Spectroscopic studies on Rhodamine B intercalated K-10 montmorillonite aqueous dispersions

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Abstract: In this paper, the optical absorption and fluorescence studies on rhodamine B (RB) intercalated acid activated K-10 montmorillonite dispersions is presented. The aqueous dispersions were prepared from the dried dye intercalated montmorillonite. The absorption and fluorescence peaks of RB dispersions show a bathochromic shift with respect to the dye concentrations. The samples have a fluorescent emission at 421 nm which is having an intensity variation depending on the concentration of the dyes. The behaviour of samples of same concentration prepared by two different routes is also presented.

1. Introduction:
Clay minerals are attractive hosts for the intercalation of dye molecules. Dye molecules are incorporated in the clay mineral network with strong dye and host matrix interactions. Dye intercalated materials are exploited in modern photochemistry and photophysics due to their transparency in the visible wavelength region and their optical activity [1]

2. Materials and methods:

2.1. Dye adsorption from solution
1g K-10 was treated with 100 ml RB dye solution (concentration $10^{-5}$, $10^{-4}$ and $10^{-3}$ M respectively) and stirred magnetically for 24 h. It was then centrifuged, Soxhlet extracted with deionised water and dried at 120 °C for 12 h. The samples were designated as KRB–Z where –Z denoted the concentration. To measure the maximum adsorption capacity, the same process was repeated with $10^{-3}$ M solution for three times. The sample was denoted as KRB–M [2].

2.2. Ultrasonicated dye adsorption
About 100 ml of the dye solution ($10^{-3}$ M) was mixed with 1 g clay and was subjected to ultrasonic treatment. After the required time, the solution was allowed to settle overnight, centrifuged, washed and air dried. It was subjected to Soxhlet extraction with distilled water to remove any weakly adsorbed dye and further dried at 120°C for 12 h. The sample was designated as KRB-S.
2.3. Dispersions of dye intercalated montmorillonite

The aqueous dispersions of the above mentioned samples were prepared by ultra-sonicating 0.1g of each of the samples in 100 ml water for 10 minutes. To check the absorption behaviour of K-10, 0.1g was dispersed in 20ml.

2.4. Optical characterisation

The absorption and the fluorescence spectra of the aqueous dispersions were noted using spectrophotometer (JASCO V-570) and fluorescence spectrophotometer (Varian, Cary Eclipse).

3. Results and Discussions

3.1. Optical Absorption Studies

The main absorption peak of RB at 555 nm in all samples was bathochromically shifted (figure 1). KRB-3 and KRB-S showed the same peak around 580 nm but the intensity of KRB-S was higher. The other main peaks (357 and 257 nm) of RB appear as the RB concentration in the clay mineral increases. KRB-M showed broad absorption spectra with peaks at 537, 560, 572 and 590 nm. The absorption spectra of the KRB-5 and K-10 were similar as the amount of dye loaded was very low in KRB-5. K-10 had a shoulder near 250 nm as in the case of all montmorillonites [3] and the RB had a peak around the same wavelength. The highly concentrated K-10 (0.1g in 20ml water) dispersion had small peaks near 371, 421, 521 and 683 nm (inset of figure 1).

All the dye intercalated samples showed bathochromic shift which may be due to the formation of J- aggregates [4]. The more absorbance shown by KRB-S with respect to KRB-3 may be due to the more uniformly distributed dye molecules and the minimisation of cluster formation by ultra sonication. However, they had the same dye concentration and showed the same peak at 580nm. KRB-M showed a broad absorption spectrum due to dye molecular aggregation on the surface of the clay minerals arising from the hydrophobic interactions and the molecular exciton model explains this [4].

Though montmorillonites are weak absorbers in the visible and NIR range [3], the weak peaks of K-10 (figure 1- inset) can be attributed to the silica and alumina layers present in their network. The presence of the dye in the network of the RB intercalated K-10 enhances the absorption at these peaks.

The adsorption of rhodamine onto clays usually leads to the metachromatic effect in the absorption spectra, whereby the main absorption band is shifted to higher energies [1]. In montmorillonite,
metachromasy results from \( \pi \) interactions between the adsorbed dye and the oxygen plane of the aluminosilicate [5].

