Chapter 2

Thermal and optical characterization of dye intercalated montmorillonites

Abstract

The first section of the chapter presents thermal diffusivity (TD) measurement on dye intercalated commercial K-10 and KSF montmorillonites carried out by photoacoustic (PA) technique. Methylene blue (MB) adsorbed K-10 samples showed distinct TD changes due to a regular decrease in specific surface area and pore volume as a result of pore filling by dye molecules when compared to the ordered KSF samples which do not have a regular change in specific surface area and pore volume. PA method was carried out to determine TD of some other industrially important dyes - auramine O (AO), malachite green (MG) and rhodamine B (RB) - adsorbed K-10. The repeatedly adsorbed MB and AO samples showed a lesser TD than the samples which have adsorbed once. The sintered MB samples showed a higher TD though they exhibited a similar trend as un-sintered pellets. The optical absorption and fluorescence studies on RB and MG intercalated acid activated K-10 montmorillonite dispersions prepared from the dried dye intercalated montmorillonite are presented in the second section. The absorption and fluorescence peaks of RB dispersions showed a bathochromic shift with respect to the dye concentrations. The samples exhibited a fluorescence emission at 421 nm which is attributed to silica and is having an intensity variation depending on the concentration of the dyes.
Dye intercalated montmorillonites

2.1. Prologue 95
2.2. Sample details 96
2.3. Dye molecular aggregates- Molecular exciton coupling theory 96
2.4. Section I - Thermal characterization of dye intercalated montmorillonites using photoacoustics 101
   Part A: Thermal diffusivity dependence on host montmorillonite 104
   Part B: Thermal diffusivity dependence on sintering temperature 111
   Part C: Thermal diffusivity dependence on dye 114
2.5. Section II - Spectroscopic studies on dye intercalated K-10 montmorillonite aqueous dispersions 122
   Part A: Rhodamine B intercalated K-10 123
   Part B: Malachite green intercalated K-10 131
   Part C: Dispersions of KSF and K-10 134
2.6. Summary 136
2.7. References 137

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2.1. Prologue:

The developments of complex materials necessitate a finer characterization of their physical properties and a better knowledge of the physical phenomena that determine their behaviour at the macroscopic level. Synthetic dyestuffs are used extensively in textile, paper, printing industries and dye-houses. The dyestuff usage has been increasing day by day because of the tremendous increase of industrialisation and man’s urge for colour.\textsuperscript{[1]} Dye stuff pollution through the waste-water generated in the industry causes adverse aesthetic effects on organisms.\textsuperscript{[2-5]} Although various industries are responsible for contributing hazardous organic wastes into our water supplies, the textile industry is of particular concern. Anywhere from 1% - 20% of the world’s production of dyes are lost during dyeing processes and is released as textile effluents. These effluents are generally quite toxic. Of all the dyes available, approximately 50% to 70% are aromatic azo compounds, which are known carcinogens. Waste-waters from dyeing and textile industries easily produce toxic trihalomethanes when chlorinated.\textsuperscript{[6]} Removal of colour from dye bearing waste-water is a complex problem because of the difficulty in treating such waste-waters by conventional treatment methods.\textsuperscript{[7]} Several physico-chemical processes\textsuperscript{[1, 8-17]} like electro and chemical coagulation,\textsuperscript{[17-25]} ozonization,\textsuperscript{[26, 27]} membrane filtration,\textsuperscript{[28-35]} electrolysis,\textsuperscript{[20, 36]} oxidation,\textsuperscript{[20-22, 37-42]} biodegradation,\textsuperscript{[10, 42-57]} flocculation,\textsuperscript{[19, 27]} precipitation,\textsuperscript{[58-61]} crystallisation,\textsuperscript{[58]} froth flotation, anaerobic decolourisation,\textsuperscript{[62]} reverse osmosis,\textsuperscript{[17, 63, 64]} ion exchange,\textsuperscript{[21-23, 61, 65-70]} reduction,\textsuperscript{[43]} biological stabilisation\textsuperscript{[71-73]} and adsorption\textsuperscript{[74, 75]} by activated charcoal\textsuperscript{[5]} or carbon\textsuperscript{[76]} have been developed for the dye exclusion during the waste-water treatment.\textsuperscript{[77]} Some of these methods are selective,\textsuperscript{[78]} expensive, less efficient,\textsuperscript{[40, 79]} of limited applicability, may need special infrastructure and even produce wastes, which are difficult to dispose of. Among all these treatment processes adsorption is found to be highly effective and non-destructive in nature.\textsuperscript{[5]} A variety of physical, chemical and biological methods have been used for the dye exclusion during the waste-water treatment\textsuperscript{[80-92]} and diverse clays can be employed for dye adsorption.\textsuperscript{[93-99]}

Nano-composite materials, which contain organic dyes incorporated in a solid matrix, are used in various applications, such as optical sensors, devices for photo-induced switching, solid lasers and in memory media.\textsuperscript{[100]} The optical properties of the dyes crucially depend on the properties of the hosts which are extremely vital in the applied research of materials.\textsuperscript{[101]}
2.2. Sample details:

2.2.1. Commercial clay samples: KSF and K-10:
The commercially available montmorillonites K-10 and KSF were purchased from Fluka, Sigma- Aldrich Chemicals Pvt. Ltd. KSF and K-10 are two differently modified acid-activated montmorillonites; the extent of leaching is lower for KSF than for K-10. K-10 clay mineral has a layered structure. Each layer is composed of one octahedral alumina sheet sandwiched between two tetrahedral silica sheets. The sheets are connected via Si-O-Al linkages. In the silica sheet, isomorphous substitution of Si by Al occurs whereas in the Al sheet, isomorphous substitution by Mg and Fe occurs. This leads to a net negative charge on the layers which are compensated by exchangeable cations Na\(^+\), K\(^+\), Mg\(^{2+}\) and Ca\(^{2+}\). Many such layers are stacked together with an inter-layer spacing of ~ 1 nm. Acid leaching leads to the removal of some Al and Fe from the framework and also results in the replacement of the exchangeable cations with H\(^+\) which imparts acidity to the system. As a result of acid treatment, de-lamination takes place and a disordered structure results. Acid activated clays in nature can be used as efficient decolourising agents due to their enhanced bleaching power arising from increased specific surface area (SSA), meso/ micro- pore volume (PV) and surface acidity of clay samples.

2.2.2. Sample preparation- Dye adsorption from solution:
1g of clay was treated with 100 ml dye solution (10\(^{-5}\) M, 10\(^{-4}\) and 10\(^{-3}\) M concentration respectively) and stirred magnetically for 24 hours. It was then filtered, Soxhlet extracted with deionised water and dried at 120 °C for 12 hours. To measure the maximum adsorption capacity, the same process was repeated with 10\(^{-3}\) M solution for three times. These powdered samples were used for the experiments.

2.3. Dye molecular aggregates - Molecular exciton coupling theory:
Organic dyes may change their colour and other optical and chemical properties in relation to their chemical environment. Therefore, dyes have often been used as probes or sensors in various scientific fields. The idea of using dyes to help identification of clay minerals or to probe their properties first appeared several decades ago. The molecular aggregation is due to hydrophobic interactions, which is a general tendency of non-polar molecules to associate physically in aqueous solutions. The presence of non-polar molecules in water disrupts the hydrogen bond network of water molecules, resulting in a loss of translational and rotational degrees
of freedom of the solvent within the hydrophobic hydration shell. Such a mechanism is generally referred to as a loss of entropy of the system.\textsuperscript{[116]}

2.3.1. The exciton model:

Absorption spectra of dye molecular aggregates usually show large differences when compared to the individual molecules. Optical properties of the dye molecular aggregates are explained by the molecular exciton model\textsuperscript{[117]} (Figure. 2.1). The model considers electrostatic interactions between transition moments of individual dye molecules, called an exciton coupling. Exciton coupling leads to the splitting of the excited electronic state of the molecule, the magnitude of which depends on distances between interacting transition dipoles and their arrangement in space. Two excited energy levels are the result of electrostatic attraction and repulsion between the transition moments.\textsuperscript{[118]} According to exciton theory, the dye molecule is regarded as a point dipole and the excitonic state of the dye aggregate splits into two levels through

\* Exciton is an electrically neutral excited state, often regarded as a bound state of an electron and a hole.
Dye intercalated montmorillonites

the interaction of transition dipoles. A transition to the upper state in parallel aggregates having parallel transition moments and to a lower state in a head-to-tail arrangement with perpendicular transition moments leads to hypsochromic† (blue) and bathochromic‡ (red) shifts, respectively (Figure 2.1).

2.3.2. Angle of slippage (α):
The angle between the long axis (line passing through the center of the aggregates or parallel to it) and one of the parallel molecule is called the ‘angle of slippage’ or the ‘slip angle’ or the ‘slippage angle’. Large molecular slippage (α < 32°) results in a bathochromatic shift (J-aggregate), and small slippage (α > 32°) results in a hypsochromic shift (H-aggregate). Most importantly, the exciton theory is valid only when the interaction between orbitals of constituent molecules is negligible.[116]

2.3.3. H and J aggregates:
There are two main types of dye molecular aggregates, formally and originally assigned according to their optical properties, but closely related to their structure and the type of intermolecular association. Certain molecular aggregates consisting of organic dyes are remarkable in exhibiting an intense and very narrow absorption peak, known as a J-band§ or Scheibe-Peak, which is red-shifted away from the region of monomer absorption. Apart from those dyes showing the J-band on aggregation, there are also dyes for which the absorption maximum is shifted to higher energies forming H-band**. The width of the resulting absorption band is comparable to that of the monomeric dyes and shows a complicated vibrational structure.[119]Scheibe[120] found that for some dyes, the aggregate absorption band is red-shifted with respect to that of the monomer. These are the J-aggregates showing a very narrow band whose position is well-predicted by a theory ignoring intra-molecular vibrations. By contrast, other dyes showed a shift towards the blue (i.e. higher absorption energies) and were termed H-aggregates (hypsochromic shift). Unlike the J-band, the line-shape of the H-band

† Hypsochromic shifts are often referred to as blue shifts in photochemistry in which the frequency of an electromagnetic wave emitted by a source moving towards the observer is shifted towards the blue side of the electromagnetic spectrum (i.e., its wavelength is decreased, or its energy is increased).
‡ Bathochromic shift is a change of spectral band position in the absorption, reflectance, transmittance, or emission spectrum of a molecule to a longer wavelength (lower frequency). This can occur because of a change in environmental conditions. Bathochromic shifts are often referred to as red shifts. It has no relation to Doppler shift or other wavelength-independent meanings of redshift.
§ J for Jelley, one of the first workers who investigated these shifts.
** H for hypsochromic
Optical and thermal characterization.....

generally shows a rich vibrational structure and has a width of the order of that of the monomer band. Some substances exhibit both a J-band and a H-band on aggregation. As a result of this complicated vibrational structure, although there exists a considerable literature on the simpler case of the J-band, there have been only a few theoretical articles which address the line-shape of H-aggregates.\[119, 121-124\]

Extensive studies on J- and H- aggregates have resulted in the proposal that these aggregates exist as a one-dimensional assembly in solution that could be in (a) ladder type, (b) staircase type, or (c) brickwork type of arrangement (Figure 2.2).

