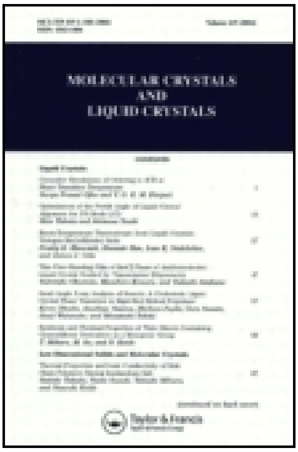

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Formation and Characterization of Anionic Dye-Polycation Molecular Films by Layer-by-Layer Adsorption Process

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Formation and Characterization of Anionic Dye–Polycation Molecular Films by Layer-by-Layer Adsorption Process

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Monolayer and multilayer films were formed by electrostatic self-assembly of poly (allyl amine) hydrochloride (PAH) and a strong fluorescent dye eosin Y (EY). In agreement with other published results, these compounds were found to form high-quality, closely packed monolayer and multilayer onto quartz substrate. The films formed on quartz substrate were then characterized in light of UV-Visible (UV-Vis) absorption spectroscopy and scanning electron microscopic (SEM) methods. Molecular movements were found to persist in the recently lifted layer-by-layer (LBL) films and about 72 h were required to get the film in stable condition. The photophysical characteristics of LBL films were found to vary with various parameters, such as number of deposited layers, dipping time in dye solution, pH of the PAH solution, and concentration of the dye. Both UV-Vis absorption spectroscopy and SEM studies also revealed the formation of molecular aggregates in the films.

Keywords Polymers; scanning electron microscopy; surface properties; thin films

1. Introduction

Many practical devices will require the formation of high-quality, closely packed, highly ordered, and, above all, stable thin films with a thickness of few micrometers. These thin films can be formed onto a solid support using the Langmuir–Blodgett (LB) technique [1–6] and electrostatic self-assembly (ESA) methods [7]. These systems are believed to have technological applications in both optical and molecular electronic devices [8,9]. The growing interest in these films among researchers throughout the world is due to their potential applications in wetting, lubrication, high-resolution lithography, adhesion [10], electroluminescent devices [11,12], and second harmonic generation [13]. Recent investigations suggest that the sequential adsorption process can be exploited to manipulate various kinds of materials, including conducting polymers [14], light emitting materials [15], nonlinear optical polymers [16], inorganic nanoparticles [17], biomaterials [18], dyes [19], and many other organic and inorganic polymeric systems [20,21]. There are various factors influencing the microstructure of the layer-by-layer (LBL) self-assembly multilayers, such as the

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molecular configuration of polyelectrolytes, stretching extent of polymer chains, average charge density, adsorption speed, etc. These factors can be adjusted by changing the temperature, nature of substrates, solubility of polyelectrolytes, charge density, concentration, pH values, and solvent composition [22–24].

The self-assembly method of organizing molecules was originally developed for sequential adsorption of oppositely charged polyelectrolytes onto solid substrates [7]. Polyions are generally preferred for this type of film deposition as assembling of such molecules basically depends on the electrostatic interaction of complimentary anion and cation pairs during successive adsorption steps.

In this article, we report the successful incorporation and detailed spectroscopic studies of an anionic dye eosin Y (EY) into LBL films along with thepoly cation, poly (allyl amine) hydrochloride (PAH). EY is a strong fluorescent anionic dye, commonly known as tetrabromofluorescein. It is water soluble, having a distinct yellowish shade. On the other hand, PAH is a cationic polyelectrolyte prepared by polymerization of allylamine. The chemical structures of both the dye and the polycation are shown in Fig. 1(a). Suri et al. [25] fabricated a dye-sensitized solar cell (DSSC) using the water-soluble organic dye EY, which is approximately 1000 times cheaper than ruthenium bipyridyl complex dyes. The micro-surface adsorption–spectral correction (MSASC) technique was described and applied to the investigation of the interaction of EY with proteins at pH 3.8 by Gao and Zhao [26]. In that particular study, it was observed that the microelectrostatic fields in proteins caused the aggregation of EY, which obeyed Langmuir isothermal adsorption [26]. It is a heterocyclic

