Role of microenvironment in the mixed Langmuir–Blodgett films

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Abstract

This paper reports the $\pi$–$A$ isotherms and spectroscopic characteristics of mixed Langmuir and Langmuir–Blodgett (LB) films of nonamphiphilic carbazole (CA) molecules mixed with polymethyl methacrylate (PMMA) and stearic acid (SA). $\pi$–$A$ isotherm studies of mixed monolayer as well as the remarkable change in collapse pressure of the mixed monolayer isotherms definitely show that CA is incorporated into PMMA and SA matrices. However, CA is stacked in the PMMA/SA chains and forms microcrystalline aggregates, as is evidenced from the scanning electron micrograph picture. The nature of these aggregated species in the mixed LB films has been revealed by UV–vis absorption and fluorescence spectroscopic studies. The presence of two different kinds of band systems in the fluorescence spectra of the mixed LB films have been observed. This may be due to the formation of low-dimensional aggregates in the mixed LB films. Intensity distribution of different band systems is highly sensitive to the microenvironment of two different matrices as well as also on the film thickness.

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1. Introduction

Carbazole (CA) and its derivatives have found extensive industrial and commercial applications in the manufacture of organic photoconductors [1] and electroluminescent devices [2–4]. CA and its derivatives are also of great interest to the spectroscopists owing to their unique photophysical characteristics such as intense and well-characterized absorption and fluorescence spectra [5,6]. Owing to their excellent optical and electronic properties, various amphiphilic derivatives of carbazole were synthesized and studied in the Langmuir–Blodgett films [5–13]. However, the synthesis of these amphiphilic carbazole derivatives and their purification are extremely difficult. In recent times it was observed that various nonamphiphilic materials could also form well-organized LB films when mixed with a long-chain fatty acid or inert polymer matrix [14–16]. A preliminary work on the photophysical characteristics of nonamphiphilic carbazole in LB films was reported [6]. In that work aggregation-induced reabsorption effect was observed. However, detailed investigations of the formation of stable LB films of carbazole doped into various matrices were not reported. Moreover, the study of the changes in photophysical properties with changing various LB parameters is also important from the point of view of various technical applications. In this communication, detailed investigations on the dependence of photophysical characteristics of mixed LB films of nonamphiphilic carbazole on various LB parameters were reported. It was observed that the longer wavelength vibrational pattern of fluorescence band system were sensitive to the mole fractions and the surface pressure of lifting as well as also to the number of layers.

2. Experimental

CA was purchased from Aldrich Chemical Company, USA, and vacuum-sublimed, followed by repeated recrystallization before use. SA (purity > 99%) from Sigma, USA and isotactic PMMA from Polyscience were used as received. The solvent chloroform (SRL, India) was of spectral grade and its fluorescence spectrum was checked before use. A commercially available Langmuir–Blodgett film deposition instrument (Apex, 2000C, India) was used for isotherm measurements and for multilayer film deposition. The subphase used was triple-
distilled deionized water. The pH of the subphase was 6.5. Solutions of CA, PMMA, and SA as well as CA–PMMA and CA–SA mixtures at different mole fractions were prepared in chloroform solvent and were spread on the subphase by a microsyringe. Surface pressure was recorded using a Wilhelmy plate arrangement as described elsewhere [17]. All isotherms were run several times with freshly prepared solutions. Deposition of multilayers was achieved by allowing the substrate to dip with a speed of 5 mm/min with a drying time of 15 min after each lift. Fluorescence-grade quartz slides were used for spectroscopic measurement. For each mole fraction of CA, 10-bilayer LB films were deposited. We chose 15 mN/m as the standard surface pressure for lifting the LB films for both the matrices. The transfer ratio was found to be 0.98 ± 0.02.

Fluorescence spectra and UV–vis absorption spectra were measured by a Perkin–Elmer LS 55 spectrophotometer and Perkin–Elmer Lambda 25 spectrophotometer, respectively. All the measurements were performed at room temperature (24 °C). Scanning electron micrographs were taken in a Hitachi (Japan) scanning electron microscope (Model S-415A).

