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6 **Adsorption of Congored in Cationic Langmuir-
7 Blodgett Films : Spectroscopic Investigations**
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11 S. A. HUSSAIN, J. BHATTACHARJEE, S. CHAKRABORTY and D.
12 BHATTACHARJEE*

13 *Department of Physics, Tripura University, Suryamaninagar-799 022, Tripura, India*

14 **Abstract** — The present paper reports the incorporation of an anionic water soluble dye congo
15 red (CR) in the cationic octadecylamine (ODA) Langmuir-Blodgett (LB) films. ATR-FTIR
16 spectroscopy confirms the presence of CR molecules in the adsorbed LB films. The adsorption
17 kinetics of the CR molecules onto ODA LB films have been demonstrated by UV-Vis absorption
18 spectroscopy. Comparison of fitted curve of the reaction kinetics to that of the observed one
19 reveals that the reaction kinetics between CR and ODA LB films is of first order kinetic process.

20
21 **Keywords** : *Langmuir-Blodgett, Layer-by-Layer, ATR-FTIR, SEM, reaction kinetics.*

22
23 **INTRODUCTION**
24

25 Ultrathin organic films have shown potentials in many areas such as integrated optics,
26 sensors, frictionless coatings, surface orientation layers etc. [1–5]. Most of these tasks
27 require preparation of well defined films composed of molecules with appropriate
28 properties in a unique geometrical arrangement with respect to each other and to the
29 substrate. The construction of multilayer assemblies from molecularly thin layers offers
30 the possibility to prepare quasi-two-dimensional layered aggregates in which the
31 distance between two molecules along the layer normal can be controlled in the
32 nanometer scale [1–3].

33 Among the several thin film preparation techniques, Langmuir-Blodgett
34 technique shows promising results in designing films with predetermined alterations
35 of layers of different amphiphilic molecules. This technique is one of the most
36 promising, reliable and powerful tool in creating carefully controlled supra molecular
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38 *Corresponding author. E-mail : debu_bhat@hotmail.com, Phone : +91381 2375317 (O), Fax :
39 +913812374802 (O)

1 structures of organized molecular assemblies. The most important advantage of this
2 technique over other techniques is that the characteristics of this film can be controlled
3 by changing various parameters, namely surface pressure, temperature, barrier speed,
4 molecular composition etc. [1–3,5–7].

5 Recently it has been observed that certain water-soluble cationic and anionic
6 types of materials when interact with the amphiphilic molecules of preformed
7 Langmuir monolayer, adsorption of these molecules are occurred in the monolayer
8 and subsequently a complex Langmuir monolayer is formed [8–14]. Employing the
9 stable monolayer of ionic amphiphiles at the air-water interface is a complementary
10 method to study the adsorption of water soluble molecules in this monolayer by
11 electrostatic interaction between the monolayer molecules and the adsorbed species.
12 But this complex monolayer at the air-water interface is usually very rigid and its
13 transfer onto solid substrates does not always lead to uniform LB film.

14 On the other hand Layer-by-Layer (LbL) self assembled techniques allows one
15 to prepare ultrathin films of oppositely charged water soluble material through
16 electrostatic interaction [4,15]. Therefore the complexity appeared during fabrication
17 of LB films using water soluble material may be avoided by using LB-LbL bi-
18 techniques for the preparation of such films [16–17]. It is a challenge to combine
19 these two techniques in order to fabricate hybrid systems of LB-LbL multilayer on
20 the same substrate. Very few reports have been found in studying the interaction
21 between LB films of charged molecules (anionic or cationic) with oppositely charged
22 water soluble materials [16–17]. In this approach LB monolayer of one type of
23 charged material (which is water insoluble) is prepared onto solid substrate which
24 is subsequently immersed into the aqueous solution of oppositely charged other
25 material. Due to electrostatic interaction spontaneous adsorption on the mono-layer
26 LB film occurs. A complex film is thus formed, one part of it is fabricated by LB
27 technique and the other is done by LbL technique.