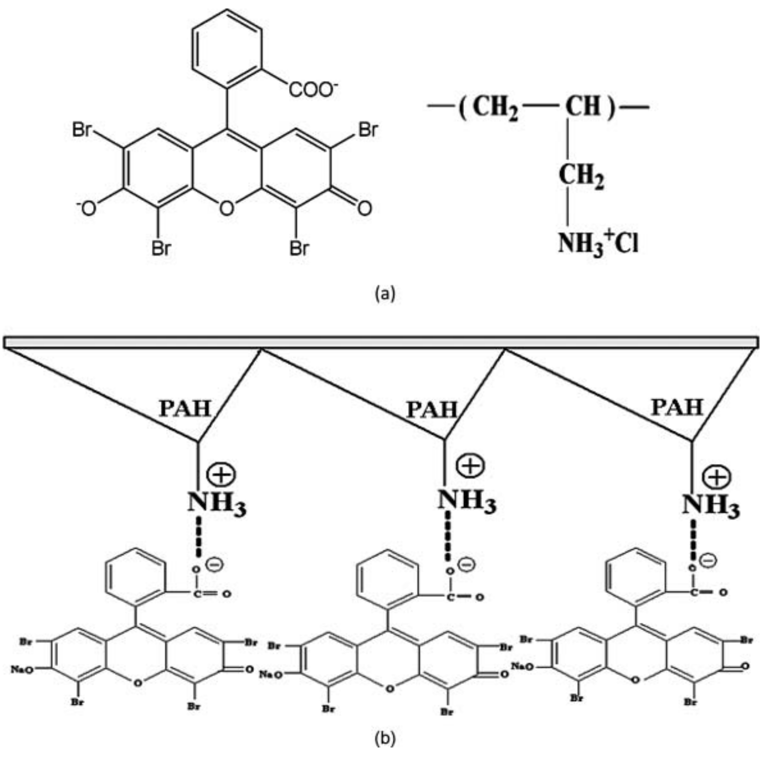


Figure 1. (a) Chemical structure of eosin Y (EY) and poly (allylamine) hydrochloride (PAH). (b) Schematic representation of PAH–EY: Self-assembled films on quartz substrate.

dye containing bromine atoms and is used in dyeing, printing, manufacturing of leather, printing ink, fluorescent pigments, etc. It is also used in paint and dye industries because of its vivid color.

2. Experimental Section

The anionic dye EY (molecular weight = 691.85, purity $> 99\%$) and the polycation PAH (molecular weight = 70,000, purity $> 99\%$) used in this work were obtained from Loba Chemie & Aldrich Chemical Co., USA, and used without further purification. Triple-distilled deionized water (resistivity about 18 MΩ cm^{-1}) was used for the preparation of solution. Thoroughly cleaned fluorescence-grade quartz substrates were used for deposition of films. The detailed technique employed for cleaning the substrate is described elsewhere [27]. LBL self-assembled films were prepared by dipping quartz substrate alternately in aqueous solutions of PAH and EY. The van der Waal interaction between the quartz substrate and the PAH molecules and charge transfer interactions between PAH and EY play important role in this method of thin-film deposition. At first, quartz substrate was dipped in PAH solution for 15 min, followed by rinsing in a water bath for 2 min to wash off additional cations attached to the surface. It was then dipped in EY solution for 15 min, followed by the same rinsing procedure. After each deposition and rinsing process, sufficient time (about 10–15 min) was allowed to dry the film, which is extremely important for the successive film deposition steps. The deposition of PAH (cation) and EY (anion) layers resulted in one-bilayer LBL film. The schematic representation of one-bilayer PAH–EY LBL films on quartz substrate is shown in Fig. 1(b). The whole sequence was repeated for fabrication of multilayer LBL films. Also, one-bilayer PAH–EY LBL films were fabricated by changing the dipping time, concentration of EY solution, and pH of PAH solution. Absorption spectra were taken after each deposition to monitor the growth of film by UV-Visible (UV-Vis) spectrophotometer (Lambda 25, Perkin Elmer). The EY solution and the EY microcrystal absorption spectra were also recorded for comparison with that of the LBL films. The scanning electron microscopic (SEM) image of 10-bilayer LBL film was recorded by a Hitachi (Japan) SEM (model S-415A).

