SPECTROSCOPIC STUDY OF THE ADSORPTION OF RHODAMINE 6G ON LAPONITE B FOR LOW LOADINGS

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ABSTRACT: The adsorption of Rhodamine 6G in aqueous suspension on Laponite B was investigated by electronic absorption and emission spectroscopies. Fluorescence spectra suggest that the monomer is adsorbed at two different surfaces, the external and the internal. A monomer is intercalated in the interlamellar space at low loading of dye (<3% CEC), whereas the monomeric state of the dye seems to be at the solid-aqueous interface in suspensions with high loading (>12% CEC). The metachromatic effect observed in the absorption spectra, for the loading interval between 1% and 15% CEC of Laponite B, is attributed to the dimerization of the dye, which seems, from X-ray diffraction measurements, to be formed at the clay interlayer. The formation constant and the absorption spectrum of the aggregate were obtained and the dimer was structurally characterized by applying the Exciton Theory. The observed fluorescence quenching for loadings lower than 15% CEC is attributed to energy transfer from monomer to the dimer, which obeys the Perrin model.

Since the first half of this century, many scientific areas such as soil science, colloid science, petroleum technology, etc. have been interested in the properties of clay-organic systems (Dixon & Weed, 1977; Theng, 1974; Newman, 1987). Nowadays, the interaction between organic matter and clay minerals is an important tool in heterogeneous catalysis (Dale Ortego et al., 1991; Laszlo, 1991), in decontamination (Srinivasan & Fogler, 1990), and in agriculture (Margules et al., 1987, 1988; Ghosal & Mukherjee, 1972). Clay-organic systems can be interesting photochemical systems as many photoprocesses can be carried out efficiently at the clay surface, as for example, long range energy transfer to fluorescent acceptors (Avnir et al., 1986).

A variety of techniques has been employed for studying clays (Tennakoon et al., 1983): X-ray diffraction (XRD), infrared spectroscopy, and 

\[ ^{13}C-^{27}Al- \text{and} \ ^{1}H-\text{nuclear magnetic resonance spectroscopies. The use of these methods is very limited when the clay is in a dilute suspension and when the organic molecules are adsorbed at very low loadings. In these cases, UV-vis and fluorescence spectroscopies can generate considerable insight into the adsorption process (Viaene et al., 1987; Cenens & Schoonheydt, 1988; Cenens et al., 1990). Fluorescent molecules have been applied to study biological systems (Lakowicz, 1983) and surfaces (Avnir et al., 1984, 1985). The spectroscopic properties of adsorbed probes provide information about the distribution of the adsorbed organic molecules on the surface and on the heterogeneity of the surface sites. In the case of clays, they are also strongly influenced by the aggregation of the clay particles in aqueous suspension (Cenens & Schoonheydt, 1988; Cenens et al., 1990).

In this work, the adsorption of Rhodamine 6G (R6G) in aqueous suspensions of Laponite B (LapB) was studied. This clay is a synthetic hectorite (Van Olphen & Fripiat, 1979) with an average particle size of 30 nm (Thompson & Butterworth, 1992) as deduced from the small effect of the light scattering, and a low proportion of iron impurity which is an efficient fluorescence quencher. Rhodamine 6G is a xanthene derivative (Fig. 1) frequently used as an active medium of dye lasers. It is an ideal probe due to its high light absorption and fluorescence capacities which are very sensitive to the environment (López Arbeloa et al., 1991a,b). Moreover, the lasing properties of rhodamines can be improved when the dye is adsorbed on a clay (Endo, 1986, 1988).
EXPERIMENTAL

Laponite B and Rhodamine 6G (laser grade) were supplied by Laporte Industries Ltd. and Kodak, respectively, and they were used without further purification. The concentration of the stock clay suspension was 2.5 g/dm$^3$ and that of the stock dye solution was $5 \times 10^{-6}$ M. The dye-clay suspensions were prepared by dropwise addition of the adequate amount of stock dye solution to the proper amount of the stock clay suspension, previously diluted. In this way and with continuous stirring, a high dye coating at the clay surface was avoided. In order to minimize the reabsorption effect on fluorescence measurements and to reduce the dye aggregation in aqueous solution, the final dye concentration was kept constant at $10^{-6}$ M (López Arbeloa, 1980; López Arbeloa et al., 1982). Since R6G adsorption on LapB takes place by cation exchange (Grauer et al., 1984), the loadings of the dye-clay suspensions were expressed as % CEC, i.e. the percentage of cation exchanged w.r.t. the total cation exchange capacity (CEC) of LapB, 73.3 mEq/100 g (Van Olphen & Fripiat, 1979). Loadings ranged from 0.10 to 15% CEC, i.e. from 0.1364 to 0.0091 g of clay/1.