28
29 In the present study we have tried to demonstrate the adsorption of congo red
30 (CR), an anionic, dichroic dye onto cationic octadecyl amine (ODA) LB films.

31

32 **EXPERIMENTAL**

33
34 Congo red (CR) and octadecyl amine (ODA) were purchased from Sigma-Aldrich
35 Chemical Co., India and used as received without any further purification. Working
36 solution was prepared by dissolving the ODA in chloroform [Spectroscopic grade,
37 Acros Organics, USA].

38 In order to obtain Langmuir films at the air-water interface, a small amount
39

1 of the dilute chloroform solution of sample was spread onto the LB trough (APEX-
2 2000C, India) filled up with ultrapure millipore water ($18.2 \text{ M}\Omega \cdot \text{cm}$). Allowing
3 15 min waiting time to evaporate the solvent, the barrier was compressed at a rate
4 of $2 \times 10^{-3} \text{ nm}^2 \text{ mol}^{-1} \text{ s}^{-1}$ to record the surface pressure - area per molecule
5 isotherm. The surface pressure (π) versus average area available for one molecule
6 (A) was measured by a Wilhelmy plate arrangement, as described elsewhere [6]. The
7 films were found to be stable and data for π -A isotherms were acquired by a computer
8 interfaced with the LB instrument. Each isotherm was obtained by averaging at least
9 five runs.

10 LB film of ODA was prepared onto polished smooth quartz plates by dipping
11 and rising vertically through the floating Langmuir film with a speed of 5 mm/min
12 at a desired fixed surface pressure to prepare monolayer LB films. The transfer ratio
13 was found to be 0.98 ± 0.02 .

14 CR molecules were adsorbed onto films by immersing the ODA LB films onto
15 the aqueous CR solution for a given time period.

16 For spectroscopic measurement UV-Vis absorption spectrophotometer (Lamda-
17 25, Perkin Elmer) and fluorescence spectrophotometer (LS-55, Perkin Elmer) were
18 used.

19 ATR-FTIR measurement of the ODA-CR hybrid film was done by a FTIR
20 spectrophotometer (Spectrum 100, Perkin Elmer). For ATR-FTIR measurement 10
21 layers of films were deposited onto clean zinc selenide substrate. An empty zinc
22 selenide substrate was used for background measurement.

23 Scanning Electron Microscopic (SEM) images were taken in a Hitachi (Japan)
24 Scanning Electron Microscope (model S-415A). Corning glass slides were used as
25 the substrate for depositing LB films for SEM measurements. Ten layers of LB films
26 were deposited by the Y-type (vertical deposition) deposition method onto the corning
27 glass substrate. LB films were coated with gold before the SEM measurement.
28 Acceleration voltage of the electron beam was maintained at 4 KV. We have used
29 low accelerating voltage in order to avoid the damage of samples due to the high
30 accelerating electron beam.

31

32 **RESULTS AND DISCUSSION**

33 **Surface pressure - area per molecule isotherms :**

34 Isotherm characteristics of ODA and CR were studied by spreading the dilute solutions
35 of ODA or CR in chloroform ($2 \times 10^{-3} \text{ M}$) on the water surface of the Langmuir
36

37

1 trough. After sufficient time was allowed to evaporate the solvent, the barrier was
2 compressed very slowly at a speed of $2 \times 10^{-3} \text{ nm}^2 \text{ mole}^{-1} \text{ s}^{-1}$.

3
4 The surface pressure - area per molecule (π -A) isotherms of ODA and CR are
5 given in Fig. 1. For ODA isotherm, the surface pressure begins to increase from
6 zero at a surface area of $0.193 \text{ nm}^2 \text{ molecule}^{-1}$ which is consistent with the area
7 occupied by densely packed alkyl chains (about 0.20 nm^2). The isotherm exhibits steep
8 rising up to the collapse pressure is reached at about 56 mN/m surface pressure. This
9 behaviour is consistent with the previously reported results [18]. When long chain
10 amine (ODA) was spread on the water the condensed monolayer with a relatively
11 small molecular area was formed, which can be considered to be due to very small
12 hydrophilicity of the amino group, being hydrated partially.