3. Results and Discussion

The UV-Vis absorption spectra of pure EY solution (concentration of 10^{-5} M), EY + PAH solution (in 1:1 volume ratio), and EY microcrystal are shown in Fig. 2. The solution absorption spectrum shows distinct and intense band systems in the 200- to 580-nm region, with an intense and sharp monomeric band having peak at 518 nm and a weak hump at 488 nm, along with high-energy bands having peaks at 306 nm and 257 nm, respectively. The mixed-solution absorption spectrum of EY and PAH also shows almost identical band profiles except the fact that in this case, the peak at 488 nm becomes prominent, which may be due to the interaction of cationic PAH and anionic EY molecules in solution. In addition, in the mixed-solution absorption spectrum, a bathochromic shift of about 10 nm (prominent peak at 528 nm) is observed with respect to pure EY solution (prominent peak at 518 nm). Also, the absorption spectrum of EY microcrystal is found to be red-shifted by 17 nm in comparison with pure EY solution spectrum.

The UV-Vis absorption spectra of different-layered PAH–EY LBL films are shown in Fig. 3. The concentrations of PAH and EY solutions were 10^{-3} M and 10^{-4} M, respectively. The inset of Fig. 3 shows the plot of absorbance of monomeric band at 543 nm

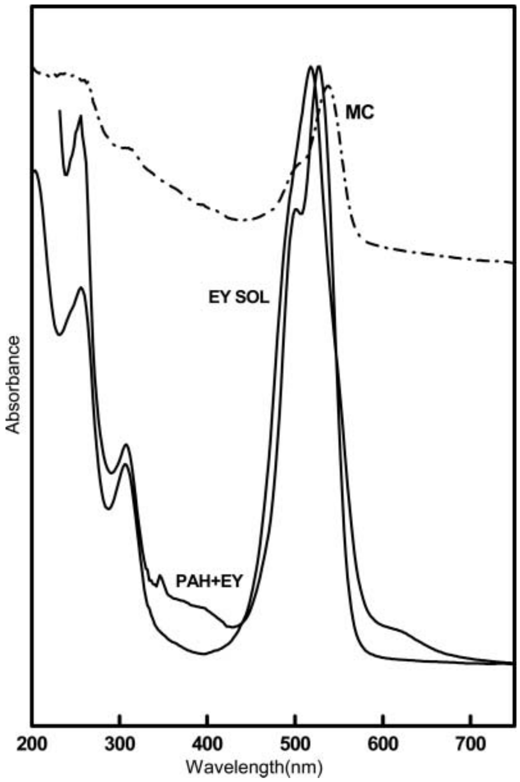


Figure 2. UV-Vis absorption spectra of EY solution (EY SOL) (10^{-5} M), PAH–EY solution (PAH + EY) (1:1 volume ratio), and EY microcrystal (MC).

versus number of layers deposited. From Fig. 3, it is observed that the absorption spectra of different-layered PAH–EY LBL films are almost identical to each other and also to that of EY microcrystal, shown in Fig. 2. The similarity in band profiles in the absorption spectra of PAH–EY LBL films and of pure EY solution and EY microcrystal confirms the successful incorporation of EY molecules in the backbone of PAH molecules onto quartz substrate. However, the red shift of the absorption spectra of LBL films and the microcrystal spectrum in comparison with the solution spectrum may be due to the change of microenvironment and closer association of EY molecules or due to the formation of PAH–EY complex in the LBL films due to electrostatic interaction, which results in aggregation. From the inset of Fig. 3, it is observed that the intensity of the monomeric band increases monotonically with the number of layer, which may be readily explained as: as the number of layer increases, the number of EY molecules attached to the substrate also increases and hence absorbance increases. Interestingly, it is observed from the inset of Fig. 3 that the intensity of the monomeric band becomes constant when the number of layers deposited is greater than or equal to 30.