![Figure 2.2: Schematic representation of the different arrangement of dyes in the solid surface and in solution. (a) ladder type, (b) staircase type and (c) brickwork type.](image)

H-aggregates are based on a sandwich-type intermolecular association\[125\](Figure 2.1a). Less frequent J-aggregates (Figure 2.1b) are formed by head-to-tail intermolecular interactions.\[126\] In the H-aggregates, coupled transition moments could be oriented in either the parallel or anti-parallel fashion. The anti-parallel orientation ($\Psi^-$) of an H-dimer has a lower energy state, due to the electrostatic attraction between the transition moments. In the J-aggregates, anti-parallel moments ($\Psi^-$) result in a higher energy due to electric repulsion. Resulting dipole for the anti-parallel arrangements of the transition moments is always zero; and therefore, the transitions to such states are symmetry forbidden. Only the transitions to the states with parallel orientations ($\Psi^+$) are allowed, which is to the lower energy state for the J-aggregates and to the higher energy state for the H-aggregates. The perfect H- and J-aggregates are just two ideal states of all possible forms and variations of molecular assemblies. Many dyes may form such assemblies, which include the structural features of both the H- and J-aggregates. In such cases, the molecular aggregates absorb light with energies corresponding to both the higher and lower energy states. The assignments of the bands absorbing at the low- and high-energy transitions indicate the structural features of the dye supramolecular assemblies. Unfortunately, there are serious problems to identify structures of molecular assemblies from the spectrum when several types of assemblies are present in a mixture.\[116\]
Dye intercalated montmorillonites

H- and J-aggregates have their optical properties according to their structural packing. Actually the difference in structure is due to the different slip angles of the stacked molecules. It is generally agreed that both H- and J-aggregates are composed of parallel dye molecules stacked plane-to-plane and end-to-end and form two-dimensional dye crystal molecule, according to exciton theory, and is regarded as a point dipole. When molecules or chromophores are aligned parallel, two new excitonic bands are generated according to a simple exciton theory: one with higher energy and the other with lower than the monomer energy level as mentioned earlier.

H-dimers or larger H-aggregates would require very short distances between neighbouring negatively charged sites. The clay surface would need to be almost fully covered with the dye in order to form homogeneous two-dimensional coverage of only H-aggregates.\(^{[101]}\) In H-aggregates, the lower state is much stabilised. So the transition from the excited state to the ground state is very fast and happens mostly between the excitonic bands with vanishing dipole moments as a result of which most of the energy losses are non-radiative like thermal losses.\(^{[116-128]}\) Due to this reason the H-aggregates have very low fluorescence which is difficult to measure by regular techniques. The H-aggregates have large stoke’s shift with low fluorescence yield. The transition energy of such aggregates is explained by the differences in the geometry of the molecular packing within the aggregates,\(^{[126, 127]}\) and thus, these aggregates are structurally distinguished by the different slip angles between the molecular transition moment and the long axis of the aggregates - small slip angle for the J-aggregates and a large slip angle for the H-aggregates.

In J-aggregates, transitions are allowed only to low energy states and as a consequence, J-aggregates are characterised by small stoke’s shift fluorescence with a high quantum yield.\(^{[129]}\) J-aggregation is due to only partial, head-to-tail association between the dye cations.\(^{[118, 130]}\) The formation of large two-dimensional J-aggregates does not require full coverage on the clay surface. The distance between two neighbouring negative charge sites is larger for the formation of stable J-dimer than that required for the formation of H-dimer. With decreasing layer-charge density the distances between neighbouring dye cations increase. Consequently, the sandwich type association with H-aggregates association breaks down in favour of J-aggregates with a ‘head-to-tail’ type association of transition dipoles and less dense packing of the dye cations.\(^{[101, 118]}\) Ordered J-aggregates usually exhibit sharp bands in the spectra.\(^{[126, 127]}\) Absence of any sharp bands of studied dyes indicates the formation of less-ordered J-aggregates.
In the systems with clay minerals, the dye aggregation is also sensitive to the surface properties of clay mineral templates and depends on the type of exchangeable cations.\cite{131, 132} It has been proven that the main parameter which controls dye molecular aggregation on clay mineral surfaces is the layer charge.\cite{116} Lower charge densities induce longer distances between adsorbed dye cations. Consequently, the monomeric form of isolated dye cations is preferentially adsorbed in such cases. If the layer charge density of clay minerals is sufficiently high, the distances between neighbouring adsorbed dye cations are smaller and H-aggregates are preferentially formed. Less densely packed J-aggregates resulting from a head-to-tail coupling\cite{127} occur less frequently under specific conditions on the surfaces of clay minerals of medium to low charge densities.\cite{116, 127, 131-134}

2.4. Section I - Thermal characterization of dye intercalated montmorillonites using photoacoustics:

2.4.1. Preamble:
The thermal diffusivity (TD), a thermo-physical parameter, determines the diffusion of the heat through the sample. In ceramics, the thermal energy is basically carried away by phonons.\cite{135} The composition, structure and arrangements of phases determine the thermal properties of the ceramics. Morphological features like pores, grain boundaries, line defects etc. influence the propagation of phonons through the ceramic body.\cite{136, 137}

The photothermal techniques, based on the absorption of pulsed or modulated optical radiation and subsequent release of the absorbed energy through non-radiative de-excitation, are widely used, well established, non-contact, simple and highly sensitive for the determination of the thermal and optical properties of a variety of materials.\cite{106, 107, 135-143} This non-radiative relaxation produces temperature fluctuations in the sample. These temperature fluctuations facilitate an indirect measurement of the thermal and optical properties of the sample.\cite{106, 107, 136, 144-147} The laser induced photoacoustic (PA) method has gained more popularity due to its simple, elegant experimental technique as well as the versatility in employing different configurations to measure the required thermo-physical parameters with great accuracy. In PA, a periodic heat flow from the solid to the surrounding gas produces pressure variations within the cell. This is the primary source of the acoustic signal and is detected by a sensitive microphone.\cite{145} Thermal characterization contributes to the development and optimisation of new materials.
Dye intercalated montmorillonites

The surfaces of clay minerals exhibit strong affinity to dye i.e., montmorillonites show an interesting capacity in separating dyes from water.\cite{97, 125, 149} They are found to be an efficient adsorbent for the uptake of the dyes\cite{102, 150} and their utilisation for further applications like ‘wall plastering’ demands their thermal characterization. The curing time required for these materials may be less if their TD is higher. Moreover, if the stability of the dye in montmorillonite host material is higher, the colour fading of the walls will also be lesser.

2.4.2. Thermal diffusivity measurement - photoacoustic theory:

The Rosencwaig and Gersho (RG) theory of the PA effect\cite{147} confirmed by more complete calculations\cite{151, 152} shows that pressure variations at the front surface of an optically thick sample depend on the TD of the sample.\cite{153} As the RG theory indicates, the PA effect is primarily dependent on the relationship between three ‘length’ parameters of the sample: the sample thickness \( l \), the optical absorption length \( l_\beta \) and the thermal diffusion length \( \mu = \left(\frac{2\alpha}{\omega}\right)^{1/2} \). While dealing with an optically very opaque solid, as long as the solid is not photoacoustically opaque (\( \mu < l_\beta \)), only the light absorbed within the first thermal diffusion length contributes to the acoustic signal. The RG theory also predicts that for an opaque material (\( l_\beta < l \)), the PA signal will vary as \( \omega^{-1} \) when \( \mu > l_\beta \) and as \( \omega^{-3/2} \) when \( \mu < l_\beta \) by varying the chopping frequency.\cite{146, 147} Charpentier et al. (1982) demonstrated that the pressure variations at the front surface of an optically thick sample can be written as the product of two terms. One depends on the modulation frequency \( f \) of excitation and the other independent of \( f \). When \( f > f_c \) the variations of the frequency dependent term is independent of the diffusivity and when \( f < f_c \) the variations in pressure depends on the sample diffusivity. Here the characteristic frequency \( f_c \) is given by the relation: \( \alpha = l^2 f_c \). As thermal diffusion length is a function of chopping frequency, PA amplitude spectrum has a slope change from -1 to -1.5 at this particular frequency \( f_c \) depending on sample thickness. Thus by knowing the sample thickness \( l \) and the transition frequency \( f_c \), the TD of the sample can be evaluated using the expression \( \alpha = l^2 f_c \). A slope variation occurs at \( f_c \) in the log (amplitude) versus log (frequency) plot and knowing the sample thickness \( l \), one can find the TD.\cite{106, 107, 136, 137, 153, 154}
2.4.3. Experimental setup:

![Schematic representation of photoacoustic experimental setup.](image)

*Figure 2.3: Schematic representation of photoacoustic experimental setup.*

The schematic representation of the experimental setup is given in *Figure 2.3*. Optical radiation from an Argon ion laser at 488 nm, 25 mW (cw, Liconix 5300) with a stability of ±0.5% was used as the source of excitation. It was intensity modulated using a mechanical chopper (HMS Light Beam Chopper 230) before it reached the sample. Detection of the PA signal was made using a sensitive electret microphone (Knowles BT 1754). The amplitude of the PA signal was measured by means of a dual phase lock-in-amplifier (Stanford Research Systems SR 830). The reflection mode geometry (*Figure 2.4*) of the open cell PA technique was used in this experiment.