13 From Fig. 1 it is observed that surface pressure for CR isotherm does not rise
14 beyond 1 mN/m . Addition of large amount of solution and sufficient compression of
15 barrier do not increase the surface pressures much. This indicates that CR molecules

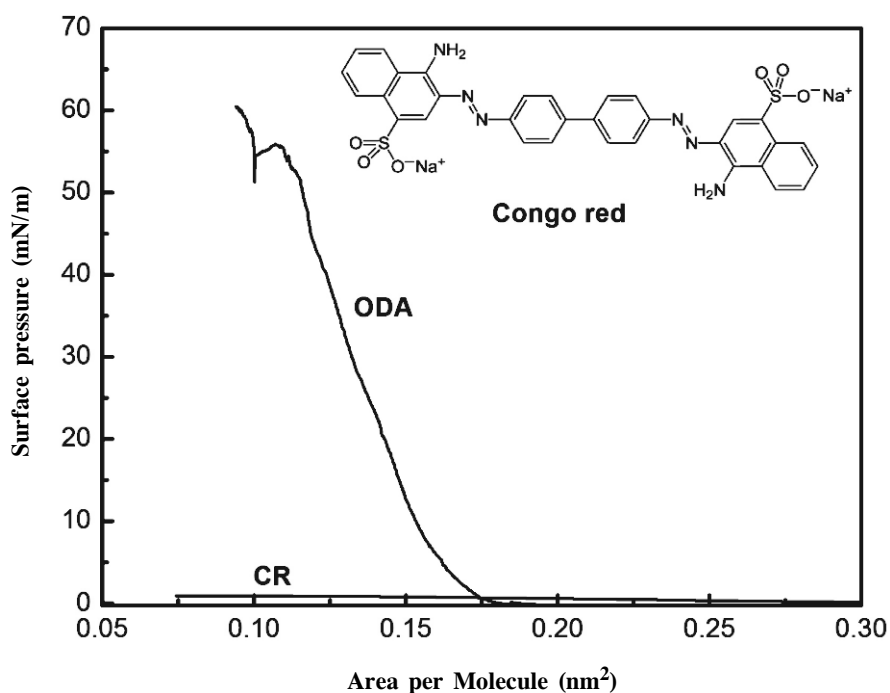
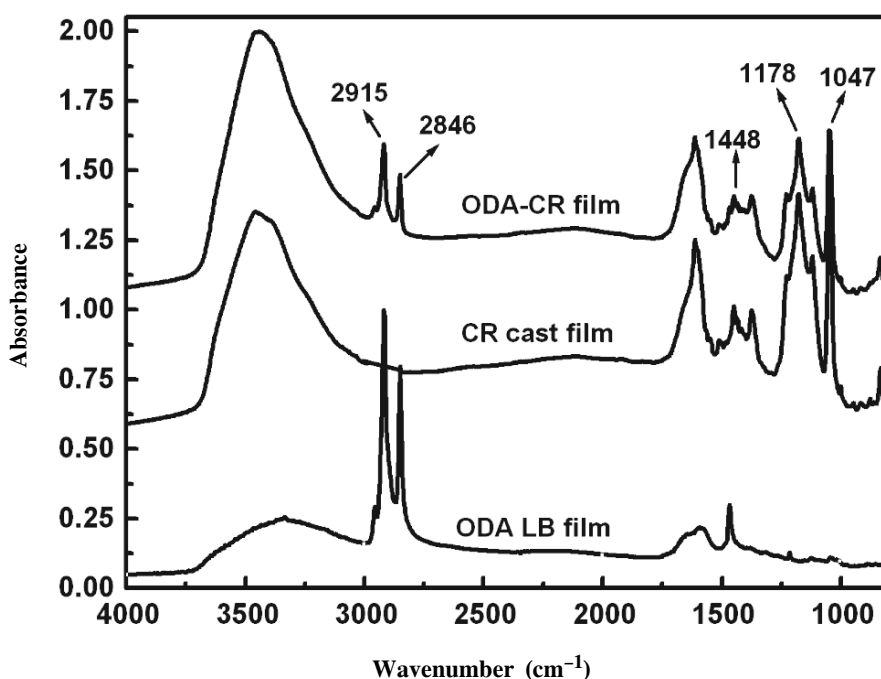