3.1 Effect of Dipping Time

One of the parameters that plays a vital role in determining the photophysical properties of LBL films is the dipping time (time of interaction) in dye solution. Figure 4 shows the

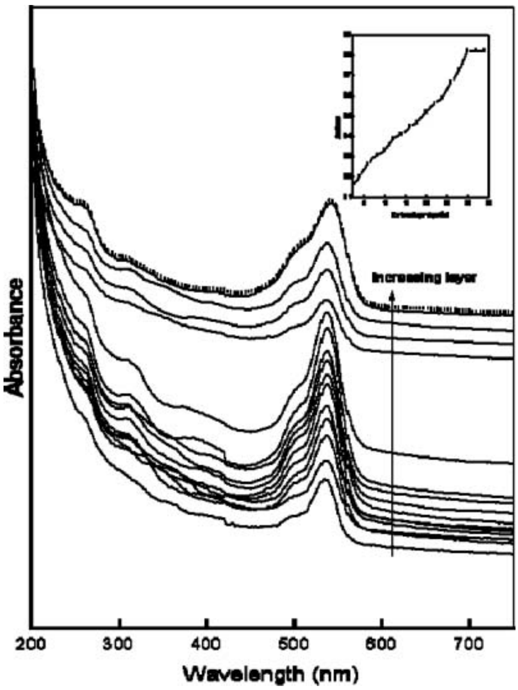


Figure 3. UV-Vis absorption spectra of different-layered LBL films of PAH–EY (dipping time in both PAH and EY solutions is 15 min.). Inset shows the plot of absorbance of the monomeric band versus increasing number of layers.

UV-Vis absorption spectra of one-bilayer PAH–EY LBL films with varying dipping time in EY solution, viz. 15, 30, 45, 60, 75, and 90 min. The dipping time in PAH solution was 15 min in all the cases. The inset of Fig. 4 shows the plot of absorbance of peaks at 495 nm and 538 nm versus dipping time in EY solution.

From the figure, it is observed that the intensity of the monomeric band increases with the increase in dipping time in dye solution, which attains maximum value when the dipping time is about 75 min and stabilizes when the dipping time is greater than or equal to 75 min. This may be due to the fact that after 75 min, all the PAH molecules attached to the substrate have interacted with the EY molecules and almost no PAH molecules are left free for further interaction, thus indicating saturation.

3.2 Aging Effect

Various technological applications demand thin films in stable form and hence checking the stability of a thin film is of great importance to avoid any molecular movements that may lead to major changes in spectroscopic and aggregating behaviors of such films, which may not suit to any technological applications. Hence, we have also investigated the time-dependent change in the UV-Vis absorption spectra of one-bilayer PAH–EY LBL films and recorded absorption spectra after every 24 h.

Figure 5 shows the UV-Vis absorption spectra of one-bilayer PAH–EY LBL films observed after a time interval of 24 h. The inset of Fig. 5 shows the plot of absorbance at 495 nm and 538 nm versus time elapsed. From the figure, it is observed that the band

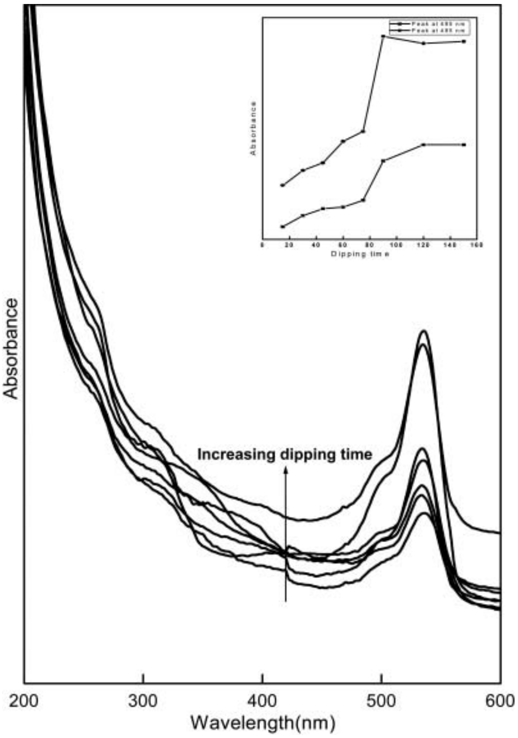


Figure 4. UV-Vis absorption spectra of one-bilayer LBL films at different dipping times in PAH solution (15, 30, 45, 60, 75, 90, and 120 min). Inset shows the plot of absorbance of the monomeric band versus increasing dipping time in EY solution.