![Reflection mode geometry of photoacoustic setup.](image)

*Figure 2.4: Reflection mode geometry of photoacoustic setup.*

2.4.4. Sample details:

Pelletised samples were used for PA studies. The pellets were prepared using a hydraulic pellet press at a pressure of $10^6$ kgm$^{-2}$. The sample thickness was measured using Mitutoyo micrometer, which can measure thickness with an accuracy of ± 1µm.
2.4.5. Part A: Thermal diffusivity dependence on host montmorillonite:

A1. Introduction:
The variation in TD of the dye intercalated montmorillonites was investigated and the results are presented. The effect of dye loading on TD in two types of montmorillonites- KSF and K-10- was studied using the PA technique. The effect of repeated adsorption on the TD of the clay samples was also studied. The TD dependence of selective dye adsorption and porosity of two types of montmorillonites are presented here. An attempt is made to understand the change in TD of methylene blue (MB) adsorbed montmorillonites and to make suitable materials with tuneable thermal properties because TD is a thermo-physical quantity which can be obtained directly from the PA studies.[155]

MB is a toxic, halogenated, aromatic hydrocarbon that is seen in the textile factory effluent streams. Clay mineral surfaces have strong affinity to MB ions.[125, 156, 157] ‘Montmorillonites’ exhibit a remarkable capacity in separating MB from water[149] and are found to be a competent adsorbent for the uptake of the dyes.[102] The thermal characterization of the dye-montmorillonite complexes is necessary to find out further applications.[158]

A2. Materials and methods:

A2.1. Sample details:
MB was purchased from Sd fine Chem. The MB adsorbed samples were prepared as described in 2.2.2. The MB intercalated K-10 samples were designated as MB–Z where –Z denoted the concentration. The repeated adsorbed K-10 sample was denoted as MB–X. Similarly MB adsorbed KSF samples were named as KSFMB-Z. The repeated adsorbed KSF sample was designated as KSFMB-X.

A2.2. Reflectance spectra measurement:
The MB intercalated K-10 and KSF samples taken in pellet form were employed for the PA studies. The Model SLM-468 single reflection attachment of a JASCO V-570 UV/VIS/NIR spectrophotometer was used to measure the relative reflectance of these samples using the forward reflected light from the aluminium-deposited plane mirror as reference at an angle of incidence ~ 5˚.
A2.3. Specific surface area and porosity measurement:
The Specific surface area (SSA) and porosity measurements were made in a Micromeritics Tristar 3000 surface area & porosity analyser. SSA was calculated using the BET (Brunauer Emmett Teller) interpretation of the nitrogen adsorption isotherm at $p/p_0 < 0.3$. Pore size distribution was calculated from t-plot measurements using the Barrett Joyner Halenda (BJH) method. Prior to the analysis, the samples were degassed in nitrogen at 120 °C for 12 hours.

A2.4. TG/DTA measurement:
Perkin Elmer, Pyris Diamond TG/DTA instrument was used for the TGA measurement at a rate of 20°C/min under nitrogen atmosphere conditions.

A3. Results and discussions:
A3.1. Optical reflectance study:

Figure 2.5: Reflectance spectra of methylene blue (MB) intercalated K-10 pellets. Inset: Absorption spectrum of 0.1mM methylene blue aqueous solution.

†† DTA- differential thermal analysis.
‡‡ The thermo-gravimetric analysis (TGA) is a commonly used method to determine the degradation temperature of the organic and inorganic components in the materials.
Dye intercalated montmorillonites

All samples under investigation were visibly well opaque and hence a transmission spectrum of the specimen was impossible at 488nm. Lindberg and Snyder\cite{159}(1972) from their diffuse reflectance spectral studies of clay minerals observed that montmorillonite minerals had a higher absorption coefficient in the near UV and blue regions of the visible spectrum. The qualitative character of the absorption spectra of the material could be obtained from the reflectance spectrum. The reflectance spectra of the MB intercalated K-10 and KSF samples are given in Figure 2.5 and Figure 2.6 respectively.

The bandwidth and the location of the monomer band are affected by the increasing loading. An increase of loading also induces the formation of dimers and higher aggregates.\cite{160}

![Figure 2.6: Reflectance spectra of methylene blue (MB) intercalated KSF pellets Inset: Absorption spectrum of 0.1mM methylene blue aqueous solution.](image)

A3.2. Photoacoustic study:

A typical variation of the PA amplitude spectrum for MB-5, characterised by the slope change is given in Figure 2.7. All other samples showed similar behaviour, in accordance with the RG theory\cite{147}. The measured TD values of the MB intercalated K-10 samples are given in Table 2.1 and those of KSF samples are given in Table 2.2. Clay samples and soils possess TD of the order of $10^{-7}$ to $10^{-4}$ m$^2$s$^{-1}$.\cite{106, 107, 144, 161-165}
However, TD is a transient thermo-physical parameter which measures how effectively phonons carry heat through the sample. In the case of pelletised samples, particles are compressed together. Hence, the average inter-particle distance is less and allows easy propagation of thermal waves through the sample. Thereby, they yield relatively high TD values. The preparation conditions and procedure affect the thermal parameters of these kinds of ceramic materials. As shown in Figure 2.8, MB decomposed at > 200 °C while the dye intercalated clay mineral was stable up to 400°C.

*Figure 2.7*: Photoacoustic (PA) amplitude plot of the MB-5 pellet.

*Figure 2.8*: TGA of (a) MB-X, (b) pure methylene blue and (c) KSFMB-X.
### A3.3. Effect of pore volume on thermal diffusivity:

The porosity of a pellet is an important property to ascertain its quality. In general, it affects the compressive strength, thermal conductivity and also plays an important role in controlling its swelling during its reduction. Nishioka reported that, not only porosity but pore size and their distribution also have an effect on thermal conductivity. It was explained that pellet with lower average pore size has more solid/pore interface area for same porosity which adds resistance to heat transfer. This effect of solid/pore interface area will be more predominant in small pore size ranges, where increase in specific surface area of pore is more for a similar decrease in pore sizes. The porosity of a pellet controls thermal conductivity by two ways:

1. Decrease in porosity increases solid/solid contact area and increases solid state conduction.
2. At the same porosity level, decrease in average pore size increases the pore/solid surface area, which in turn increases resistance to heat conduction.

The net change in thermal conductivity with porosity will depend on the contribution by the above two factors. At high porosity level and with larger pores, decrease in porosity or PV will increase particle to particle contact area and decrease the pore/solid interfacial area. However, after certain pore volume/size the increase in contact area is likely to be less predominant than change in particle pore surface area. The decrease in pore size, at constant porosity, will increase pore/particle interface area with almost no change in contact area. This adds resistance to heat flow and decreases thermal conductivity. The decrease in porosity reduces the free zones of particle contact leading to a considerable increase in the material density. In porous materials this parameter may affect deeply the permeability and as a consequence, the TD and the thermal conductivity.
Effective thermal conductivity and TD of the pellet decreases gradually with increase in porosity. The decrease in TD and thermal conductivity must hence be attributed to the increase in SSA of pores and added resistance to heat conduction.\textsuperscript{[170]}

\textit{Table 2.2: Thermal diffusivity (TD) values of the KSF samples obtained at room temperature.}

<table>
<thead>
<tr>
<th>Dye loading (mg/g clay)</th>
<th>KSF samples</th>
<th>Sample thickness×10^{-3} m</th>
<th>TD ×10^{-4} m^{2}s^{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>32.0</td>
<td>KSFMB-3</td>
<td>0.982±0.001</td>
<td>0.931±0.002</td>
</tr>
<tr>
<td>3.2</td>
<td>KSFMB-4</td>
<td>0.971±0.001</td>
<td>0.898±0.002</td>
</tr>
<tr>
<td>0.32</td>
<td>KSFMB-5</td>
<td>0.980±0.001</td>
<td>0.893±0.002</td>
</tr>
<tr>
<td>96.0</td>
<td>KSFMB-X</td>
<td>0.931±0.001</td>
<td>0.864±0.002</td>
</tr>
<tr>
<td>0.0</td>
<td>KSF</td>
<td>1.029±0.001</td>
<td>0.625±0.002</td>
</tr>
</tbody>
</table>

The TD increased with increasing dye concentration. The dye adsorption changes the TD value and by controlled adsorption, samples with desired TD can be prepared. The presence of air in the porous network of K-10 contributed to a low TD value of 0.676×10^{-4} m^{2}s^{-1}. When a small amount of MB enters the matrix, it displaces some of the air which reduces the PV as seen in MB-5 and increases TD to 0.753×10^{-4} m^{2}s^{-1}. When larger amounts of MB was adsorbed, more of air was displaced resulting in decrease of porosity and subsequent increase in TD.\textsuperscript{[136]} The PV of the K-10 was decreased with increase in concentration of the dye molecules (\textit{Table 2.3}). The pores in the structure act as scattering centres for phonons and hence affect the phonon mean free path and consequently the TD value.\textsuperscript{[136]}

\textit{Table 2.3: Specific surface area (SSA) and pore volume (PV) obtained from N}_{2} adsorption measurements for the methylene blue (MB) intercalated K-10 samples.}

<table>
<thead>
<tr>
<th>Sample</th>
<th>SSA (×10^{3} m^{2}kg^{-1})</th>
<th>PV (×10^{-3} m^{3}kg^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>MB–3</td>
<td>166±5</td>
<td>0.307±0.001</td>
</tr>
<tr>
<td>MB–4</td>
<td>177±5</td>
<td>0.318±0.001</td>
</tr>
<tr>
<td>MB–5</td>
<td>181±5</td>
<td>0.336±0.001</td>
</tr>
<tr>
<td>MB–X</td>
<td>117±5</td>
<td>0.276±0.001</td>
</tr>
<tr>
<td>K-10</td>
<td>202±5</td>
<td>0.369±0.001</td>
</tr>
</tbody>
</table>

