

Study of Adsorption Behaviour of a Highly Fluorescent Laser Dye in a Long Chain Fatty Acid Matrix of Stearic Acid

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Abstract: Dyes are well-known to be utilised in the textile, printing, food, and cosmetic industries. Since the introduction of synthetic dyes in 1856, these huge families of chemical substances have enriched chemistry. Every year, more than 800,000 tonnes are produced. Dyes are organic molecules that contain chromophore and auxochromic groups and are grouped into numerous groups with varying structures for varied purposes. These applications are dependent on the chemical structure of the dye, its hue, and the complete light absorption system. The chromophores are the groups of atoms responsible for the dye colour, and auxochromes are electron withdrawing or donating substituents that cause or intensify the colour of the chromophores by shifting adsorption towards longer wavelengths and increasing absorption intensity. The adsorption behaviour of a highly luminous laser dye Rhodamine B (RhB) integrated into ultra thin films in a long chain fatty acid matrix of Stearic acid is described in this study.

Keywords: Dyes, Synthetic Dyes, Fluorescent Laser Dye, Chemical Structure, Adsorption and Ultra Thin Films

Introduction:

Ultrathin organic films have recently been a hot topic, with a focus on diverse applications such as integrated optics, sensors, friction-reducing coatings, and so on. To generate well-defined films with intriguing photophysical properties, most of these applications require a unique geometrical arrangement of the constituent molecules with them other and also with the substrate. Despite being a common method for mono/multi layered film preparation, the Langmuir Blodgett (LB) technique produces interesting results in fabricating films with predetermined alterations of different LB parameters

such as deposition surface pressure, pH, sub phase temperature, and so on using various amphiphilic molecules in general.

Recent studies show that when certain water soluble cationic or anionic materials engage electrostatically with the amphiphilic molecules of a prepared Langmuir monolayer, adsorption of these molecules results in the development of a complicated monolayer.

Based on the electrostatic interaction of opposite charges, another approach for synthesising water soluble molecules in ultra thin films was recently devised. The creation of multilayer assemblies is caused by the sequential change of anionic and cationic molecule adsorption on the substrate. This method is also known as Layer by Layer (LBL) or Self Assembled. As a result, combining these two processes to create a super lattice film with intriguing properties is a difficult task.

The production of an insoluble monolayer with ionic amphiphilic at the air-water interface, followed by the transfer of mono/multi-layered LB films onto a solid substrate, has received a lot of attention. Our present strategy is bi-technical, integrating LB and LbL. At a specific surface pressure, a stable amphiphilic mono/multilayer is transferred on solid quartz substrates using the LB technique. When this substrate is immersed in an aqueous solution containing an oppositely charged fluorescent dye, adsorption occurs. The luminous behaviour of organic dyes is heavily influenced by the relationship that molecules can make with nearby molecules to avoid the formation of dimers or aggregates. The integration of fluorescent dye in the confined geometry frequently results in significant departures from typical solution behaviour.

Experimental

Rhodamine B (RhB) and Stearic acid (SA) with purity greater than 99% were used. The chloroform (SRL, India) utilised as a solvent for SA is of spectroscopic grade, and its purity was verified before to use using fluorescence spectroscopy. For solution preparation and as a sub phase, ultra pure Milli - Q (resistivity 18.2 - cm) water was used. Throughout the experiment, the temperature was kept at 240 degrees Celsius. The LB deposition instrument- APEX 2000 C is utilised for film creation with the standard amphiphilic molecule SA in the LB process.

First, 200 l of SA chloroform solution was applied to the LB trough's air-water interface. After allowing 15 minutes for the solvent to evaporate, the barrier was compressed to achieve the desired surface pressure of 15 mN/m before beginning vertical Y-type deposition of stable SA monolayer by dipping the fluorescence grade quartz substrate at a speed of 5 mm/min with a drying time of 5 minutes after each lift. As a result, the required mono/multilayered SA film is obtained. The substrate is then immersed in an aqueous solution of Rhodamine B at a concentration of 10^{-4} M in a beaker for adsorption of oppositely charged molecules using the LBL method.

