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Metal ion-induced H-aggregation of a water-soluble anionic dye Congo red (CR) in Langmuir–Blodgett (LB) film

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ABSTRACT
1. Introduction

In recent time, dye aggregation in ultra-thin films has attracted considerable interest owing to their technological applications in non-linear optics (1–4), optical memory (5, 6), organic solar cells (7–9), gas sensors (10–13), molecular electronics (14, 15), laser technology (16), etc. In ultra-thin films, molecular aggregates are formed due to strong coupling among the molecules resulting in the closer molecular association and organisation. Nature of molecular organisations can be controlled by changing various film forming parameters during the process of fabrication of films.

Depending on the molecular organisations, different types of aggregated species are formed in ultra-thin films. Formation of aggregates modifies the photophysical properties of the dyes. It causes either a blue shift or a red shift in the absorption band of the aggregates. For a J-type aggregate (side by side arrangement of molecules), the absorption band is red-shifted relative to the monomer, while a blue shift in the absorption band is observed for H-aggregate (face-to-face arrangement of molecules) (17).

Among several techniques of producing organised molecular assemblies, Langmuir–Blodgett (LB) film preparation technique is one of the most versatile techniques for making well-ordered ultrathin films wherein molecules are expected to maintain a highly ordered arrangement (18). Especially, the immobilised functional groups of molecules in LB films have great advantages for the practical applications such as chemical sensors, molecular electronics, optoelectronic devices and in the field of various biologically important processes.

Generally, amphiphiles are LB compatible materials (19). In certain cases, water-insoluble non-amphiphilic materials were also observed to form LB film when mixed with inert building matrices (20). In some cases, water-soluble materials were also used for LB film preparation (21–25). Meral et al. (21) studied the spectroscopic characteristics of mono and multilayer LB film of water-soluble Pyronin B (Py B) and Pyronin Y (Py Y) mixed with stearic acid (SA). Depending on dye concentrations, different types of aggregated species were formed. Modlinska et al. (22) studied the aggregation properties of tetrachloroperylene-tetracarboxylic acid in binary Langmuir and LB films. Hybrid films of water-soluble dye Nile blue were prepared by LB technique using a surfactant as a building matrix (23). Nano clay platelets laponite played a significant role in controlling the molecular aggregation of the dye.

LB films of water-soluble highly fluorescent cationic dye RhB were prepared by adsorbing it onto a cationic template ODA monolayer via anionic nano clay platelets Hectorite (24). Inglot et al. (25) studied the monolayer formation of azo dyes at the air–water interface by LB technique. Studies revealed that depending on dye concentrations different types of aggregated species were formed.

In these cases, water-soluble ionic (cationic and anionic) materials were used. They were dissolved in the aqueous subphase of the Langmuir trough and allowed to be adsorbed onto a preformed template Langmuir monolayer of oppositely charged amphiphiles. Due to electrostatics interactions, the ionic water-soluble materials interacted with the oppositely charged amphiphiles of the preformed Langmuir monolayer. Thus, a complex Langmuir monolayer was formed at the air–water interface. When some inorganic metal ions or inorganic nanoparticles were used in this process then organic–inorganic hybrid Langmuir monolayer was formed (26). The complex/hybrid Langmuir monolayer could be transferred onto suitable solid substrates to form mono- and multilayered LB films. Depending on the process of adsorption, organisations and orientations of the molecules in the Langmuir film may change. Surface pressure vs. area per molecule isotherms as well as compressibility vs. surface pressure characteristics studies, at the air–water interface gave valuable information in this respect.

In the present communication, detail investigations have been carried out to study the nature of organisation of a water-soluble anionicazo dye Congo red (CR) in LB film in the presence of divalent cationic metal ion Mg2+. Here, anionic SA monolayer was used as a template monolayer and the anionic CR molecules were adsorbed onto the anionic SA monolayer via cationic divalent metal ions Mg2+. In this case, Mg2+ ions acted as mediators to tag CR molecules into the anionic SA monolayer. A detailed investigation has been carried out to investigate the nature of molecular organisations of CR in the LB film under different conditions.