3. Monolayer characteristics of CA at the air–water interface

To study the behavior of pure CA at the air–water interface, 100 µl of chloroform solution of CA (2 × 10⁻³ M) was spread on the water surface. After allowing the solvent to evaporate for 20 min, the barrier was compressed very slowly at a speed of 2 × 10⁻³ nm² mol⁻¹ s⁻¹. It was observed that the surface pressure rose up to 8 mN/m and the area per molecule was found to be very small. Addition of larger amount of CA solution resulted in the formation of crystalline domains at the air–water interface upon compression, which were visible to the naked eye. Moreover, the islets once formed as a result of barrier compression did not degenerate at the molecular level but remained as smaller islets upon relaxation of surface pressure. Repeated attempts to transfer this floating layer onto solid substrate were failed. However, when CA was mixed with a supporting matrix of either SA or PMMA, the floating layer was found to be highly stable and could be transferred onto quartz substrate.

Figs. 1a and 1b show the surface pressure (π) vs area per molecule (A) isotherms of CA mixed with PMMA and SA respectively at different mole fractions of CA, along with pure PMMA and SA. The area per molecule of pure PMMA and SA is 0.11 and 0.23 nm², respectively, at a surface pressure of 15 mN/m, which is consistent with the reported result [14].

Pure PMMA isotherm shows an inflection point at about 20 mN/m [18]. It is also observed that this inflection point gradually loses its distinction with increasing mole fractions of CA in PMMA and at and above 0.7 M of CA, the CA–PMMA mixed isotherms show steep rising without any transition point. At about or above this inflection point, the collapsing of monolayer occurs and the monolayer remains no longer stable [18]. This is why a surface pressure of 15 mN/m has been chosen for the film deposition.
The most interesting feature of CA–PMMA mixed isotherm is that at lower mole fractions of CA up to 0.3 M, the area per molecule of mixed film is larger than that of pure PMMA. Although it gradually decreases with increasing mole fractions and from 0.4 M and above mole fractions of CA, the area per molecule is lower than that of PMMA. The most plausible explanation seems to be that at lower mole fraction of CA, the PMMA matrix behaves as an excellent microenvironment, where CA molecules can accommodate. Thus a monolayer of CA–PMMA is formed. However, with increasing mole fraction of CA, phase separation between CA and PMMA moieties occurs, which may originate from the immiscibility of the components owing to their differences in molecular structure and physical and chemical properties, which generates aggregates. In case of isotherms of CA–SA mixed films (Fig. 1b), the area per molecule also decreases consistently with increasing mole fraction.

However, negligible small area per molecule of pure CA and at higher mole fraction of CA of mixed monolayer may lead to the conclusion that CA molecules may form aggregates and may be sandwiched between PMMA or SA chains and squeezed into the matrices and out onto the air–water interface. Another possibility may be the loss of CA molecules through precipitation into the water subphase.

To confirm whether the CA molecules at the air–water interface were lost through precipitation in the bulk of the subphase, small amounts of water from just below the air–water interface were sucked out and the fluorescence of the water sample was recorded. It was confirmed from the failure to detect any fluorescence that CA molecules were not lost through submerging below the air–water interface.

Therefore the most likely explanation may be that they are pushed up in between the SA or PMMA chains in such a way as not to occupy any area at the air–water interface.

Moreover, an increase in the absorption and fluorescence intensities with increasing number of layers and mole fractions of CA in the mixed film (figure not shown) definitely confirms the incorporation of CA molecules into the mixed LB films.

The plot of collapse pressure versus mole fraction of CA in the mixed films of CA with PMMA and SA is also shown in the insets of Figs. 1a and 1b, respectively. It is evident from the figures that collapse of the mixed monolayer occurs at much higher surface pressure than that of pure PMMA and SA. This certainly gives evidence that CA molecules are definitely stacked between PMMA and SA chains and do not precipitate out. Moreover, the collapse pressures at various mole fractions do not match with the ideality (solid) curve, which indicates that CA molecules and PMMA/SA molecules are totally immiscible in the mixed monolayer [6]. This immiscibility or complete demixing between CA and PMMA or SA may lead to the formation of crystalline aggregates of CA molecules in the mixed LB films, which has been confirmed by scanning electron micrograph (SEM). The nature of these aggregates has been revealed by UV–vis absorption and fluorescence spectroscopic studies.

