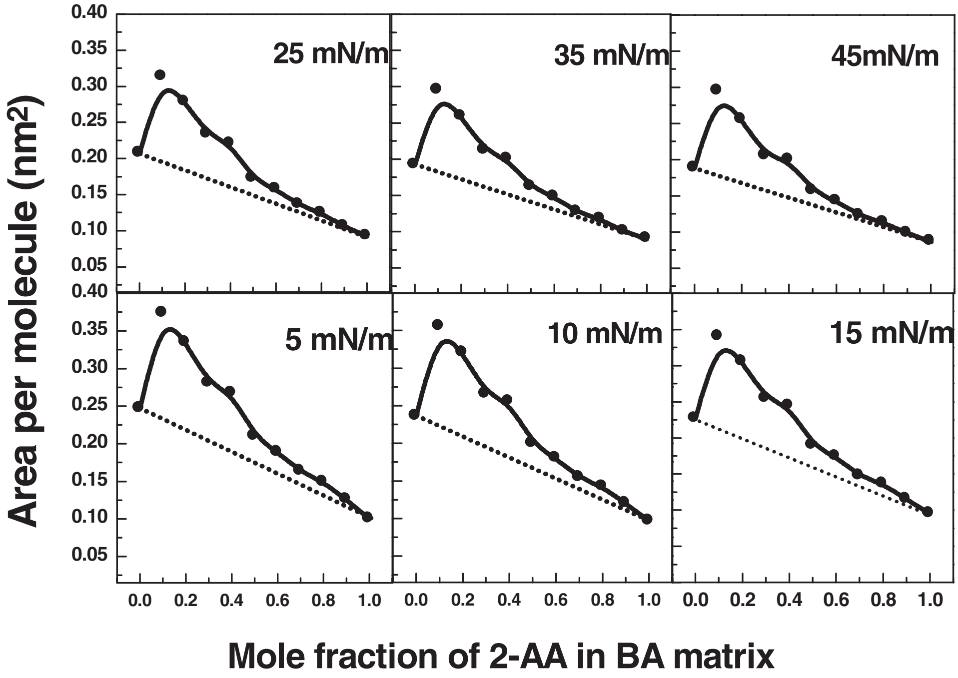

Figure 3. Plot of area per molecule versus mole fraction for 2-AA/BA mixed monolayers on water subphase at various surface pressures.

The formation of aggregates can also be explained by considering the interactions between the molecules in the mixed films at the A–W interface. There are three types of interactions: BA/BA, 2-AA/2-AA, and BA/2-AA. Among these three, BA/2-AA interaction helps in the formation and stability of the monolayer. But, if the other two interactions are strong, aggregation is formed and area per molecule is expected to decrease.

The collapse pressure is an important parameter in judging the miscibility behavior or phase separation of the components in the mixed monolayers. According to surface phase rule [3, 24], if there is only one surface phase in equilibrium with a bulk phase at the A–W interface, there are three degrees of freedom among the intensive variables, including temperature, external pressure, monolayer surface pressure, and film composition. Therefore, if the two components in the monolayer are miscible at the A–W interface, there is only one degree of freedom at the given temperature and external pressure. This indicates that the two components in the mixed monolayer are miscible at the interface if collapse pressure varies with the composition. On the other hand, for a two-component immiscible system, collapse pressure is independent of the film compositions.

The plot of collapse pressure versus mole fraction of 2-AA in 2-AA/BA mixed films is described in the Fig. 4. The dotted line indicates the ideality characteristics. From the close inspection of the Fig. 4, it is seen that the experimentally observed values of collapse pressures for 2-AA/BA mixed films are independent of compositions. This suggests that 2-AA and BA are totally immiscible at all mixing ratios at the A–W interface. This immiscibility or complete demixing between 2-AA and BA may lead to the formation of aggregates of 2-AA molecules in the mixed films.