Fig. 1 Surface pressure - area per molecule (π -A) isotherms of ODA and CR in aqueous sub phase. Inset shows the molecular structure of congo red (CR).

1 are water soluble and do not form stable Langmuir monolayer at the air-water
 2 interface.

3 **ATR-FTIR spectroscopy :**

4 Fig. 2 shows the ATR-FTIR spectra of CR adsorbed onto 10 layer ODA LB film
 5 along with CR cast film and 10 layer ODA LB film for comparison. The FTIR
 6 spectrum of ODA LB film shows strong prominent band at 2846 and 2915 cm^{-1} along
 7 with other bands. These two bands are the diagnostic bands of ODA and identified
 8 as the stretching vibration of $-\text{CH}_2$ group of ODA [18]. These two bands are also
 9 present in the CR adsorbed ODA LB film spectrum. On the other hand the FTIR
 10 spectrum of CR cast film possesses prominent bands at around 1047, 1178, 1448
 11 cm^{-1} along with several other bands. These 1047 and 1178 cm^{-1} bands are due to
 12 S=O stretching vibration of CR [19] and the 1448 cm^{-1} band is due to the azo N=N
 13 vibration [20]. This band is mainly the diagnostic band for azo dyes [20]. In the FTIR
 14



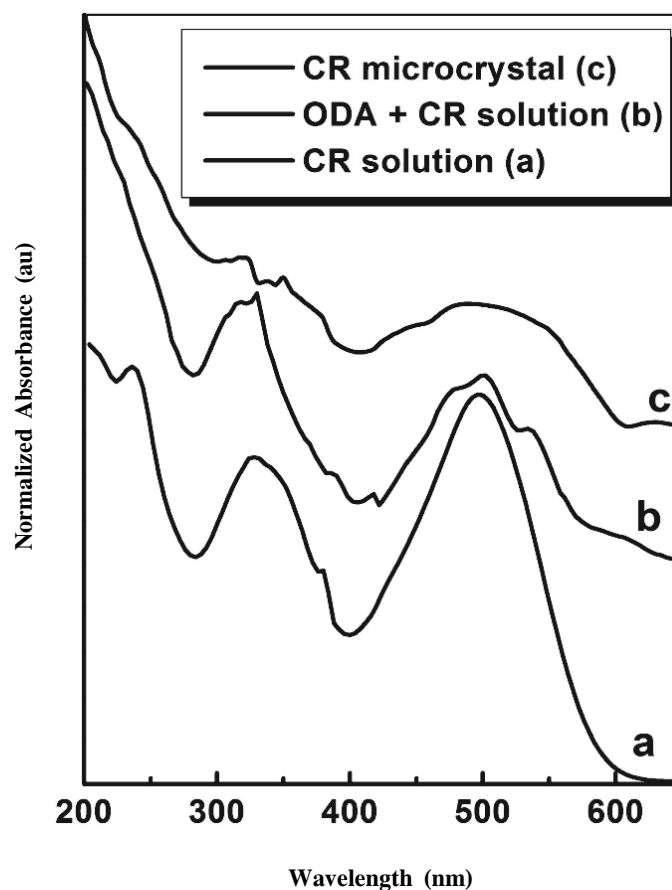
37 Fig. 2. ATR-FTIR spectra of CR adsorbed onto 10 layer ODA LB film along with CR cast
 38 film and 10 layer ODA LB film.