profiles of the absorption spectra of LBL films observed at various time intervals are almost identical as far as their peak positions are concerned. However, the intensity of monomeric bands is found to increase with the passage of time (as evidenced from the inset of Fig. 5), and almost 72 h are required for films to get in stable condition. This may be due to the fact that some molecular movements exist in the recently lifted LBL films (0 h), and with the passage of time, these molecular movements cease and the dye molecules get strongly attached to the backbone of the PAH molecules to form a stable film (72 h).

3.3 Scanning Electron Microscopy

To confirm the formation of microcrystalline aggregates in PAH–EY LBL films, and also to compare the nature of crystalline aggregates between the recently lifted LBL films (0 h) and a stable LBL film (after 72 h), we have employed traditional structural studies, viz. SEM. Figures 6(a) and (b) show the SEM micrographs of 10-bilayer PAH–EY LBL films (a = recently lifted LBL films and b = LBL films after 72 h, i.e., in stable condition) at room temperature (concentrations of PAH and EY solutions were 10^{-3} M and 10^{-4} M, respectively). The microcrystalline aggregates with sharp and distinct edges correspond to three-dimensional aggregates of EY in the LBL films. The formation of distinct crystalline domains in EY molecules, as evidenced from the SEM image, provides a compelling visual evidence of aggregation of EY in the LBL films. Also, the SEM image of the recently lifted

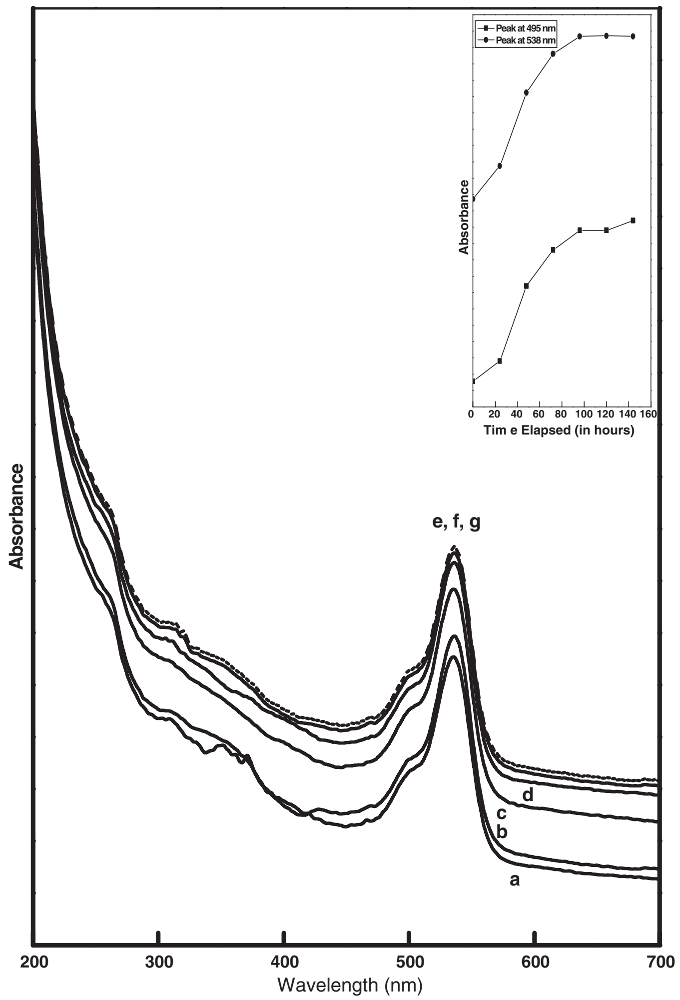
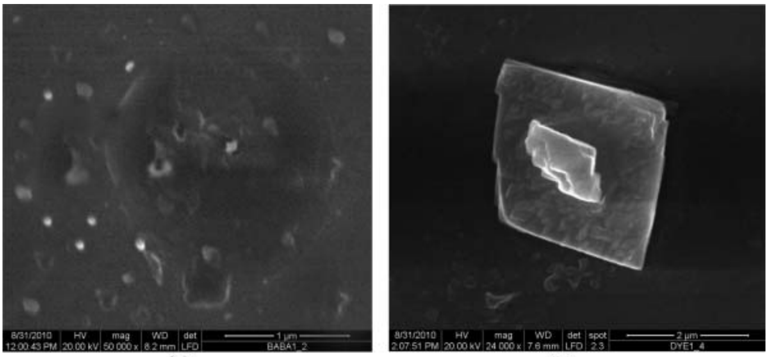