4. Scanning electron microscopy

To visualize the phase separation between unlike molecules and to confirm the formation of microcrystalline aggregates of CA molecules in mixed LB films, a traditional imaging method, namely, scanning electron micrography (SEM), has been employed. Fig. 2 shows a scanning electron micrograph (SEM) of the 10-layer mixed LB film of 0.5 M of CA in SA matrix. The aggregates with sharp and distinct edges correspond to the three-dimensional aggregates of CA in LB films. The smooth background corresponds to the SA matrix. In the case of CA–PMMA mixed LB films (figure not shown), crystalline aggregates of CA are also observed. The formation of distinct crystalline domains of CA, as evidenced from the SEM, provides compelling visual evidence of aggregation of CA in the LB films.

5. UV–vis absorption and fluorescence spectroscopic study

Figs. 3a and 3b show the UV–vis absorption and fluorescence spectra of mixed LB films of CA (0.1–0.8 M) in PMMA and SA matrices, respectively, along with the spectra in chloroform solution and CA microcrystal for comparison.

Absorption spectrum of CA in chloroform shows distinct bands within the regions 225–350 nm, with intense and sharp high-energy bands having peaks at 247 and 292 nm along with a weak hump at around 258 nm, owing to S2 → S0 (1L→1A) transition [6] that is directed parallel to the long axis of the molecule. There are two other low-intensity but prominent vibrational bands in the regions 300–350 nm, with maxima at around 319 and 331 nm corresponding to S1→S0 (1L→1A) transition [6] that is directed parallel to the short axis of the molecule. The vibrational band system in the CA microcrystal spectrum is almost identical in position and shape except an increase in intensity. However, the high-energy bands in the microcrystal spectrum become broadened and blue-shifted. Also, the band with peak at 292 nm in CA solution spectrum is totally absent in microcrystal spectrum.

It is interesting to note that the absorption spectra of the mixed LB films of CA in PMMA/SA matrices, for almost all the mole fractions are observed to be diffused, broadened, and less intense compared to the solution absorption spectrum, except the absorption spectra of mixed LB film of 0.8 M of CA.
in PMMA. Also, the vibrational bands are too weak to be distinguished. However, the mixed LB film absorption spectrum of 0.8 M of CA in PMMA matrix becomes almost identical to that of CA microcrystal spectrum. The broadening of the band system may arise due to aggregation. The close similarity of the absorption spectra of the mixed LB films at higher mole fractions to that of the microcrystal spectrum may be due to the formation of low-dimensional microcrystalline aggregates in the mixed LB films.

It may be mentioned in this context that there are certain rigid nearly planar platelike molecules, namely pyrene [19], or rodlike molecules, anthracene [20] or biquinoline [14], that form aggregates in the mixed LB films. These molecules are sandwiched among the matrix molecules (SA/PMMA) to form aggregates in the LB films and partial or total binary demixing occurs in the mixed LB films. In the present work, the CA molecule has an almost linear rodlike structure. For aggregation to occur in the mixed LB films of CA molecules, the best possibility is a sandwich of CA molecules among SA or PMMA molecules in the mixed LB films.

Fluorescence spectrum in chloroform solution (also shown in Figs. 3a and 3b) shows a distinct and prominent vibrational band profile within the region 325–400 nm with the 0–0 band at 338 nm and the other prominent, intense band at 352 nm. There is a shift of the 0–0 bands at about 7 nm in fluorescence spectrum in comparison to solution absorption spectrum. This may be due to slight deformation of electronic states of the molecules.

The fluorescence spectrum of CA microcrystal is totally different from that of CA solution spectrum. The high-energy band system in solution spectrum is totally absent in CA microcrystal, and a longer wavelength band system with intense vibrational peaks at 393 and 413 nm along with a weak hump at 436 nm is observed. The origin of this longer wavelength band system is not readily explicable. One possible explanation is that due to closer association of molecules in CA microcrystal, deformation in the electronic structure occurs, resulting in the formation of favorable conditions for transition to the upper vibrational levels of the ground electronic state.