\textbf{A3.4. Effect of repeated adsorption on K-10:}
Repeated adsorption (sample MB–X) decreased the TD value (0.461×10^{-4} m^{2}s^{-1}) showing that the thermal properties of the samples could be changed by repeated
Dye intercalated montmorillonites

adsorption. On repeated adsorption of the dye the effective TD was reduced because of the low TD values of the dye. Dyes exhibit typical diffusivities of the order of 10^{-2} \text{ cm}^2\text{s}^{-1}.^{[140, 141]} \text{MB–X} had a well defined reflectance spectrum compared to MB–3 due to the larger amount of MB adsorbed (Figure 2.5). In MB–X, the thermal wave generation or propagation was less due to the presence of strongly interlinked dye molecules and these samples showed less TD. At maximum loading (MB-X), there was a drastic decrease in SSA and porosity as evidenced from N\textsubscript{2} adsorption measurements (Table 2.3). The lower TD may be due to the clustering and dense packing of MB molecules.^{[106, 107]}

A3.5. Pore volume effect on the thermal diffusivity of dye adsorbed KSF:
The dye intercalated KSF samples had higher TD than the pure KSF. But, TD of MB adsorbed samples did not show appreciable variation. Initially, SSA and PV increase due to the inter-layer expansion as a result of dye intercalation (Table 2.4). Dye molecules prevent access of nitrogen molecules into the pores at higher loadings resulting in lowering SSA and PV. The TD values of KSFMB-4(0.898 \times 10^{-4} \text{ m}^2\text{s}^{-1}) and KSFMB-5 (0.893 \times 10^{-4} \text{ m}^2\text{s}^{-1}) were similar (Table 2.2). This may be attributed to the greater SSA and PV of KSFMB-4 than that of KSFMB-5. The interlayer expansion may increase SSA and PV of the KSFMB-5 and KSFMB-4. As the dye concentration is increased, the enrichment of dye molecules decreases SSA and PV of the samples, as seen in case of KSFMB-3 and KSFMB-X (Table 2.4).

Table 2.4: Specific surface area (SSA) and pore volume (PV) obtained from N\textsubscript{2} adsorption measurements for the methylene blue (MB) intercalated KSF samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>SSA ($\times 10^3$ m$^2$ kg$^{-1}$)</th>
<th>PV ($\times 10^{-3}$ m$^3$ kg$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KSFMB–3</td>
<td>76±5</td>
<td>0.171±0.001</td>
</tr>
<tr>
<td>KSFMB–4</td>
<td>98±5</td>
<td>0.186±0.001</td>
</tr>
<tr>
<td>KSFMB–5</td>
<td>57±5</td>
<td>0.160±0.001</td>
</tr>
<tr>
<td>KSFMB–X</td>
<td>39±5</td>
<td>0.110±0.001</td>
</tr>
<tr>
<td>KSF</td>
<td>14±5</td>
<td>0.075±0.001</td>
</tr>
</tbody>
</table>

A3.6. Effect of repeated adsorption on KSF:
The multiple adsorbed KSFMB-X had a lesser TD (0.864 \times 10^{-4} \text{ m}^2\text{s}^{-1}) than the single adsorbed KSFMB-3 (0.931 \times 10^{-4} \text{ m}^2\text{s}^{-1}). This is due to the presence of heavily loaded dye in the host material, which is evident from the distinct reflectance spectra of KSFMB-X when compared to that of KSFMB-3 (Figure 2.6). A steep decrease in PV
and SSA was also seen in the case of KSFMB-X (Table 2.4). Thus, the clustering and dense packing of the dye molecules contributed to the lower TD of the KSFMB-X.\[106\]

**A3.7. Thermal diffusivity of methylene blue adsorbed K-10 and KSF – A comparison:**
The dye intercalated K-10 samples showed considerable changes in the TD values compared to the dye intercalated KSF samples. Though PV and SSA of KSF were small compared to K-10, it had a smaller TD ($0.625 \times 10^{-4}$ m$^2$s$^{-1}$) than K-10 ($0.676\times 10^{-4}$ m$^2$s$^{-1}$). This may be due to their more highly ordered structure with respect to K-10. SSA and PV of KSF were much lower than that of K-10. As the amount of the loaded dye increased, the PV and SSA of dye intercalated K-10 samples gradually decreased while that of KSF samples initially increased and then decreased. The initial increase in PV and SSA was due to the interlayer expansion and pore filling reduced PV and SSA. Thus, a substantial change in TD was not observed in the dye intercalated KSF samples.\[106\]

**A4. Conclusions:**
The selective adsorption of dye by montmorillonite can be used for obtaining samples with desired TD. The contribution of MB towards TD becomes more significant as the amount of dye increases. Repeatedly adsorbed samples have a lower porosity and TD due to the clustering and dense packing of the MB molecules in the clay mineral network. The decomposition temperature of the intercalated dye was higher than that of the pure dye. The dye intercalated K-10 showed significant changes of TD with the amount of MB adsorbed compared to KSF. Hence, K-10 is more suitable for obtaining samples with desired TD values by MB adsorption.

**2.4.6. Part B: Thermal diffusivity dependence on sintering temperature:**

**B1. Introduction:**
Sintering is broadly defined as a consolidation of a loose mass to a dense mass through heating. Generally, it causes a decrease in both the SSA and the porosity, but an increase in the density of the samples.\[172\] Sintering expels organic material, volatile impurities and moisture content in the sample. The sample becomes more uniform on sintering. Thus the phonon scattering due to various scattering mechanisms is reduced. During the process of sintering, there is the diffusion of different elements that compose the material. This provides mass transport and gives rise to better homogeneity in terms of pore distribution.\[173\] Thus lattice connectivity is enhanced,
Dye intercalated montmorillonites

the scattering centres are reduced and the mean free path is increased. This increase in mean free path of heat carrier results in an increased value for TD of the sintered samples.\[137, 142] With the increase of sintering temperature, the sintering driving force increases and the self-diffusion and inter-diffusion of atoms enhance as well, which accelerates the densification of materials. On the other hand, due to components of low fusing point in the matrix, some liquid phase will appear at higher temperature, which can fill some pores and then strengthen the densification of the composites to a certain extent.\[174]

The thermal characterization of MB intercalated montmorillonites - K-10 and KSF - revealed that K-10 samples have well defined changes compared to KSF samples.\[106] Hence, the variation in TD of the MB intercalated K-10 montmorillonites at various sintering temperatures and the effect of dye loading on TD were studied using the PA technique.

B2. Experimental details:
The reflectance spectra of the pelletised samples were obtained with the help of a JASCO V-570 UV/VIS/NIR spectrophotometer. The same samples were employed for the PA studies. The details of the PA measurement are given in section 2.4.3.

B3. Sample details:
The samples, prepared by the methods described earlier in 2.2.2. and 2.4.4, were sintered at 300 °C and 500 °C for overnight. The dye (MB) adsorbed K-10 samples are employed here for the TD measurements.

B4. Results and discussion:

B4.1. Samples sintered at 300 °C:
Figure 2.9 shows the reflectance spectra of the sintered pellets used for the PA study. Still, the dye intercalated samples have noticeable changes in the reflectance compared to the K-10 pellet.

Table 2.5 shows the TD values of the MB intercalated K-10 samples sintered at 300°C. It is known that the TD values of the ceramic samples can be modulated by varying the sintering temperature.\[136] All the sintered samples have a higher TD value compared to un-sintered samples.\[106]
Optical and thermal characterization.....

Figure 2.9: Reflectance spectra of methylene blue intercalated K-10 pellets sintered at 500 °C.

Figure 2.10: Reflectance spectra of methylene blue adsorbed K-10 pellets sintered at 500 °C.

Table 2.5: Thermal diffusivity (TD) values of methylene blue (MB) intercalated K-10 montmorillonites sintered at 300 °C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Thickness×10^{-3}m</th>
<th>TD×10^{-4} m^2s^{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>MB–3</td>
<td>0.959±0.001</td>
<td>0.972±0.002</td>
</tr>
<tr>
<td>MB-4</td>
<td>0.924±0.001</td>
<td>0.870±0.002</td>
</tr>
<tr>
<td>MB-5</td>
<td>0.849±0.001</td>
<td>0.830±0.002</td>
</tr>
<tr>
<td>MB-X</td>
<td>0.930±0.001</td>
<td>0.889±0.002</td>
</tr>
<tr>
<td>K-10</td>
<td>1.003±0.001</td>
<td>1.006±0.002</td>
</tr>
</tbody>
</table>

MB intercalated sintered samples (at 300 °C, Table 2.5) also show the same trend as the un-sintered ones.[106] But, it is observed that the TD of MB-5 is less than that of K-10. The higher TD of K-10 can be due to the enhanced lattice connectivity.[137,142,173] Here also, the repeatedly adsorbed sample, MB-X, has a lesser TD than the single adsorbed sample, MB–3, which may be due to the densely packed dye molecules as in the case of the un-sintered samples.[106]

B4.2. TGA analysis of methylene blue intercalated K-10:
The TGA of pure MB and MB-X (Figure 2.8) shows that MB decomposes after 200°C while the dye intercalated K-10 is stable even near 400°C. Hence, the decomposition temperature of the dye within the clay is higher than that of the pure dye.[106]

B4.3. Samples sintered at 500 °C:
Studies were also carried out on the pellets sintered at 500 °C. The reflection spectra of the samples are given in Figure 2.10. All the samples showed the same nature in the
Dye intercalated montmorillonites

visible range. They are found to be bleached and the TD measurements on K-10 and MB-X samples with thickness $(0.985 \pm 0.001) \times 10^{-3}$ m and $(0.910 \pm 0.001) \times 10^{-3}$ m respectively, which are the two extremes of the present study, show a value of $(1.017 \pm 0.002) \times 10^{-4}$ m$^2$s$^{-1}$ and $(0.961 \pm 0.002) \times 10^{-4}$ m$^2$s$^{-1}$ respectively. The reduced TD of MB-X at 500 °C can be attributed to the presence of only a few MB molecules, which are still present in the clay network. However, it is obvious that the dye doped samples are slowly approaching the TD value of the pure K-10 as the sintering temperature increases.\[107\]

B5. Conclusions:
The sintered samples exhibit higher TD values. When the sintering temperature increases, the dye starts decomposing and the TD values of the MB intercalated samples gradually approach to that of the pure montmorillonite. Thus a variation in the sintering temperature and dye concentration can be used for changing the effective TD values of the ceramic samples.