39

1 spectrum of CR adsorbed LB film all these bands are present. It confirms the
2 adsorption and consequent presence of CR molecules onto the LB films.

3 **Photophysical behaviour :**

4 The UV-Vis absorption spectrum of CR aqueous solution (10^{-6} M), CR & ODA
5 mixed solution (1 : 1 volume ratio), and CR cast film are shown in Fig. 3. The CR
6 aqueous solution absorption spectrum shows intense band at 498 nm along with other
7 high energy bands with peaks at around 236, 328 nm. The 498 nm band is mainly
8 due to $\pi\pi^*$ transitions of CR [21]. The CR - ODA mixture solution absorption
9



38 Fig. 3. UV-Vis absorption spectra of CR in aqueous solution (curve a; concentration 10^{-6} M),
39 CR & ODA mixed solution (curve b; 50 : 50 volume ratio), and CR cast film (curve c).

1 spectrum shows two additional weak humps at around 478 and 538 nm, along with
2 all other bands, which are present in the pure CR solution spectrum. Hasegawa et
3 al. [22] observed a band at around 550 nm for concentrated CR solution and
4 interpreted as due to be related to CR molecules in associated forms. In the present
5 case anionic part of CR molecule interacts with the cationic part of the ODA
6 molecule. Thus into the complex species, the CR molecules get closer side by side
7 and closer association of CR molecules take place, which is manifested by the
8 emergence of new bands in the ODA-CR mixed aqueous solution absorption spectrum.
9 Changes in the UV-Vis absorption spectrum provide evidence of complex formation
10 or possible interaction between ODA and CR. This inference leads us to study the
11 reaction kinetics of CR molecules with ODA LB films. CR microcrystal shows a
12 broad band pattern in the 400–600 nm region. This broad band profile may be an
13 overlapping of main CR characteristics band at 498 nm along with two weak humps
14 at 478 and 537 nm. In microcrystal, the CR molecules remain in aggregated form
15 resulting into closer association of CR molecules.

16 Fig. 4 shows the UV-Vis absorption spectra of CR adsorbed onto different
17 layered ODA LB films. In all cases the immersion time was kept fixed at 15 minutes.
18 The absorption spectra of CR adsorbed onto ODA LB films are almost similar with
19 respect to spectral profile to that of ODA - CR mixed aqueous solution absorption
20 spectrum. Here also the two weak humps are present at around 484 and 543 nm along
21 with the prominent band centered at 501 nm. This is an indication that closer
22 association of CR molecules occurred in the CR adsorbed ODA LB films due to
23 interaction with the ODA molecules in LB films. Here all the bands are slightly red
24 shifted with respect to solution. It is worthwhile to mention in this context that red
25 shifting of CR absorption bands occur when CR binds with poly (L-lysine), insulin,
26 poly (vinyl alcohol) and peptide [23–26]. Such changes are attributed to formation
27 of ordered aggregates. In the present case the observed red shift in CR absorption
28 bands may be due to formation of ordered aggregates or associated species in LB
29 films.