Almost all the bands of CA solution and microcrystal spectra are present in fluorescence spectra of LB films of CA in both the PMMA and SA matrices at different mole fractions of CA having 0–0 band at 341 nm, which appears to be slightly shifted with respect to the solution fluorescence spectrum. In comparison to the CA solution spectrum, new bands are observed within the region 350–450 nm in the mixed LB films of CA in both the matrices having prominent peaks at 397 and 416 nm along with a weak hump at around 437 nm. It is interesting to note that in the case of PMMA matrix with increasing mole fraction, the band systems in the region 325–375 nm decrease in intensity and at a mole fraction of 0.8 M the band systems totally disappear. However, in the case of the SA matrix, the band system within the region 325–375 nm become broadened with peak at around 346 nm and remain present in all the mole fractions of CA in SA. The decrease in intensity of the high-energy band system of the region 325–375 nm with respect to the longer wavelength band system in the region 350–450 nm of mixed LB film spectra is an indication of a strong aggregation-induced re-absorption effect [6] owing to the formation of microcrystalline aggregates in the mixed LB films.
6. **Layer effect**

Various technical applications may sometimes require thick films. Here we have also studied the dependence of photophysical characteristics on the number of layers. Figs. 4a and 4b show the UV–vis absorption and steady state fluorescence spectra of different layered mixed LB films of CA in PMMA and SA matrices, respectively, at two different mole fractions of 0.1 and 0.5 M of CA.

No appreciable change in band position is observed in the UV–vis absorption spectra of the mixed LB films in both the matrices except a little change in intensity distribution. However, their fluorescence spectra are quite interesting. The fluorescence spectra of the mixed LB films of the CA in PMMA matrix (Fig. 4a) show that when the number of layers is small, namely five, then at both the mole fractions of 0.1 and 0.5 M, the longer wavelength band system with prominent vibrational peaks at 397, 416, and 436 nm are quite intense in comparison to the high-energy band. The high-energy band system is quite low-intensity, having several overlapping diffuse vibrational peaks. However, 25-layered LB films for both the mole fractions show intense high-energy bands with prominent vibrational peaks at 342 and 353 nm and a quite low-intensity longer wavelength band system. However, in the case of an SA matrix, even in 25-layer LB films, both the longer and shorter wavelength band systems remain stronger.

The increase in high-energy band in the case of a PMMA matrix at a higher number of layers may be due to the fact that some conformational changes in CA molecules occur in the microenvironment of the PMMA matrix. As a result, deformation in electronic structure tends to decrease. Moreover, a comparison of the two different matrices may definitely lead to the conclusion that the conformational and organizational changes of CA molecules are largely affected by the different kinds of microenvironment in two different matrices.

7. **Pressure effect**

By changing the surface pressure of lifting, the morphology and crystal parameters of the LB films may be controlled precisely. Fig. 5 shows the spectroscopic characterizations of the mixed LB films of CA in SA matrix at two different mole fractions (0.1 and 0.5 M) of CA using 15, 20, 25, and 30 mN/m surface pressure. All the films are 10 layers thick.

No appreciable change in fluorescence spectra is observed with change in pressure. Only at a higher surface pressure of 30 mN/m and also at a higher mole fraction of 0.5 M do the longer wavelength band systems become intense in comparison to the high-energy band. A comparison with the microcrystal fluorescence spectrum of CA shows that at higher surface pressure, the CA molecules in the mixed LB films are organized in a large-dimensional microcrystal form.

8. **Conclusion**

In conclusion, our results show that carbazole molecules form an excellent Langmuir monolayer at the air–water interface when incorporated into PMMA or SA matrices and can easily be transferred onto a solid substrate to form monom and multilayered Langmuir–Blodgett (LB) films. \( \pi - \Delta \) isotherm studies of mixed monolayers as well as the remarkable change in collapse pressure of the mixed monolayer isotherm definitely
show that CA is incorporated into PMMA and SA matrices. The collapse pressure versus mole fraction plot of CA in SA mixed films clearly reveals the nature of complete demixing of binary components. Scanning electron micrography gives visual evidence of microcrystalline aggregates of CA molecules in the mixed LB films. UV–vis absorption and steady state fluorescence spectroscopic studies definitely conclude that CA molecules form microcrystalline aggregates in the mixed LB films in case of both the matrices. Fluorescence spectra of mixed LB films of CA in both the matrices of PMMA and SA at different mole fractions reveal two different band systems in the longer wavelength region and in the shorter wavelength or high-energy region.

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