Figure 5. UV-Vis absorption spectra of one-bilayer LBL films observed at different time intervals: a = 0 h, b = 24 h, c = 48 h, d = 72 h, e = 96 h, f = 120 h, and g = 144 h. Inset shows the plot of absorbance of the monomeric band versus elapsed time (in hours).

LBL film shows microcrystalline aggregated species with relatively small patchy structures throughout the substrate, which is indicative of some molecular movements. However, all these small patchy crystalline structures submerged together with the passage of time to form relatively larger crystalline structure, as shown in Fig. 6(b).

3.4 pH Dependence Study

In recent years, much effort has been devoted to control the properties and function of multilayer films through the use of pH-responsive polymers [28,29]. One of the most promising potential uses for pH responsive multilayer films is in the area of controlled release, with implications in drug delivery, personal care products, sensors, and filtration [30].



(a) (b)

Figure 6. Scanning electron microscopy (SEM) of 10-bilayer PAH–EY LBL films at room temperature (concentrations of EY and PAH are 10^{-4} M and 10^{-3} M, respectively): (a) recently lifted LBL film (0 h), (b) stable LBL film (72 h).

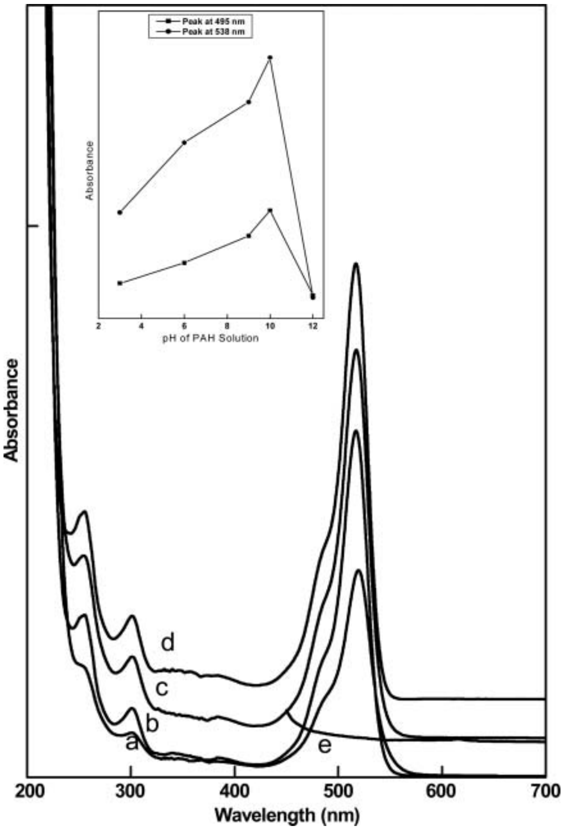


Figure 7. UV-Vis absorption spectra of one-bilayer LBL films at different pH values of PAH: a = pH 3, b = pH 6, c = pH 9, d = pH 10, and pH = 12. Inset shows the plot of absorbance of the monomeric band versus pH of PAH solution.