UV-Vis absorption and fluorescence spectra were obtained using UV-Vis absorption and fluorescence spectrophotometers, respectively. For ATR-FTIR measurements, a complex film was created using dye adsorption on a zinc selenide single crystal substrate. For background measurement, a clean zinc selenide substrate was used. ATR - FTIR measurements were performed using an FTIR spectrophotometer.

Results and discussions:

UV-Vis absorption and Fluorescence Emission Spectroscopy:

To evaluate the adsorption behaviour, ten layers of LB film were formed onto a spectroscopic grade quartz slide and then dipped into an aqueous solution of RhB at a concentration of 10^{-4} M. The spectra of pure RhB solution contains a strong band with a peak at 553 nm and a shoulder at around 515 nm. The 553 nm band is attributed to monomer absorption and trace, but the 515 nm weak shoulder is attributed to monomer vibronic transition trace. These two bands are redshifted to 567 and 528 nm in the microcrystal absorption spectrum, respectively. The spectral profile of thin film is substantially identical to that of microcrystal.

The observed red shift in thin film and microcrystal absorption spectra could be attributed to a change in microenvironment when molecules are transported from solution to solid surface. This, in turn, has an impact on the electronic energy levels, resulting in a change and band shift in the spectrum. RhB aqueous solution fluorescence spectrum reveals a strong band with a peak at 573 nm. The RhB microcrystal spectrum contains an intense longer wavelength band at around 635 nm, whereas the 573 nm band becomes a weak hump. The spectral profile of the fluorescence spectra of SA - RhB thin films is extremely close to that of the microcrystal spectrum.

The longer wavelength band appears in film spectra because the energy levels are altered by the orientational change in molecular packing that occurs when molecules are transferred to a solid surface. The closeness between the thin film and microcrystal spectrums suggests that RhB molecules are integrated into complex films and stacked to produce microcrystalline aggregates.

The immersion time was kept constant in all cases at 30 minutes. It's worth noting that the absorption spectra of different stacked films have essentially identical band patterns. Monitoring the UV-Vis absorption spectra of RhB adsorbed onto different layered SA LB films allowed us to estimate the quantitative dependency of adsorption amount of RhB in the SA LB films. It has been discovered that the specific absorbability of RhB molecules rises as the number of layers increases. The full adsorption of the RhB molecule demands a longer immersion time as the number of SA layers increases. As a result, RhB molecule penetration into SA LB sheets is a rate-determining phase in the adsorption process.

Time Effect:

To track the reaction kinetics, LB SA films were deposited on a quartz substrate and submerged in an aqueous solution of RhB (10⁻⁴M) over various time intervals. UV-Vis absorption spectra of RhB adsorbed LB films were examined to determine the adsorption kinetics.

The adsorption kinetics show that the adsorption equilibrium is reached after nearly 30 minutes. It is quite fascinating to see that the absorbance first increases very quickly, but this rate slows as the immersion period grows. This suggests that as time passes, the adsorption process becomes slower. This is due to the fact that the RhB molecules initially travel towards the LB monolayer in a fast diffusive process. Following then, a few RhB molecules on the film surface should alter conformation to accommodate additional RhB molecules in films, slowing the adsorption process. We attempted to model the absorbance vs. time data using a single function, as shown in equation (1).

$$A = K[1 - \exp(-t/\tau)] \quad (1)$$

Where A = absorbance taken as proportional to the amount of adsorbed material

K = constant

τ = characteristic time.

The calculated results are found to be in good agreement with the experimental data. This implies that the adsorption behaviour is a first order kinetic process with time constants of 10 minutes and $k = 0.036$.

Conclusion:

The findings reveal that the water-soluble cationic laser dye Rhodamine B may be successfully integrated onto the fatty acid matrix of SA in Langmuir-Blodgett (LB) films via adsorption. The cationic dye in aqueous solution interacted electrostatically with the long chain fatty acid molecule in LB films. ATR-FTIR spectroscopy verified the existence of RhB molecules in the adsorbed extremely thin films. UV-Vis absorption spectroscopy was used to evaluate the kinetics of adsorption. It has been discovered that the specific absorbability of RhB molecules rises as the number of SA layers increases. The penetration of RhB molecules into SA LB sheets, on the other hand, achieves adsorption equilibrium in less than thirty minutes. A comparison of the fitted and actual reaction kinetics curves demonstrates that the reaction kinetics between RhB and SA films is a first order kinetic process.

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