30 It is interesting to note that the absorption spectra of different layered films
31 show almost similar band pattern. The quantitative dependence of adsorption amount
32 of CR in the ODA LB films was determined by monitoring the UV-Vis absorption
33 spectra of CR adsorbed onto different layered ODA LB films [Fig. 4]. It has been
34 observed that the specific absorbability of the CR molecules increases with increasing
35 numbers of layers up to 8 layers. The adsorbed amount of the CR dyes shows almost
36 constant absorbance above 8 layers (inset of Fig. 4). This suggests that the CR
37 adsorption quantitatively occurs with the deposited amount of the cationic materials
38 (ODA) on the substrate. With increasing number of ODA layers, it has been observed
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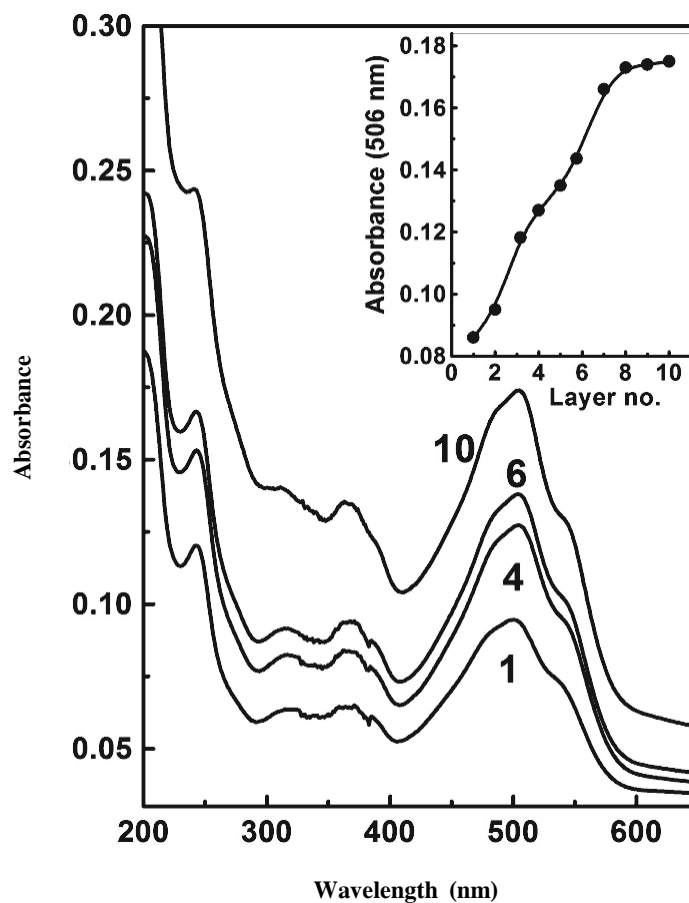


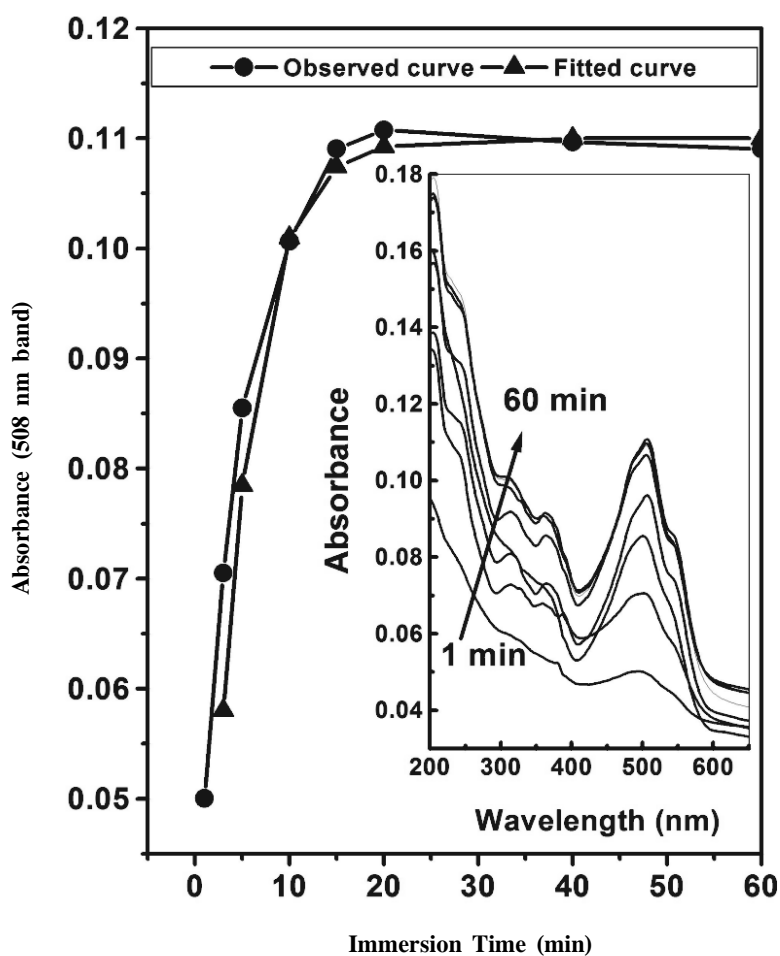
Fig. 4. UV-Vis absorption spectra of CR adsorbed in different layered ODA LB films. The numbers denote the layer number. Inset shows the plot of absorbance (506 nm band) as a function of layer numbers.