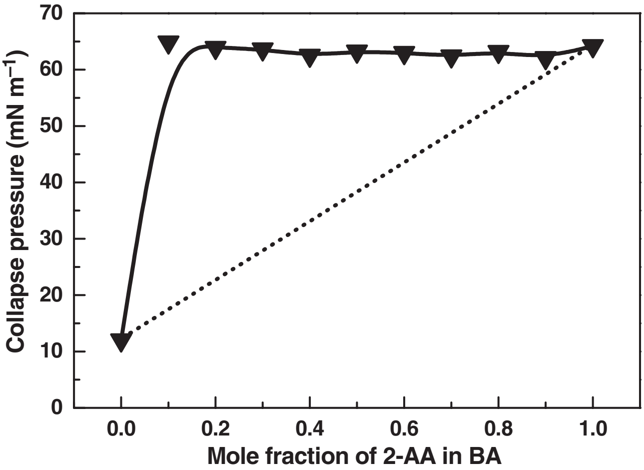

Figure 4. Plot of collapse pressure versus mole fraction for 2-AA/BA mixed monolayers.

3.3. Spectroscopic Study of Mixed LB Films

Figure 5 compares the UV-vis absorption spectrum of mixed LB films of 2-AA and BA with the solution spectrum of 2-AA in chloroform. The microcrystal absorption spectrum is also shown for comparison. The 2-AA solution spectrum shows a broad band maximum at 407 nm and this is in good agreement with the result published elsewhere [17]. The LB film and microcrystal spectra show red shifted and broadened spectra in comparison with the solution spectrum. The broadening along with the red shift may be due to the formation of aggregates in the mixed LB films.

According to the exciton model suggested by McRae and Kasha [25], dipole–dipole interaction leads to the formation of an exciton band, which may be located above or below

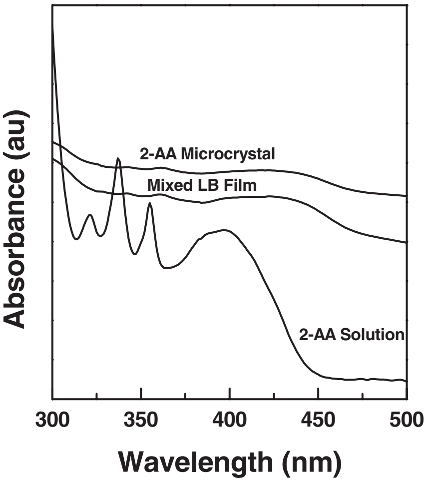

Figure 5. UV-vis absorption spectra of 2-AA solution in chloroform, Mixed LB film of 2-AA/BA, and 2-AA microcrystal.