CR is a carcinogenic benzidine-based anionic diazo dye, which comes in the effluents of textile industries during the dyeing and the rinsing process and despite its wide industrial use in combination with surfactants, there are few reports on investigation of interactions in CR/surfactant mixtures (27–31). Xia et al. (27) used two surfactants octadecylamine (ODA) and cetyltrimethylammonium bromide (CTAB) for selective removal of the CR from an aqueous solution. Bagha et al. (28) studied the interaction of CR with some cationic surfactants and found that a stronger interaction occurred for gemini surfactants compared to the conventional ones. Interaction of CR with CTAB was investigated in submicellar aqueous solution in the presence of Ag+ ions and Ag nanoparticle (29). CR molecules formed stable complex in the presence of Ag nanoparticles. Shahir et al. (30) investigated the electrostatics interaction between the CR molecules and oppositely charged surfactant and showed that oppositely charged surfactant
simplifies dye aggregation. CR molecules formed different species such as dye–surfactant complexes, dye surfactant aggregation and surfactant micelle formation as a function of surfactant concentration (31).

Congo red is often used to stain amyloid fibrils. It has been shown that CR can interact with any secondary structure and the strength of the interaction is mostly determined by the particle side chains presented by the protein. The CR molecules have strong self-aggregating nature which can be removed by detergent (32).

2. Experimental section

2.1. Chemicals

Water-soluble anionic dye CR (MW = 696.66), [purity 97%] and SA [purity 99%] were purchased from Aldrich Chemical Co. and used as received. Magnesium chloride (MgCl₂) salt [purity > 98%] used in this study was obtained from the Merck Specialties Pvt. Ltd., India. Spectroscopic grade chloroform was purchased from SRL India Pvt. Ltd.

2.2. Instruments

A commercially available LB film deposition instrument (Apex-2006C) was used for surface pressure vs. area per molecule (n–A) isotherm measurements and LB films preparation. Ultrapure Milli-Q water (Electrical resistivity 18.2 MΩ-cm) was used as the subphase of the Langmuir trough and was also used to prepare aqueous solution of CR and aqueous MgCl₂ salt solution. Different concentrations of MgCl₂ salt solutions were prepared and sonicated for 10 min prior to use. The temperature was maintained at 24 °C throughout the experiment. UV–Vis absorption spectrophotometer (Lambda 25, Perkin Elmer) was used to record the UV–Vis absorption spectra. For spectroscopic characterisations, thoroughly cleaned quartz substrates were used for LB films preparation. Atomic Force Microscopic (AFM) image of SA-Mg-CR hybrid LB monolayer was taken in air with a commercial AFM system (Bruker Innova). Experiment was performed at room temperature (24 °C). Relative humidity was kept under 60% (noncondensing). First of all the film was deposited on fresh silicon wafer and then AFM image was taken in ambient air. The AFM image presented here was obtained in intermittent contact (tapping) mode. Typical scan area was 1 × 1 μm².

2.3. Methods

Stock solution of SA was prepared by dissolving them in spectroscopic grade chloroform (SRL). Concentration of stock solution was 0.5 mg/ml. Stock solution of CR was made by dissolving it into ultra-pure Milli-Q water (10⁻³ M). Same water was used as the subphase in the Langmuir trough. MgCl₂ aqueous solutions at different salt concentrations (1, 2, 3, 5, 10 g/L) were prepared in the ultra-pure Milli-Q water and sonicated for 10 min prior to use.

Being anionic, CR molecules could not be directly adsorbed into the template anionic SA monolayer at the air–water interface. In this case divalent cationic metal ions Mg²⁺, dissociated in the aqueous solution of MgCl₂ in the Langmuir trough, acted as mediator to incorporate anionic CR molecules into the SA monolayer. Here, Mg²⁺ ions bound CR molecules and SA molecules together by electrostatic interaction. Thus, CR molecules got adsorbed into the SA monolayer via Mg²⁺ ions. As a result, SA-Mg-CR hybrid monolayer was formed at the air–water interface.

For the preparation of this hybrid Langmuir monolayer at the air–water interface, first of all the Langmuir trough was filled up with dilute aqueous solution of MgCl₂ (at different concentrations of 1, 2, 3, 5, 10 g/L). Then 2000 μL aqueous solution of CR (10⁻³ M) was mixed with the dilute MgCl₂ aqueous solution in the Langmuir trough. In the aqueous solution, Mg²⁺ cations were dissociated and bound the anionic CR molecule electrostatically.

After waiting for 30 min, 100 μL chloroform solution of SA was spread onto the subphase of the Langmuir trough by a microsyringe. Adsorption of Mg-tagged CR molecule onto the SA monolayer was started immediately. After waiting for one hour to complete the adsorption process, isotherms were recorded. To prepare the mono- and multilayered LB films, the hybrid monolayer was transferred onto solid substrates at 20 mN/m surface pressure and at the speed of 5 mm/min.