2.4.7. Part C: Thermal diffusivity dependence on dye:

C1. Introduction:
From the studies described in the earlier parts of this section, K-10 is found to be showing noticeable changes in TD values on dye intercalation. This part of the studies deals with the TD dependence of fluorescent and non-fluorescent dye adsorbed K-10.

C2. Experimental setup:
The absorption spectra of the samples taken in a thin-film form were obtained with the help of a JASCO V-570 UV/VIS/NIR spectrophotometer. The same samples taken in a pellet form were employed for the PA studies. The PA measurement details are given in section 2.4.3. The pore volume (PV) and specific surface area (SSA) measurements were carried out as described in A2.3.

C3. Sample details:
The samples were prepared as described in 2.2.2. The samples were designated as D–Z where –Z denoted the dye concentration and D represented the corresponding dye (AO, MG and MB). The repeatedly adsorbed sample was denoted as D–X. The dye AO was purchased from Loba Chemie and the oxalate salt of MG from Sigma.
C4. Results and discussions:

C4.1. Absorption studies on dye intercalated samples:

Figure 2.11: Absorption spectra of methylene blue intercalated K-10 montmorillonites. Inset: Absorption spectrum of 0.1 mM aqueous solution of methylene blue (MB).

Figure 2.12: Absorption spectra of auramine O intercalated K-10 montmorillonites. Inset: Absorption spectrum of 0.1 mM aqueous solution of auramine O (AO).
Dye intercalated montmorillonites

The absorption spectra of the MB intercalated samples (Figure 2.11), taken as a film, showed a broadened nature with respect to the pure dye at $10^{-4}$ molar concentration. The absorption spectra of AO and MG intercalated samples, taken as films, are given in Figure 2.12 and Figure 2.13 respectively.

The observed broadening and shifts in the absorption spectra are due to the formation of clusters. The excitonic interactions between the chromophores in a very dense packed structure result in a red shift in the spectra. Moreover, the phonon scattering of excitons results in a strong reduction of the peak height of each constituent absorption band and the broadened band overlap each other. The superposition of lattice phonon spectra on the absorption spectrum of the dye makes the spectrum broad as observed in the present case. It should also be noted that the dye gets immobilised in a solid matrix. The shape of the absorption peak and the position of its maximum depend much on the matrix quality. In solution, the maximum wavelength of the cationic dyes depends on the relative permeability of the solvent. In a solid matrix, the absorption peak becomes broader and the maximum wavelength is shifted towards higher values. Due to the van der Waals intermolecular interactions, deviations from planarity may decrease in solid matrix, so that it can be reasonably expected that the maximum absorption wavelength of the dyes will be much higher in a solid matrix than in a solution. It is very likely that the distribution of the strength of...
the solid matrix-dye interactions is much broader than that of the solvent dye interaction. Consequently, the solid matrix-dye interaction also brings about the broadening of the absorption bands.\cite{178}

**C4.2. Photoacoustic study:**

The PA amplitude spectrum of the pellets, characterised by the slope change, is similar\cite{106} to that given in the previous section A3.2. The measured TD values of the samples under investigation are given in Table 2.1, Table 2.6 and Table 2.7.

*Table 2.6: Thermal diffusivity (TD) values of auramine O (AO) intercalated K-10 montmorillonites obtained at room temperature.*

<table>
<thead>
<tr>
<th>Sample</th>
<th>Thickness $\times 10^{-3}$m</th>
<th>TD ($\times 10^4$ m$^2$s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AO-5</td>
<td>0.965±0.001</td>
<td>0.987±0.002</td>
</tr>
<tr>
<td>AO-4</td>
<td>0.982±0.001</td>
<td>0.990±0.002</td>
</tr>
<tr>
<td>AO-3</td>
<td>0.939±0.001</td>
<td>1.029±0.002</td>
</tr>
<tr>
<td>AO-X</td>
<td>0.928±0.001</td>
<td>0.927±0.002</td>
</tr>
</tbody>
</table>

*Table 2.7: Thermal diffusivity (TD) values of malachite green (MG) intercalated K-10 montmorillonites obtained at room temperature.*

<table>
<thead>
<tr>
<th>Sample</th>
<th>Thickness $\times 10^{-3}$m</th>
<th>TD ($\times 10^4$ m$^2$s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MG-5</td>
<td>0.811±0.001</td>
<td>0.481±0.002</td>
</tr>
<tr>
<td>MG-4</td>
<td>0.835±0.001</td>
<td>0.687±0.002</td>
</tr>
<tr>
<td>MG-3</td>
<td>0.888±0.001</td>
<td>0.695±0.002</td>
</tr>
<tr>
<td>MG-X</td>
<td>0.878±0.001</td>
<td>0.805±0.002</td>
</tr>
</tbody>
</table>

The TD of the dye intercalated samples increases with increase in dye concentration. When a small amount of dye ($10^{-5}$ M) enters the matrix, it displaces some of the air and cations in K-10 which leads to a reduction in porosity and hence the TD is increased.\cite{136} The PV of the samples decreases with the increase in concentration of the dye molecules within the clay network\cite{106} (Figure 2.14, Table 2.3, Table 2.8 and Table 2.9). As more of dye gets adsorbed, more of air gets displaced, and an increase in TD is expected due to the decrease in porosity.\cite{136} For samples under the present investigation, not only PV but the dye concentration is also changing. This suggests that the dye also contributes to the TD and this contribution becomes more significant as the amount of dye increases.
Dye intercalated montmorillonites

Figure 2.14: Pore volume (PV) of different dye intercalated K-10 montmorillonites. Here S=MB- methylene blue, AO- auramine O and MG- malachite green. S0=K-10. Details of the samples are given in Table 2.3, Table 2.8 and Table 2.9.

<table>
<thead>
<tr>
<th>Sample</th>
<th>SSA (m$^2$kg$^{-1}$) × 10$^{3}$</th>
<th>PV(m$^3$kg$^{-1}$) × 10$^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>AO-5</td>
<td>191±5</td>
<td>0.365±0.001</td>
</tr>
<tr>
<td>AO-4</td>
<td>182±5</td>
<td>0.337±0.001</td>
</tr>
<tr>
<td>AO-3</td>
<td>166±5</td>
<td>0.293±0.001</td>
</tr>
<tr>
<td>AO-X</td>
<td>116±5</td>
<td>0.271±0.001</td>
</tr>
</tbody>
</table>

Table 2.8: The specific surface area (SSA) and pore volume (PV) obtained from N$_2$ adsorption measurements for the auramine O (AO) intercalated K-10 samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>SSA (m$^2$kg$^{-1}$) × 10$^{3}$</th>
<th>PV(m$^3$kg$^{-1}$) × 10$^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MG-5</td>
<td>190±5</td>
<td>0.359±0.001</td>
</tr>
<tr>
<td>MG-4</td>
<td>180±5</td>
<td>0.326±0.001</td>
</tr>
<tr>
<td>MG-3</td>
<td>145±5</td>
<td>0.270±0.001</td>
</tr>
<tr>
<td>MG-X</td>
<td>103±5</td>
<td>0.257±0.001</td>
</tr>
</tbody>
</table>

Table 2.9: The specific surface area (SSA) and pore volume (PV) obtained from N$_2$ adsorption measurements for the malachite green (MG) intercalated K-10 samples.

As the concentration of the dye increases, the porosity gets reduced by the filling of dye molecules in the pores thereby increasing the TD. Repeated adsorption of the dye reduces the effective TD of the system because of the low TD values of the dye.\textsuperscript{[140]}

- 118 -
This confirms that the dye also contributes to the TD. Thus the controlled adsorption can be used to obtain samples with the desired TD.

*Figure 2.15:* Specific surface area (SSA) of different dye intercalated K-10 montmorillonites measured by (a) BET (Brunauer Emmett Teller) and (b) Langmuir methods. Here S=MB- methylene blue, AO- auramine O and MG- malachite green. S0=K-10. Details of the samples are given in Table 2.3, Table 2.8 and Table 2.9.

*Figure 2.15* shows the SSA obtained for the dye intercalated K-10 montmorillonites using BET and Langmuir methods. At maximum loading, there is a drastic decrease in SSA and PV (*Figure 2.14*) as evidenced from N₂ adsorption measurements.

MB–X, AO-X and MG-X have a more broadened spectrum compared to MB–3, AO-3 and MG-3 respectively (*Figure 2.11, Figure 2.12 and Figure 2.13*). Pore volume and specific surface area show a steep decrease in the case of repeatedly adsorbed samples (*Figure 2.14* and *Figure 2.15 & Table 2.3, Table 2.8 and Table 2.9) and a higher TD can be expected due to the decrease in porosity. However, a lesser TD was observed in this case; except for MG-X. The lower TD may be due to the clustering and dense packing of dye molecules. These dye molecules usually exhibit low TDs of the order of 10⁻⁶ m²s⁻¹. In this case, the contribution of the dyes towards TD is more and so the effective TD is less.

**C4.3. Anomalous behaviour of repeatedly adsorbed MG-X sample:**

The repeated adsorption decreases the TD value in the case of MB-X and AO-X. But, MG-X does not show this property which may be due to the very small absorbance of MG at 488 nm (*Figure 2.13*). Since the absorption of MG at 488 nm is low, there is limited non-radiative relaxation of MG in the case of MG-X. The only contribution towards PA signal arises from the clay mineral. Moreover, the pore volume is again decreased due to the filling of dye molecules. Hence, as stated
earlier, the TD increases due to the decrease in porosity.\textsuperscript{[136]} Thus, the thermal properties of the clay samples can be changed by the selective dye adsorption. The dye adsorption changes the TD value and samples with the desired TD can be obtained with a change in adsorption.