Figure 7 shows the UV-Vis absorption spectra of one-bilayer PAH–EY LBL films at different pH values of PAH solution, viz. pH 3, 6, 9, 10, and 12. The inset of Fig. 7 shows the plot of absorbance of peaks at 495 nm and 538 nm versus pH of PAH solution. From the figure, it is observed that the intensity of the monomeric band is found to increase for pH $\leq$ 10; however, it sharply reduces for pH $>$ 10 and almost becomes parallel to the wavelength axis when the pH is equal to 12. One of the possible explanations of this result is that amine is basic in nature, so at lower pH, i.e., in a strong acidic medium, amine undergoes protonation and hence its basic character is almost lost. However, when the acidity decreases, i.e., pH increases, at pH = 6, which is feebly acidic, protonation of amine does not take place. After pH $\approx$ 7, the medium is basic and hence maximum UV-Vis absorption occurs. At higher pH (pH = 12), hydrolysis of PAH takes place, which means that no –COO$^-$ ions are free and hence almost no interaction occurs between PAH and EY molecules. So, a sharp decrease in the intensity of the monomeric band is observed (as shown in the inset of Fig. 7).

3.5 Dependence on Concentration of Dye

The photophysical characteristics of LBL films are found to vary with various parameters, such as number of layers, concentration of dye, pH of polyelectrolytes, temperature etc. For this reason, we have also investigated the UV-Vis absorption spectra of one-bilayer

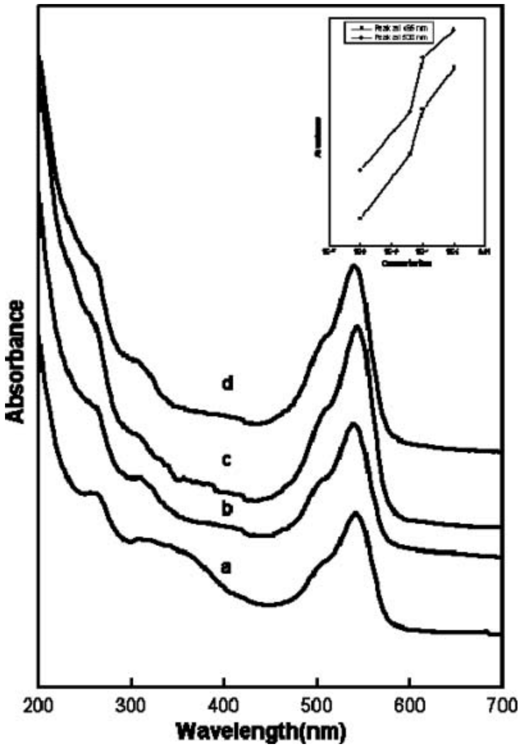


Figure 8. UV-Vis absorption spectra of one-bilayer LBL films at different concentrations of eosin Y, a = 10^{-6} M, b = 10^{-5} M, c = 10^{-4} M, and d = 10^{-3} M. Inset shows the plot of absorbance of the monomeric band versus concentration of EY solution.

PAH–EY LBL films at different concentrations of dye, viz. 10^{-2}, 10^{-3}, 10^{-4}, and 10^{-5} M, as shown in Fig. 8. The inset shows the plot of absorbance versus concentration of EY. In all the cases, the concentration of PAH is kept fixed at 10^{-3} M.

From Fig. 8, it is observed that the absorption spectra of LBL films at different concentrations of EY are almost identical except the fact that as the concentration of EY increases, the intensity of the monomeric band also increases. This may be certainly due to the fact that as the concentration of the dye increases, the number of EY molecules in the film increases. The absorption spectra of EY solution at different concentrations (10^{-5} M to 10^{-8} M) are found to be almost identical as far as their band profile and peak positions are concerned (figure not shown). The plot between the absorbance of the monomeric band versus dye concentration (figure not shown) indicates that with increasing dye concentration, the absorbance of the monomeric band also increases, which is indicative of closer association of EY molecules with increasing concentration in solution.

4. Conclusion

In conclusion, our results show that self-assembled films of the dye EY and the polycation PAH can be fabricated by alternate LBL adsorption process. The van der Waal interaction between quartz and PAH molecules and the electrostatic attraction between oppositely charged polyelectrolytes are mainly responsible for the formation of such films. UV-Vis absorption and SEM confirm the formation of microcrystalline aggregates in the PAH–EY LBL films. The intensity of the monomeric band is found to increase with the rise in concentration of the dye solution. Some molecular movements persist in the recently lifted LBL films, and almost 72 h are required for the film to become stable. In addition, the interaction between PAH and EY molecules depends largely on the pH of PAH solution.

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