For the preparation of SA-Mg hybrid Langmuir monolayer, same procedure was followed but no CR solution was added to the subphase of the Langmuir trough.

3. Results and discussions

3.1. Molecular structure

The molecular structure of CR is shown in Figure 1(a). CR becomes divalent anion in an aqueous solution. Two Na⁺ ions from the two sulfonate groups of a CR molecule are dissociated in an aqueous solution resulting in the formation of two SO₃⁻ ions in the two positions of the CR. This is shown in Figure 1(b). Divalent metal cations Mg²⁺ may electrostatically attach both CR and SA molecules forming a hybrid structure as shown in Figure 1(c). Thus, two SA molecules were tagged to one CR molecule. At the air–water interface of the Langmuir trough, the two SA-tagged CR molecules would be oriented almost vertically with the hydrophobic alkyl chains of SA molecules point upward. Thus, the vertically oriented CR molecules would stack
together at the air–water interface of Langmuir monolayer. In this type of molecular arrangement, area per molecule of the complex monolayer became largely reduced due to vertical orientation of CR molecules at the air–water interface. This has been discussed in the isotherm characteristics studies in the next section. In the monolayer LB film, this stacking was also retained. This has been discussed in the ‘schematic representation’ section.

However, in the presence of excess amount of Mg$^{2+}$ cations in the aqueous solution, not all the Mg$^{2+}$ ions acted as mediators to form SA-Mg-CR hybrid molecules. It might be that in such case, while one cationic site of a Mg$^{2+}$ ion was tagged to the one anionic position of a CR molecule, the other anionic position of the CR molecule might be attached to the SA molecule via another Mg$^{2+}$ ion. As a result, CR molecules might be organised in a tilted orientation in the hybrid Langmuir monolayer. This tilted orientation resulted in an increase in the area per molecule of complex monolayer as compared to the vertical orientation. In the Langmuir monolayer, stacking of tilted CR molecules at the air–water interface resulted in an increase in the area per molecule. This has been discussed in the section ‘isotherm characteristic studies’. In the monolayer LB films, this stacking was also retained and discussed in the section ‘schematic representation’.

3.2. Surface pressure vs. area per molecule isotherms studies: adsorption of water-soluble anionic CR molecules onto the preformed Langmuir monolayer of anionic SA via divalent metal cations Mg$^{2+}$

Being anionic, CR molecules could not be directly adsorbed from the aqueous subphase onto the preformed anionic SA monolayer at the air–water interface. Divalent metal cation Mg$^{2+}$ acted as mediator to bind both SA and CR molecules. Thus, SA-Mg-CR hybrid molecules were formed at the air–water interface. The hybrid Langmuir monolayer thus formed consisted of SA-Mg-CR hybrid molecules.
molecules were bound to the SA monolayer by Mg\textsuperscript{2+} ions, the molecular area of the hybrid molecule became greater than that of Mg-St molecule. This resulted in the increased molecular area of the hybrid Langmuir monolayer at the air–water interface. It is also noted that there was a phase transition of the hybrid monolayer at around 25 mN/m surface pressure in case of both lower and higher MgCl\textsubscript{2} concentrations. The phase transition might lead to particular orientations of CR molecules in the hybrid monolayer.

The most interesting point to note is that it became evident from the two isotherms of the hybrid monolayer (graphs II and III), the area per molecule in case of graph II was less than that of graph III. That is the hybrid monolayer at the air–water interface when formed at 1 g/L aqueous MgCl\textsubscript{2} solution has less area per molecule than that formed at higher MgCl\textsubscript{2} concentration of 10 g/L in the aqueous subphase. As discussed in the previous section, the vertical orientation of CR molecules in the hybrid monolayer might lead to the decrease in area per molecule in the first case in comparison to the tilted orientation of CR molecules in the second case. These two different types of orientation of CR molecules in the two types of hybrid monolayer might lead to two different types of molecular organisation. This has been discussed in the next section 'schematic representation'.