**C4.4. Thermal diffusivity of rhodamine B intercalated K-10 samples:**
A similar experiment with rhodamine B (RB) intercalated K-10 pellets was also conducted and the result was similar to that of AO intercalated K-10. The reflectance spectra of the samples are as shown in Figure 2.16. The TD values of the samples obtained using PA technique is given in Table 2.10. In this case also the repeatedly adsorbed RB-M showed a low TD compared to the single adsorbed RB-3.

![Reflectance spectra of rhodamine B intercalated K-10 montmorillonites. Inset: Absorption spectrum of 0.1 µM aqueous solution of rhodamine B (RB).](image)

*Figure 2.16: Reflectance spectra of rhodamine B intercalated K-10 montmorillonites. Inset: Absorption spectrum of 0.1 µM aqueous solution of rhodamine B (RB).*

**C4.5. Ultrasonicated dye adsorbed sample:**
Many researchers have studied the effects of ultrasound on adsorption processes because ultrasonic waves accelerate mass transport phenomena and thus enhance and improve the sorption rate.\textsuperscript{[179]}

**C4.5.1. Sample preparation:**
About 100 ml of the dye solution ($10^{-3}$ M) was mixed with 1 g clay and was subjected to ultrasonic treatment in a Sartorius Labsonic® M ultrasonicator (maximum amplitude 125 mm, maximum sound rating density 130 W/cm$^2$) fitted with a 10mm Ti
probe at an operating frequency of 30kHz at room temperature for a period of 3 hours. A continuous time cycle was provided with 60% amplitude. 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 hours. The sample was designated as RB-S.

C4.5.2. Thermal diffusivity of the sample:
Both RB-S and RB-3 pellets were of same concentration and showed almost similar reflectance spectra. But the ultra-sonication helped the dye to distribute more uniformly into the clay network and its contribution to TD was more prominent. The sonication produces significant de-lamination and lateral size reduction while the crystalline structure is retained. This improves the surface characteristics and enhances the dye uptake capacity.\cite{120} The increased adsorption of dye on ultra-sonication, makes a contribution to the TD analogous to the repeatedly adsorbed sample, RB-M. Hence RB-S has a TD lesser than that of RB-3 and it is very close to that of RB-M.

Table 2.10: Thermal diffusivity (TD) values of rhodamine B (RB) intercalated K-10 montmorillonites obtained at room temperature.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Thickness×10⁻³m</th>
<th>TD (×10⁻⁴ m²s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RB-5</td>
<td>0.870±0.001</td>
<td>0.648±0.002</td>
</tr>
<tr>
<td>RB-4</td>
<td>0.947±0.001</td>
<td>0.845±0.002</td>
</tr>
<tr>
<td>RB-3</td>
<td>0.970±0.001</td>
<td>0.997±0.002</td>
</tr>
<tr>
<td>RB-M</td>
<td>0.942±0.001</td>
<td>0.778±0.002</td>
</tr>
<tr>
<td>RB-S</td>
<td>0.963±0.001</td>
<td>0.796±0.002</td>
</tr>
</tbody>
</table>

C5. Conclusions:
The PA based TD studies on dye intercalated K-10 montmorillonites showed that the intercalation of dye in the clay network remarkably affect the TD values of the samples. The adsorption of more concentrated dye resulted in increasing the TD while the repeatedly adsorbed sample showed a low TD than the single adsorbed one, except in MG-X. The case of MG-X is explained as a result of the relatively low absorption of MG near 488 nm. The ultrasonicated dye adsorbed sample showed a low TD compared to the sample prepared by the direct dye adsorption from solution which is attributed to the presence of more adsorbed and uniformly distributed dye in the clay network without the chances of forming aggregates.
2.5. Section II - Spectroscopic studies of dye intercalated K-10 montmorillonite aqueous dispersions:

2.5.1. Preamble:
Clay minerals are very attractive matrices for the intercalation of dye molecules. Clay particles are structurally lamellar and often highly colloidal in nature which makes them suitable substrates for studying photoactive species in aqueous solution and for intercalating dye molecules.[181] The adsorption of organic cations by clay minerals has been studied over the past 70 years.[182] Aqueous dispersions of swelling clay minerals are known for their colloidal and rheological properties and have several industrial applications.[183] The guest photoactive species, which occupy spaces within the microstructure of the host clay assemblies, are generally organic compounds that are intercalated in the layers of the inorganic substrate. Dye cations are strongly adsorbed on the clay mineral surfaces[101] and the organisation of the photoactive species within the microstructure is entirely dependent on the host-guest and guest-guest interactions within the microstructure.[181] Due to the negative charge of their interlayer, the smectites have a suitable host structure for the intercalation of various guests like metals, inorganic complexes and organic cations. Dye intercalated materials are exploited in modern photochemistry and photophysics due to their transparency in the visible wavelength region and their optical activity.[184-187] The increasing interest in dye/inorganic nano-composites is focused on changes in optical and thermal properties during adsorption and/or intercalation of the dye in an inorganic matrix. Intercalation of organic dyes into layered silicates is one method of producing ordered organic-inorganic hybrid materials with interesting photo-functions[186-188] and thermal properties.[106, 107] Various dye-clay systems offer an interesting area of research, and spectroscopic techniques have been successfully used to study such systems.[102, 186-191]

Montmorillonites belong to the dioctahedral smectite group of 2:1 phyllosilicate class.[102, 186, 187, 192-194] Smectites are generally nanomaterials with negatively charged elementary platelets of a few nanometre thicknesses; the exact thickness depends on the number of adsorbed water layers. One can transform a clay particle, consisting of a number of more or less well oriented elementary platelets, into an aqueous suspension with randomly moving, elementary clay platelets in which the degree of swelling depends on the charge density of the clay mineral, size and shape of the elementary platelets and particles, the type and charge of the exchangeable cation and the chemical and thermal history of the clay mineral sample.[195] Smectite group is used as a very convenient host structure for the intercalation of organic dyes.[102, 184, 186-188, 193]
The blue emission from the K-10 dispersions is important to be discussed as this emission possesses many advantages useful for potential applications since the emission is located partly in the UV-B spectral region.\textsuperscript{[106]} The novelty of the work is that the dispersions are prepared from the dried dye intercalated samples with same clay amount and different dye concentrations.

2.5.2. Dispersions of dye intercalated montmorillonite:
The aqueous dispersions of the dye adsorbed samples, obtained by the method described in 2.2.2., were prepared by ultra-sonicating 0.1 g of each of the samples in 100 ml water for 10 minutes. To check the absorption behaviour of K-10, 0.1 g was dispersed in 20 ml and the spectrum was taken.

2.5.3. Optical characterization:
The absorption spectra of the aqueous dispersions at room temperature, taken in a 1cm quartz cuvette (Hellma\textsuperscript{\textregistered}, Precision Cells made of Quartz SUPRASIL\textsuperscript{\textregistered} 300, 100-QX), were noted using a spectrophotometer (JASCO V-570 UV/VIS/NIR) and the fluorescence spectra of all the samples were recorded under the same conditions using a fluorescence spectrophotometer (Varian, Cary Eclipse).

2.5.4. Part A: Rhodamine B intercalated K-10:

D1. Introduction:
Rhodamines, an active medium of dye lasers, have a high absorption coefficient and fluorescent yield. They are convenient dyes for probing heterogeneous systems because of their strong dependence of the absorption and fluorescence capacity on the matrix of the solvent. Similar to other organic dyes with molecules having a flat structure or containing planar chromophore groups, rhodamine dyes form molecular assemblies (aggregates), which are characterised by various types of intermolecular associations and optical properties. The formation of such assemblies is usual in aqueous solutions of higher concentrations. It may be enhanced by the adsorption on solid surfaces.\textsuperscript{[100]} It is seen that rhodamine dye can be intercalated into clay interlayers and form aggregation states due to the electrostatic intercalation with the cationic charges.\textsuperscript{[108]} RB has a strong tendency for aggregation, depending on the concentration in the intercalation solution and on the charge distribution in the solvent matrix.\textsuperscript{[185, 188]}

The goal of the present work is to investigate the optical absorption and fluorescence properties of the RB intercalated K-10 montmorillonites in aqueous dispersions.
Dye intercalated montmorillonites

check the dependence on the sample preparation route, one sample is prepared using ultra-sonication and the result is compared. The fluorescence emissions at different wavelengths are also explained.

D2. Experimental- Materials and methods:
Cationic, organic, RB of GR grade was bought from Loba Chemie. Dispersions of RB intercalated K-10 were prepared as described in 2.5.2. The RB intercalation was done as follows

D2.1. Dye adsorption from solution:
These samples were prepared by the methods described earlier in C3. The samples were named as RB-Z, where Z denoted the concentration. The repeatedly adsorbed sample is designated as RB-M.

D2.2. Ultrasonicated dye adsorption:
The sample RB-S was prepared by the method described in C4.5.1., which involved ultrasonicated dye adsorption of 10\(^{-3}\) M dye solution by K-10.

D3. Results:

D3.1. Optical absorption studies:

*Figure 2.17: Absorption spectra of rhodamine B (RB) intercalated K-10 montmorillonite aqueous dispersions (0.1g sample in 100 ml water). Inset: Absorption spectrum of 0.1\(\mu\)M rhodamine B aqueous solution.*
Optical and thermal characterization…..

The absorption spectra (Figure 2.17) showed that the main absorption peak of RB at 555 nm \(^{(5)}\) in all samples was bathochromically shifted. The samples RB-3 and RB-S exhibited maximum intensity at around 580 nm but the intensity of RB-S was higher. The other important peaks (357 nm and 257 nm) of RB appear in the spectra as the RB concentration in the clay mineral increases. The RB-M samples showed broad absorption spectra with peaks at 537, 560, 572 and 590 nm. The absorption spectra of RB-5 and K-10 were similar as the amount of dye loaded was very low in the case of RB-5. It was also observed that K-10 had a shoulder near 250 nm as in the case of all montmorillonites \(^{197,198}\) and the RB had a peak around the same wavelength.