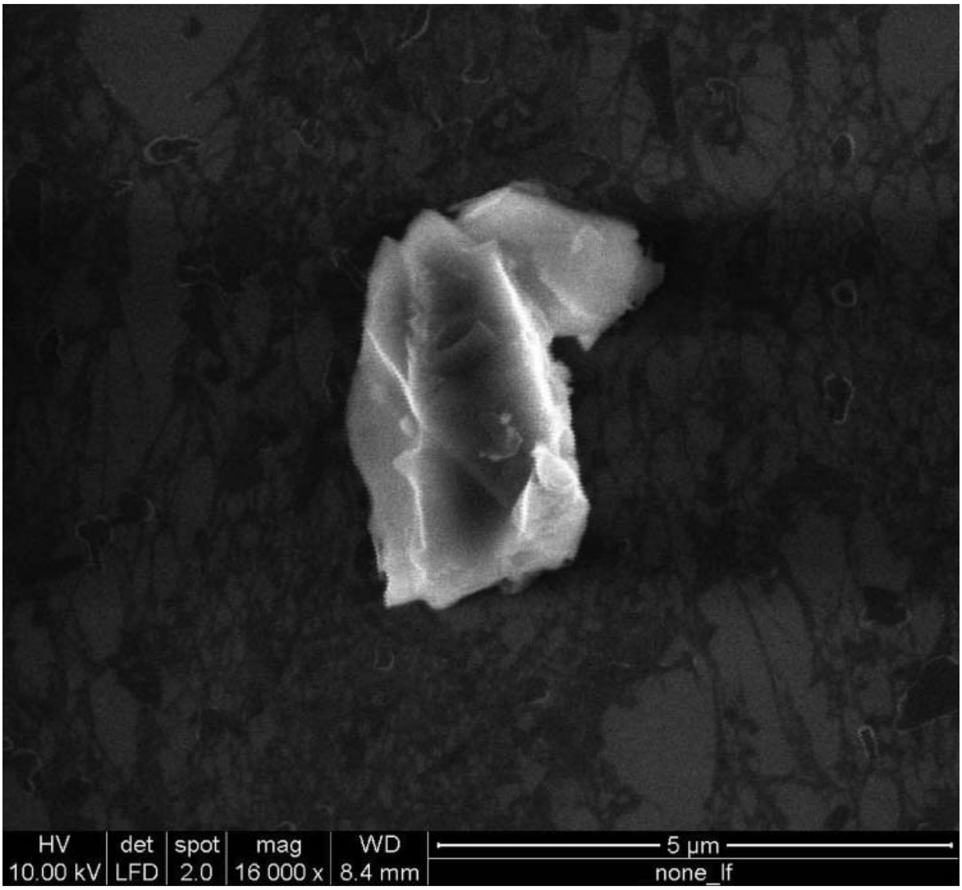

Figure 6. Scanning electron micrograph of 10-layered 2-AA/BA mixed LB film.

the monomeric energy level. The amount of shift depends on the angle (θ) made by the dipole moment of the molecule with the vector joining the centers of the diploes and the distance of the separation (r) of the centers of the dipoles. The amount of the shift (ΔE) is given by the relation

$$\Delta E = \frac{2\mu^2\left(1 - 3\cos^2\theta\right)}{r^3}$$

where μ is the dipole moment of the molecules. When $0^\circ < \theta < 54.7^\circ$, the exciton band is energetically located below the monomeric band that causes a red shift and the corresponding are referred to as the J-aggregates, while for $54.7^\circ < \theta < 90^\circ$, the exciton band is located energetically above the monomeric band that causes a blue shift and the corresponding are referred to as the H-aggregates. Corresponding to the magic angle $\theta = 54.7^\circ$, no shift in the absorption spectrum is observed and the corresponding aggregates are referred to as I-aggregates. In the investigated 2-AA/BA mixed LB films, we observed red shifts. Hence, these aggregates are identified as J-aggregates according to the exciton model.

3.4. Surface Morphology of Mixed LB Film

Figure 6 shows a SEM of LB film of 2-AA mixed with BA. The clusters with sharp and distinct edge corresponds to the three dimensional aggregates of 2-AA formed in the mixed film. As described earlier, it seems likely that dissimilar physical and chemical properties of 2-AA and BA molecules and strong interaction between similar molecules result in phase separation of 2-AA and BA molecules, which leads to the aggregate formation in the LB films. The formation of 2-AA aggregates as evidenced from SEM provides compelling visual evidence of aggregation of nonamphiphilic 2-AA molecules in the mixed LB films that also supports the conclusions drawn from the spectroscopic studies.

4. Conclusion

In summary, our work demonstrates that nonamphiphilic 2-aminoanthracene (2-AA) mixed with BA forms stable Langmuir monolayers at the A–W interface that could be easily transferable onto solid substrates. The surface pressure versus area per molecule isotherms studies indicate repulsive type of interaction between 2-AA and BA molecules. It is likely that strong repulsive interaction between dissimilar molecules (2-AA/BA) and strong attractive interactions between similar molecules (2-AA/2-AA and BA/BA) result in a phase separation of components into microcrystalline aggregates. Absorption spectroscopy complemented with scanning electron microscopic studies definitely proves the thesis of aggregate formation.

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