The J-aggregates, which are formed more rarely than the H-aggregates, absorb light of lower energies and exhibit luminescent properties [6]. The bathochromic shift in the absorption spectra of the samples was due to the formation of J-aggregates. But, KRB-M showed the presence of the H-aggregates as evident from the hypsochromic shift and the broadened nature of the main absorption peak of RB.

3.2. Fluorescence studies

The samples showed a fluorescence peak at 421 nm when excited with 371 nm (figure 2). This may be arising from the silica layer. All the samples were excited at the same conditions and it was observed that the peak intensity increased for KRB-5 than that of K-10. The fluorescence intensity was decreased for all other samples as the dye concentration was increased. Similar results were obtained with 250 nm excitations (figure 3).

Samples excited using 555 nm showed a bathochromic shift as the amount of the intercalated dye increases (figure 4). Since KRB-3, KRB-S and KRB-M were prepared from dye solutions of same molarity, they showed almost same emission intensity, but KRB-M peak was bathochromically shifted.

The fluorescence peak intensity comparison of KRB-3 and KRB-S from figures 2-4 shows that the emission peak intensity for KRB-S is slightly less than that of KRB-3. KRB-S also shows a broadened nature for fluorescence though both KRB-S and KRB-3 have the same absorption peak at 580 nm. But, KRB-S has a higher absorption.

When dye molecules are excited, their excitation energy gets transferred to silica in the matrix so that fluorescence of silica at 421 nm is enhanced as in figure 2. The 421 nm emission of silica showed fluorescence quenching due to the presence of more dye molecules in the clay network which inhibits the emission from the silica layers. As the concentration of the RB is increased the radiative relaxation of dyes become more predominant resulting into fluorescence quenching at 421 nm and enhancement in 580 nm region. The same intensity of KRB-3 and KRB-S also confirms the emission from the silicate layer because they are of the same concentration though they are prepared by different methods. Porous silicon [7], silica spheres [8] and silicon nanoparticles [9] when excited near 370 nm.
showed an emission around 420 nm. Since, no peak shift is observed for this emission for all the samples we can conclude that the emission arises from the montmorillonite itself. The fluorescence emission of the K-10 colloid also confirms this. However, the presence of a small amount of dye in the network enhances the fluorescence intensity. Moreover, fluorescence quenching can be observed as the amount of dye in the dispersions increases. The fluorescence quenching is due to the energy transfer from the excited state of the monomers to the aggregated species. This transfer can be via either an electron exchange or coulombic interactions. There could also be other effects like light scattering, adsorption by the solid surface [10], deformation to a non-planar conformation upon adsorption etc., on the fluorescence of the dye in the adsorbed state, which may significantly reduce the fluorescence yield [6]. Montmorillonite intercalated with RB cations showed that the bands corresponding to the silicate layer remained unchanged after intercalation [11]. This means that the silicate layers can be treated as rigid bodies during energy minimization.

The fluorescence band of the rhodamine-clay system is shifted to higher wavelength compared with that of the rhodamine in aqueous solution [11]. In addition, the emission band becomes broader as a consequence of the structural inhomogeneity of the rhodamine-clay system, where the surface structure may differ significantly from that in the interlayer space [11]. The bathochromic shift observed in the case of KRB-M (figure 4) is due to the clustering and dense packing of the dye molecules which arises from the repeated adsorption. The fluorescence intensity of the KRB-M was less compared to KRB-3 and KRB-S which was attributed to the usual fluorescence quenching in highly concentrated solutions. The changes in fluorescence band profile with increasing RB concentration reflect the changes in relative proportions of monomers, dimers, and higher aggregates adsorbed on the external surface and intercalated into the interlayer space.

4. Summary
The emission intensity of K-10 montmorillonite can be enhanced by the addition of a small amount of dye in the network. The dye addition increases the absorption peak intensity of K-10. The increase in dye concentration shows bathochromic shift in peaks due to the formation of J-aggregates. The emission intensity decreases as the amount of the dye increases which is due to the fluorescence quenching. KRB-S prepared by ultra-sonication method shows more absorption and less fluorescence than KRB-3 due to the uniform distribution and minimised clustering of dye molecules.

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