that the complete adsorption of the CR molecule requires a longer immersion time. Therefore, the penetration of CR molecule into ODA LB films is a rate determining steps in the adsorption process.

Adsorption kinetics of CR molecules onto ODA LB films :

Anionic CR molecules interact with the cationic ODA LB films. To monitor this reaction kinetics LB films of ODA were deposited onto quartz substrate and this ODA

1 film has been immersed into the aqueous solution of CR (1×10^{-4} M) for different
 2 time interval. In order to quantify the adsorption kinetics, UV-Vis absorption spectra
 3 of CR adsorbed LB films have been measured. Fig. 5 shows the adsorption kinetics
 4 of anionic CR molecules onto cationic ODA LB films (black : fitted curve, red :
 5 observed curve) along with the absorption spectra of CR adsorbed ODA LB films
 6 at varying immersion time (inset of Fig. 5).



37 Fig. 5. Adsorption kinetics of anionic CR molecules onto cationic ODA LB films : absorbance
 38 of 508 nm band as a function of immersion time (red : observed, black : fitted curve). Inset
 39 shows the UV-Vis absorption spectra of CR adsorbed ODA LB films at varying immersion time.

1 From the adsorption kinetics it is seen that the adsorption equilibrium is
2 achieved after 20 minutes. The absorbance of long wavelength band reaches its
3 maximum with immersion time 20 minutes. It is very interesting to note that initially
4 the absorbance increases very fast however, this rate becomes slow with increase in
5 immersion time. This indicates that the adsorption process becomes slow with
6 increasing time. This is because initially the CR molecules move towards octadecyl
7 amine LB monolayer in a fast diffusive process. After that few CR molecules on the
8 film surface should change their conformation to accommodate further CR molecules
9 in films. This is a slow process as the steric and electrostatic hindrance must be
10 overcome. Thus slow down the adsorption process. If we look at the absorption
11 spectra it is observed that the absorbance band positions for the films with immersion
12 time up to 10 minutes remains same. For 15 minutes immersion time the band shifts
13 by 5 nm and for 20 minutes or more immersion time the red shift is about 7 nm.
14 This may be due to the conformational change of CR molecules. The conformational
15 change of CR molecules starts with immersion time greater than 10 minutes.
16 Consequently it affects the absorption spectra.

17 The kinetics of adsorption of conducting polymer in self assembled films has
18 been discussed by Rubner *et al* [27]. They observed that in the first 3 minute of
19 adsorption the amount of adsorbed polymer increased with $t^{1/2}$, thus suggesting that
20 the adsorption could be diffusion controlled as in a Langmuir-Schaefer type adsorption
21 [27]. However, the calculated effective diffusion coefficient for various polymer
22 concentrations varied over four orders of magnitude which prompted them to conclude
23 that the Langmuir-Schaefer relationship is not valid for their system in the time regime
24 accessible by UV-vis experiments. Raposo *et al* [28] demonstrated the kinetics of
25 adsorption of poly (O-methoxyaniline) (POMA) via self assembly. The showed that
26 the adsorption of POMA can't be explained by a $t^{1/2}$ dependence even for the first
27 minutes of immersion, as a very sharp increase occurs in the initial stage. Rather a
28 two step process during adsorption has been suggested [28].