Figure 2(b) shows compressibility vs. surface pressure characteristics curves of the three Langmuir monolayers corresponding to Figure 2(a).
compressibility which decreased with increasing surface pressure. Graphs (II) and (III) show the compressibility curve of SA-Mg-CR hybrid Langmuir monolayer at lower salt concentration (1 g/L) and higher salt concentration (10 g/L), respectively. Both these curves show higher compressibility and there is a kink at 23 mN/m surface pressure for graph (II) and 27 mN/m for graph (III) which are the phase transition points as shown in the isotherm characteristic curves in Figure 2(a). It is clearly observed that after the phase transition point compressibility decreased rapidly. It indicates the attainment of solid phase. Compressibility curves also confirmed that hybrid monolayer was more compressible resulting in the more favoured molecular organisation.

3.3. Schematic representation of CR molecules in the complex of LB monolayer

Figure 3 shows the schematic representation of CR molecules in the hybrid Langmuir monolayer prepared at lower and higher salt concentrations at the aqueous subphase.

At lower MgCl₂ concentration (1 g/L) in the aqueous subphase, divalent anionic CR molecules were tagged to the two SA molecules via two Mg²⁺ cations. The two hydrophobic alkyl chains of SA molecules pointed upward and CR molecules became vertically oriented in the hybrid SA-Mg-CR molecule. This is schematically shown in Figure 3(a). In the monolayer LB film, this situation was retained and thus vertically oriented CR molecules were stacked in the LB monolayer forming H-aggregated sites as shown schematically in Figure 3(b), where stacking direction is perpendicular to the molecular plane. This is in conformity with the molecular arrangement for H-aggregate in monolayer film as discussed by Huang et al. (23).

At higher salt concentration (10 g/L) in the aqueous subphase due to the abundance of Mg²⁺ cations, one anionic site of CR molecule might get tagged to the one SA molecule via one Mg²⁺ cation, while other anionic site of CR molecule might be attached to only Mg ion. This resulted in the tilted orientation of the CR molecule. This is shown schematically in Figure 3(c). Stacking of these tilted CR molecules in the LB monolayer film might lead to J-aggregated site as shown schematically in Figure 3(d). This representation of J aggregation in monolayer film is in conformity with the result as discussed by Sato et al. (34). Experimental conformation of the formation of H-aggregate and J-aggregate sites in the LB films has been confirmed by UV-Vis absorption spectroscopic studies.

3.4. AFM studies

Figure 4 shows the AFM image of the monolayer LB film of SA-Mg-CR hybrid film which was fabricated at 1 g/L MgCl₂ concentration and the surface pressure was maintained at...
films depositions were done at 20 mN/m surface pressure. Distinct oval shape crystalline domain is clearly visible in the AFM image. The surface coverage is more than 80%. In some cases, the oval-shaped nanocrystalline domains overlapped each other. Each encircled region on the AFM image showed several nanocrystalline aggregates having dimensions varying from 25 to 50 nm. The SA and CR molecules as well as the Mg\(^{2+}\) cations are not distinguishable since their dimensions are beyond the resolution of AFM system. This AFM image gives clear visible evidence of the formation of SA-Mg-CR hybrid films.

3.5. UV–Vis absorption spectroscopic studies of SA-Mg-CR hybrid LB film

UV–Vis absorption spectroscopic studies give valuable information about the nature of molecular organisations in the LB film. Once the hybrid monolayer was formed at the air–water interface, the monolayer was transferred onto solid substrate by Y-type deposition technique to form mono- and multilayer LB films. For UV–Vis absorption spectroscopic studies, quartz substrates were used for LB film deposition.

Figure 5 shows the UV–Vis absorption spectra of (I) aqueous solution of CR (10\(^{-3}\) M), (II) thin cast microcrystal film of CR and (III–IV) monolayer hybrid LB films of SA-Mg-CR with different concentrations of MgCl\(_2\) (1 and 10 g/L) in the aqueous subphase of Langmuir trough. LB films depositions were done at 20 mN/m surface pressure. CR solution absorption spectrum gives a longer wavelength intense band at 498 nm along with a low intense high-energy band at 340 nm. The 498 nm band arises due to \(\pi-\pi^*\) transition of azo group, whereas the 340 nm bands are \(\pi-\pi^*\) transition of –NH (29). CR microcrystal absorption spectrum gives a longer wavelength band with peak at around 503 nm. The 5 nm red shifting while going from aqueous solution to microcrystal phase may be due to the changes in microenvironment.