The highly concentrated K-10 (0.1 g in 20 ml water) dispersion had small peaks near 371, 421, 521 and 683 nm as seen in Figure 2.18 and these peaks were not observed in Figure 2.17 due to the very low concentration of K-10 in the dispersion. These peaks were found to be enhanced in dye intercalated samples under the same conditions which were not shown here as most of the peaks got saturated as the concentration was high.

![Absorption spectrum of K-10 montmorillonite aqueous dispersion (0.1g K-10 in 20 ml water).](image)

**Figure 2.18:** Absorption spectrum of K-10 montmorillonite aqueous dispersion (0.1g K-10 in 20 ml water).

**D3.2. Fluorescence studies:**

The samples showed a fluorescence peak at 421 nm when excited with 371 nm (Figure 2.19a). This may be arising from the silica layer. The samples were excited at the same conditions and it was observed that the peak intensity increased for RB-5 than that of K-10. The fluorescence intensity was decreased for all other samples as the dye concentration was increased. Figure 2.19b shows the fluorescence emission at
Dye intercalated montmorillonites

421 nm from samples when they were excited using 250 nm. This figure also showed the same behaviour as in the case of 371 nm excitation.

*Figure 2.19*: Fluorescence spectra of rhodamine B (RB) intercalated K-10 montmorillonite aqueous dispersions (0.1g sample in 100 ml water) peaked at 421 nm when excited using (a) 371 nm (b) 250 nm.

When the dye intercalated samples were excited using 555 nm, they showed a bathochromic shift as the amount of the intercalated dye increases (*Figure 2.20*). Since the samples RB-3, RB-S and RB-M were prepared from dye solutions of same molarity, they showed almost same emission intensity, but RB-M peak was bathochromically shifted. The spectrum of sample K-10 is not given as it had no absorption at 555 nm.

*Figure 2.20*: Fluorescence spectra of rhodamine B (RB) intercalated K-10 montmorillonite aqueous dispersions (0.1g sample in 100 ml water) when excited using 555 nm.
The fluorescence peak intensity comparison of RB-3 and RB-S from *Figures 2.19 & 2.20* shows that the emission peak intensity for RB-S is slightly less than that of RB-3. RB-S also shows a broadened nature for fluorescence though both RB-S and RB-3 have the same absorption peak at 580 nm. But, RB-S has a higher absorption.

*Figure 2.21*: Fluorescence spectra of rhodamine B (RB) intercalated K-10 montmorillonite aqueous dispersions (0.1 g sample in 100 ml water) when excited using various wavelengths (a) RB-4, (b) RB-3, (c) RB-S and (d) RB-M.

*Figure 2.21* shows the fluorescent emissions from RB-4, RB-3, RB-S and RB-M near 600 nm when different excitation wavelengths were used. The fluorescent emission of RB is reported to be near 580 nm when it is excited with 555 nm. From *Figure 2.21a*, for RB-4, the emission peak near 580 nm was observed when the excitation wavelength was 555 nm. However, in other cases, both absorption and emission peaks of RB were bathochromically shifted and the main fluorescent peak appeared after 600 nm (*Figure 2.21 b-d*). The fluorescent emission from RB-5 was found to be too weak to be presented as it had no absorption peak near 555 nm (*Figure 2.17*).
Dye intercalated montmorillonites

D4. Discussions:

D4.1. Optical absorption studies:
All the dye intercalated samples showed bathochromic shift which may be due to the formation of J-aggregates\(^{[116]}\). The greater absorbance shown by RB-S with respect to RB-3 may be due to the more uniformly distributed dye molecules and the minimisation of cluster formation by ultra-sonication. Moreover, greater amount of dye can be adsorbed by ultra-sonication\(^{[180]}\). However, they had the same dye concentration and exhibited the peak at 580 nm.

The RB-M sample showed a broad absorption spectrum due to the dye aggregations. The dye molecular aggregation on the surface of the clay minerals is due to the hydrophobic interactions, which is a general tendency of non-polar molecules to associate physically in aqueous solutions. The molecular exciton model gives a clear-cut explanation for this phenomenon as given by various authors\(^{[116, 200]}\).

Though montmorillonites are weak absorbers in the visible and NIR spectral range\(^{[198]}\), the weak peaks of K-10 (Figure 2.18) 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 clay samples usually leads to the metachromatic effect\(^{[8]}\) in the absorption spectra, whereby the main absorption band is shifted to higher energies\(^{[160, 185]}\). The proportion of the dimers to the monomers increases with increasing concentration of the dye. The interaction of dye with the montmorillonite runs on the principle of the ion-exchange reaction. This process is controlled by coulombic and van der Waals interactions, H-bonds, and also non-bond energy contributions between guest and host and between the guest and guest\(^{[184]}\). In montmorillonite, metachromasy results from π interactions between the adsorbed dye and the oxygen plane of the alumino-silicate\(^{[201]}\).

The J-aggregates, which are formed more rarely than the H-aggregates, absorb light of lower energies and exhibit luminescent properties. They are assemblies with a head-to-tail association\(^{[100]}\). However, the present studies showed that the bathochromic shift in the absorption spectra of the samples was due to the formation of J-aggregates. But,\(^{[8]}\) Relating to the property of certain chemical substances to appear as different colours

- 128 -
RB-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.

H-dimers have been observed in polar and low-viscosity solutions. J-dimers may be formed in weakly polar solvents or in the adsorbed state. At the absorbed state, the electrostatic interaction of the molecule with the polar surface and with other monomer molecules governs the formation of aggregates. The fluorescent character of dimers is due to the allowed transition from the J-dimer level to the ground level.\textsuperscript{200}

**D4.2. Fluorescence studies:**

Dye molecules are incorporated in the clay mineral network with strong dye and host matrix interactions. 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 shown in Figure 2.19a. 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 in enhancement in 580 nm region (Figure 2.21) and decrease in fluorescence intensity at 421 nm. The same intensity of RB-3 and RB-S also confirms the emission from the silicate layer because they are of the same concentration though they are prepared by different methods. It was reported that porous silicon\textsuperscript{202}, silica spheres\textsuperscript{203} and silicon nanoparticles\textsuperscript{196} when excited near 370 nm showed an emission around 420 nm. Since, no peak shift is observed for this emission for all the samples, it may be concluded that the emission arises from the montmorillonite itself. The fluorescence emission of the K-10 colloid also confirms this (2.5.6.). 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. Dipole-dipole type coulombic interactions are long range and are effective for the systems with a large overlap between the fluorescence spectrum of the donor and absorption spectrum of the acceptor.\textsuperscript{204} Besides dye aggregation, there could also be other effects like light scattering, adsorption by the solid surface,\textsuperscript{189} 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.\textsuperscript{100, 205} It is reported that montmorillonite intercalated with RB cations showed that the bands corresponding to
Dye intercalated montmorillonites

the silicate layer remained unchanged after intercalation.\[^{185}\] This means that the silicate layers can be treated as rigid bodies during energy minimisation.

The less intense fluorescence behaviour of RB-S compared to RB-3 when excited near 580 nm (Figure 2.21b and Figure 2.21c) can also be attributed to fluorescence quenching. For RB-3 the aggregation may be more than that of RB-S and the light scattering will be more. The number of photons absorbed by the RB-3 sample will be less due to scattering and hence less absorption. This can cause a lesser fluorescence quenching and can result in more intense fluorescence emission. Thus, the light absorbed is less and quenching of fluorescence will be less and so a slightly higher fluorescence for RB-3. The RB-S had a more uniform distribution and dye intercalation as it was carried out under ultra-sonication and the dye aggregation was less. This may result in absorbing more photons and higher absorption. Consequently, fluorescence quenching becomes more prominent due to the presence of more number of absorbing molecules. Moreover, when two identical fluorescent molecules are in close proximity, their fluorescence emission is quenched due to the intermolecular interaction. Increasing the distance between the two molecules will decrease their interaction and thus increase their fluorescence intensity. Attaching the two fluorophores to a host molecule then allows to sense the conformational change of the host molecule.\[^{206}\]

The fluorescence band of the rhodamine-clay system is shifted to higher wavelength compared with that of the rhodamine in aqueous solution.\[^{188, 189, 207, 208}\] 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.\[^{188}\] The bathochromic shift observed in the case of RB-M (Figure 2.20) is due to the clustering and dense packing of the dye molecules which arises from the repeated adsorption. The fluorescence intensity of the RB-M was less compared to RB-3 and RB-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.\[^{188}\]

D5. Conclusions:
The effect of RB on the fluorescence emission of silica layer at 421 nm with two excitation wavelengths at 250 nm and 371 nm showed that the emission intensity of
K-10 montmorillonite can be enhanced by the addition of a small amount of dye in the network. The addition of dye 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. The RB-S sample prepared by ultrasonication method shows more absorption and less fluorescence than the sample RB-3 due to the uniform distribution, increased adsorption and minimised clustering of dye molecules.

2.5.5. Part B: Malachite green intercalated K-10:

E1. Introduction:
The consequence of a fluorescent dye RB intercalated K-10 dispersions are presented in 2.5.4. In this part, the effect of a non-fluorescent dye MG intercalated K-10 dispersions is discussed.

MG shows strong absorption at the red end of the visible spectrum.\textsuperscript{[210]} The dye itself is not fluorescent.\textsuperscript{[209]} Tahir and Naseem\textsuperscript{[211]} (2006) studied the ability of bentonite to remove MG from aqueous solutions for different adsorbate concentrations by varying the amount of adsorbent, temperature, pH and shaking time. Shivaji et al.\textsuperscript{[212]} (2004) reviewed the toxicological effect of MG on various fish species and certain mammals. MG can be photocatalytically degraded from textile industry waste-water.\textsuperscript{[77]} Juraj and Nobuo\textsuperscript{[101]} investigated the aggregation behaviour of MG in dispersions on montmorillonites. The optical absorbance and fluorescence behaviour of the dispersions prepared from the triphenylmethane (TPM) cationic dye MG adsorbed K-10 montmorillonite is presented.