29
30 In an attempt to fit the adsorption vs. time data we tried using a single function
31 given in equation (1).

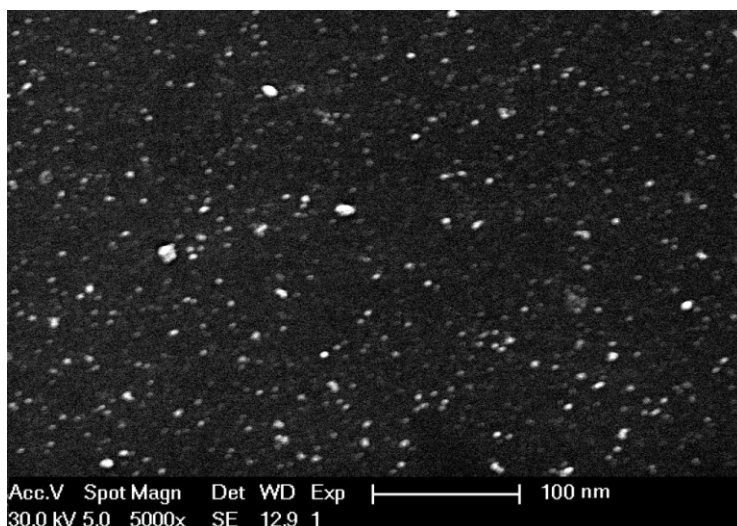
$$32 \quad A = K[1-\exp(-t/\tau)] \quad [1]$$

33 Where A is the absorbance taken as proportional to the amount of adsorbed material,
34 K is constant and τ is the characteristics time. The fitted curve is also shown in Fig.
35 5 (black curve).

36
37 It is found that the calculated data are in well agreement to that of the
38 experimental data. This suggests that the adsorption behaviour is of a first order
39 kinetic process with characteristics time 4 minute and $k = 0.11$.

1 **Scanning electron microscopy :**

2 UV-Vis absorption studies of ODA-CR complex film suggests the formation of ordered
 3 aggregates or associated species in LB films due to the adsorption of CR in ODA
 4 LB films. To confirm this we have employed traditional structural studies namely,
 5 scanning electron microscopy (SEM). Fig. 6 shows the scanning electron micrograph
 6 of the 10 layer ODA-CR complex film. The aggregates with sharp and distinct edges
 7 correspond to the three-dimensional aggregates of ODA-CR complex species in the
 8 complex films. The smooth background corresponds to the ODA. The formation of
 9 distinct crystalline domains of ODA-CR complex species, as evidenced from the SEM,
 10 provides compelling visual evidence of aggregation of CR in the complex LB films.
 11



29
30 Fig. 6. SEM of 10 layer congo red adsorbed ODA LB film.

31
32 **SUMMARY**

33 In conclusion our results show that water soluble CR molecules can be incorporated
 34 onto Langmuir-Blodgett (LB) films through adsorption of CR molecules onto cationic
 35 ODA Langmuir-Blodgett (LB) films. Ionic interaction occurred between the anionic
 36 dyes in aqueous solution to the long chain amine in LB films. The presence of CR
 37 molecules in the adsorbed LB films has been confirmed by ATR-FTIR spectroscopy.
 38 Reaction kinetics of adsorption has been monitored by absorption spectroscopy. It has
 39

1 been observed that the specific absorbability of CR molecules increases with increasing
2 numbers of ODA layers. However, the penetration of CR molecule into ODA LB
3 films is a rate determining steps in the adsorption process. Twenty minutes are
4 required to achieve the adsorption equilibrium. A comparison of fitted curve of the
5 reaction kinetics to that of the observed one reveals that the reaction kinetics between
6 CR and ODA LB films is of first order kinetic process.

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9
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