Hybrid monolayer LB films absorption spectra showed interesting results. LB films lifted at lower salt concentration (1 g/L) showed intense high-energy absorption band with peak at 468 nm (graph III) (30). With increasing salt concentration, LB film absorption spectra showed red shifting absorption band and at higher salt concentration (10 g/L) this band coincided with the solution absorption spectrum at 498 nm. As discussed by several authors (29), the blue shifting of the absorption band with respect to the solution absorption spectrum is due to the formation of H- aggregates of dye chromophore.

It may be mentioned in this context that in the aqueous solution, anionic CR molecules interacted with the cationic CTAB and with the change in CTAB concentration,
a maximum blue shift of 54 nm was observed in the absorption band \( (31) \). The most likely cause of this blue shift was due to dye aggregation accompanied by the formation of an ion pair. A blue shift about 48 nm was observed when small amount of tetradecyltrimethylammonium bromide (TTAB) was added to CR solution, implicating an inductive effect of TTAB on dye aggregation process \( (30) \). The inductive formation of dye aggregation in parallel form, called H-aggregation, is considered to be responsible for such a blue shift.

In monolayer of LB film, parallel orientations of dye molecules became possible due to interaction of the divalent metal cation Mg\(^{2+}\). This is schematically shown in Figure 3(b). As discussed earlier, at lower salt concentration, this type of organisation became possible and was evident from the isotherm characteristic studies. With increasing salt concentrations, the absorption band became red shifted and at higher salt concentration of 10 g/L the absorption band of monolayer LB film again red shifted to 496 nm. As discussed in Figure 3(d), this may be happened due to tilted organisation of dye molecules in the monolayer LB film. Most remarkable similarities of this spectrum at higher salt concentration with that of microcrystal absorption spectrum may further lead to the conclusion that tilted organisation of dye molecules may form microcrystalline aggregates in the LB film.

![Figure 6](image1.png)

**Figure 6.** (Colour online) UV–Vis absorption spectra of SA-Mg-CR hybrid monolayer LB films lifted at various concentrations of MgCl\(_2\) (a) 1 g/L, (b) 2 g/L (c) 3 g/L, (d) 5 g/L, (e) 10 g/L.

![Figure 7](image2.png)

**Figure 7.** (Colour online) (a) UV–Vis absorption spectra of different layered SA-Mg-CR hybrid LB films lifted at 1 g/L MgCl\(_2\) concentration in the aqueous subphase. (b) UV–Vis absorption spectra of different layered SA-Mg-CR hybrid LB films lifted at 10 g/L MgCl\(_2\) concentration in the aqueous subphase.
Figure 6 shows the UV–Vis absorption spectra of SA-Mg-CR monolayer hybrid LB films lifted at different MgCl₂ salt concentrations (1, 2, 3, 5, 10 g/L) in the aqueous subphase of the Langmuir trough. With increasing salt concentration, it was observed that 468 nm longer wavelength band gradually red shifted and at higher salt concentration it is shifted to 496 nm. As discussed previously, at higher salt concentration dye molecules became tilted and formed microcrystalline aggregates in the LB films.

Figure 7(a) shows the UV–Vis absorption spectra of different layered SA-Mg-CR hybrid LB films lifted at 1 g/L MgCl₂ concentration in the aqueous sub-phase of the Langmuir trough. With increasing layer number, it was found that the longer wavelength band gradually red shifted from 468 nm in monolayer LB film to 495 nm in eleventh layer LB film. It is evident from this figure that H-aggregates sites became destroyed with increasing layer number. Figure 7(b) shows the UV–Vis absorption spectra of different layered LB films lifted at higher salt concentration of 10 g/L in the aqueous subphase of the Langmuir trough. In the monolayer, the absorption band was at 496 nm and there was no shifting of band with layer number.

4. Conclusion

In conclusion, our results showed that anionic watersoluble dye CR adsorbed onto anionic SA monolayer via divalent metal cation Mg²⁺. Consequently, SA-Mg-CR hybrid Langmuir monolayer was formed at the air–water interface. The hybrid monolayer was transferred onto solid substrate to form stable LB films. The organisations of CR molecules in the hybrid films depend on the concentration of MgCl₂ salt in the aqueous subphase of the Langmuir trough during the formation of Langmuir film. At lower salt concentration in the aqueous subphase, CR molecules arranged in H-aggregate pattern in the hybrid film. At higher salt concentration, H-aggregate pattern could not be retained. AFM observations clearly demonstrated the formation of nanocrystalline domains in the hybrid LB films.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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