E2. Dispersions of malachite green intercalated K-10 montmorillonite:
The preparation of the dispersions of the samples, obtained by the method C3, was described in 2.5.2. The samples were designated as KMG-Z and the repeatedly adsorbed sample as KMG-M. The optical characterization was described in 2.5.3.

E3. Results:

E3.1. Optical absorption studies:
The absorption spectra of the dispersions of the samples were as shown in Figure 2. It is observed that the main peaks of the MG at 426 nm and 616.5 nm are
Dye intercalated montmorillonites

bathochromically shifted and broadened in KMG-3 and KMG-M due to the aggregation of dye molecules on the clay basal surface.

![Absorption spectra of malachite green (MG) intercalated K-10 dispersions. Inset: Absorption spectra of 10 µM malachite green aqueous solution.](image)

**Figure 2.22:** Absorption spectra of malachite green (MG) intercalated K-10 dispersions. Inset: Absorption spectra of 10 µM malachite green aqueous solution.

**E3.2. Fluorescence studies:**

![Fluorescence spectra of malachite green (MG) intercalated K-10 dispersions at 421 nm when they are excited using (a) 371 nm and (b) 250 nm.](image)

**Figure 2.23:** Fluorescence spectra of malachite green (MG) intercalated K-10 dispersions at 421 nm when they are excited using (a) 371 nm and (b) 250 nm.

MG is a non-fluorescent dye, but the presence of a small amount of dye in the clay network enhances the fluorescence behaviour of the K-10 samples at 421 nm when excited using 371 nm as seen in Figure 2.23a. Though noticeable change was not obtained in the absorption of KMG-5, it showed an enhancement in fluorescence at

- 132 -
421 nm. But the fluorescence quenching was observed as the amount of the dye adsorbed was increased. The same phenomenon was observed with RB as described in D4.2. The samples also showed fluorescence near 421 nm with vibrational spectrum when they are excited with 250 nm as shown in Figure 2. 23b. In this case also the samples have an enhanced fluorescence with a slight amount of dye in the network and the fluorescence is quenched as the amount of dye in the network increases.

E4. Discussions:
The basic change in the absorption and fluorescence spectrum of the dye intercalated montmorillonites arises from the dye aggregation on the clay network. The optical properties of dye/clay reaction systems can also be interpreted assuming charge transfer between the dye cations and the clay surface.\textsuperscript{[211]} This reaction requires the parallel orientation of dye cations on a clay basal surface. The parallel orientation of triphenylmethane (TPM) dyes like MG would be contrary to their non-flat, propeller-like structures.\textsuperscript{[214]} Moreover, a triangular plane of the cation center of the TPM dyes is tilted at a large angle to the clay surface.\textsuperscript{[210, 214]} The parallel orientation and stacking of the cations on top of each other could not lead to stable arrangements in aggregates because the cations would not be able to interact electrostatically with the negatively charged basal surface. However, if the orientation of the cations is sub-perpendicular to the basal surface of the clay, the existence of large, two dimensional dye aggregates on the clay surface is possible.\textsuperscript{[101, 125]} The more complicated structures of the cations of TPM dyes might cause the absence of the sharp bands formed by the less-ordered J-aggregates.\textsuperscript{[101]} TPM dye cations have a low degree of freedom to adjust to their shape, in order to fill the space at the clay surface. The only possibilities are a rotation of the phenyl groups.\textsuperscript{[101]} MG has only a slight change in the cation structure and/or size, such as replacing methyl groups with ethyl groups, which leads to the behaviour of the dye at the surface of clays. The low intense band near 430 nm arises from the lower symmetry in the cations of MG.

The dye aggregation quenches the fluorescence of the silica in clay network. The dye molecules aggregate on the clay network as their concentration increases which in turn inhibits the fluorescence of the silica. Thus, it can be confirmed that the presence of the dye in K-10 undoubtedly affects the fluorescence behaviour of the silica at 421 nm when excited using 371 nm. Hence dye can be used to monitor the fluorescence of clay.
Dye intercalated montmorillonites

E5. Conclusions:
The intercalation of the non-fluorescent dye MG in K-10 verifies that the 421 nm fluorescence from the K-10 dispersion arises from the silica present in clay network. The result also confirms that the presence of a small amount of dye in the clay enhances this fluorescence. Moreover, the fluorescence intensity can be monitored by the amount of dye added and it does not depend on whether the dye is fluorescent or not.

2.5.6. Part C: Dispersions of KSF and K-10:
F1. Introduction:
Many chemical reactions in soils are affected by their internal surface. In this respect, clay minerals are one of the most reactive species, due to their high SSA. Under the chemical conditions in the soil, the clay mineral particles form large aggregates which contain micropores. Shape, size, and the internal structure of these aggregates depend on the ionic concentration of the dispersion medium.

The colloidal state (stable, coagulated, or gel-like) and the rheological properties of montmorillonite dispersions are strongly influenced by organic cations. Clay minerals are distinguished from other colloidal materials by the highly anisometric and often irregular particle shape, the broad particle size distribution, the different types of charges (permanent charges on the faces, pH-dependent charges at the edges), the heterogeneity of the layer charges, the pronounced cation exchange capacity, the disarticulation (in case of smectites), the flexibility of the layers, and the different modes of aggregation.

Pure clay mineral dispersions have a tendency to aggregate.

Light absorption characteristics of clay minerals in the UV and visible range have been studied by several investigators. Visible absorption spectroscopy has been reported as a useful technique for the estimation of particle size of clays in suspension. Banin and Lahav noted that montmorillonite shows a light absorption band in the UV range, at about 245 nm. They proposed a semi-quantitative method for the estimation of the specific light absorption intensity by subtracting the estimated scattered light from the optical density at the absorption band. They further postulated that the absorption band in montmorillonite is caused by compounds which are affecting the tactoid size of the mineral while dispersed in water. This suggestion was based on the fact that a negative correlation was found between the intensity of light absorption and tactoid size.
Both K-10 and KSF are acid leached commercial montmorillonites. KSF is less acid leached than K-10. From the present study, the change in the absorption and fluorescence of the acid leached montmorillonites can be estimated.

**F2. Materials and methods:**
To measure the absorption spectrum, 0.1 g of K-10 and KSF were dispersed in 20 ml double distilled water. The fluorescence studies were conducted with dispersions made with 0.1 g montmorillonite in 100 ml double distilled water. The spectral measurements details are given in 2.5.3.

**F3. Results and discussions:**

**F3.1. Optical absorption studies:**
The absorption spectrum of the K-10 dispersion is given in Figure 2.18 and that of KSF is given in Figure 2.27. The dispersions show a significant shoulder near 260 nm which is a characteristic of the montmorillonites. The K-10 and KSF dispersions are almost transparent in the visible range with some weak peaks arising from the silica and alumina layers in the clay network. All montmorillonites exhibit either an absorption band or a shoulder at a wavelength near 245 nm.

![Absorption spectrum of KSF montmorillonite aqueous dispersion (0.1g KSF in 20 ml water).](image)

**F3.2. Fluorescence studies:**
The fluorescence spectra of the K-10 and KSF dispersions are as shown in Figure 2.25. These dispersions showed fluorescence at 421 nm when excited using 250 nm and 371 nm. The fluorescence produced by 371 nm is noticeable as it may be arising from
Dye intercalated montmorillonites

The silica layers of the clay minerals. The more acid leached K-10 showed higher absorbance near 371 nm and fluorescence at 421 nm. Hence, it may be assumed that the acid leaching enhances the absorbance and fluorescence of montmorillonites. However, more quantitative studies are to be carried out to confirm this. Though the K-10 and KSF dispersions show fluorescence at 421 nm for 250 nm excitation it is weak compared to that originating from the 371 nm excitation.

![Fluorescence spectrum of KSF montmorillonite aqueous dispersion at 421 nm when excited using 371 nm and 250 nm.](image)

**Figure 2.25:**

**F4. Conclusions:**
The optical absorption and fluorescence studies on K-10 and KSF dispersions showed that acid leaching can significantly influence these features. Out of the weak absorption peaks in the visible range arising from the silica and alumina layers of the montmorillonites, only 371 nm excitation was able to produce noteworthy fluorescence.

**2.6. Summary:**
The PA studies on MB intercalated K-10 and KSF revealed that K-10 is more suitable for obtaining desired TD. The sintered MB intercalated samples showed higher TD in K-10 matrix. As the sintering temperature increases, the TD of the dye intercalated samples tends to that of the non-intercalated sample. It is also noted that the dye adsorbed K-10 samples have different TD values depending on the amount and type of dye adsorbed. The TD studies of the dye adsorbed montmorillonites expose the possibility of these materials for further applications after the industrial waste-water treatment. The repeatedly adsorbed samples showed a low TD compared to the single
adsorbed samples except for MG adsorbed ones. The anomalous behaviour of MG may be arising from the low absorption of MG at 488 nm.

The optical absorption and fluorescence studies of the dye adsorbed montmorillonite dispersions showed that both fluorescent and non-fluorescent dye in a small amount can enhance the fluorescence of the K-10 montmorillonite at 421 nm when the wavelength of excitation is 371 nm. The presence of dye in the clay network can be used to monitor the optical properties of both. Moreover, acid leaching can significantly affect the optical properties of the montmorillonites.

Many cationic dyes and chromophores embedded in inorganic substrates are used in industry, e.g. in photography, in various materials for signal processing and memory storage media, as catalysts, as energy antennas and transducers in photochemical reactions etc. All these applications depend crucially on the optical properties of the employed dye. Therefore, the relationship between dye aggregation and the parameters of inorganic hosts might be very significant in the applied research and engineering of the materials.[101]

2.7. References:

Dye intercalated montmorillonites


Dye intercalated montmorillonites


Dye intercalated montmorillonites


Optical and thermal characterization.....


Dye intercalated montmorillonites


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Optical and thermal characterization.....


Dye intercalated montmorillonites


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Dye intercalated montmorillonites


Dye intercalated montmorillonites