When an aqueous solution of R6G was centrifuged, an absorbance gradient along the centrifugation tube was observed, even with centrifugation conditions in which LapB particles were not fully precipitated. Therefore, centrifugation cannot be used to separate both the adsorbed and non-adsorbed dye.

In order to determine the amount of non-adsorbed R6G, the dye-clay suspensions were filtered through cellulose nitrate filters (Sartorius Gmbh). A completely transparent (controlled by UV-vis spectroscopy) filtrate was obtained when a $10^{-6}$ M R6G aqueous solution was passed through a 0.65 μm pore-size filter. However, the filter did not retain the dye in a clay suspension with a loading of 0.10% CEC. These experiments suggested that the free dye in solution was retained by the filter whereas the dye adsorbed on clay passed through it. Apparently, the affinity of R6G by the cellulose filter was lost when the dye was adsorbed on clay. The amount of dye retained on the 0.65 μm filter rises by increasing the relative dye concentration on clay, i.e. 15% CEC suspension lost 12% of its absorbance after filtration. The R6G retained by the filter should be the free dye in solution and dye adsorbed on the largest particles of the clay. The results given in this work were obtained with the filtrate of the dye-clay suspensions that is considered to be free of non-adsorbed dye.

Absorption and emission spectra were recorded on a Shimadzu Spectrophotometer (model UV-240) and on a Shimadzu spectrofluorimeter (model RF-5000), respectively, using 1 cm plastic cells. The position of the d001 line of the freeze-dried clay-dye complexes was measured with a Philips PW 4025 X-ray diffractometer and Cu-$K_\alpha$ radiation.

RESULTS AND DISCUSSION

Absorption spectra

The shape of the absorption spectrum is strongly affected not only by the relative dye-clay concentration but also by the suspension stirring time. Figure 2 shows the evolution of the absorption spectrum with stirring time for a loading of 10% CEC. A decrease of the principal absorption band at 533 nm and an increase of a band between 470 and 480 nm were observed. With increasing loading the short wavelength band increased at the expense of the 533 nm band. However, the absorption spectra obtained 10 min after the sample preparation did not show a clear isosbestic point, when the relative dye-clay concentration was changed. The spectra obtained after 1.5 h stirring were coherent and showed a definitive isosbestic point. It is supposed then that the pseudo-equilibrium distribution of the dye on the surface was attained. For this reason, the results shown hereafter were obtained with suspensions stirred for 1.5 h.

The shape of the absorption spectrum of R6G ($10^{-6}$ M) adsorbed on LapB depends also on the
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Clay concentration. Several representative spectra of Rhodamine 6G-LapB suspensions (from 0.23 to 15% CEC) are shown in Fig. 3. For loadings <0.50% the shape of the absorption spectrum of R6G/LapB did not change with the clay content and is similar to that shown in Fig. 3a. The spectrum is also similar to that obtained with very dilute R6G/water solution though shifted to lower energies, i.e. the absorption maximum of R6G in LapB suspension is at 533 nm and in aqueous solution at 526 nm, as shown in Fig. 3. So, for these low loadings, R6G is considered to be adsorbed in monomeric form.

With increasing loading, the intensity of the principal absorption band centred at 533 nm diminished and the intensity at ~475 nm increased, an evolution similar to that obtained with the stirring time in Fig. 2.

The replacement of the principal absorption band by another band at higher energies is known as metachromasy. The metachromatic effect has been attributed to two different phenomena: (i) the interaction between the electron lone pairs of surface oxygens with the π-system of the dye (Grauer et al., 1984), and (ii) the association of the dye at the clay surface (Cenens & Schoonheydt, 1988; Cenens, 1988; Aznar et al., 1992). The π-interaction is proposed for clays with tetrahedral substitution of Si⁴⁺ by Al³⁺ (Yariv, 1988). Since LapB does not have this type of substitution, the metachromatic effect has to be related to dye association (Yariv, 1988). Therefore the changes observed in Figs. 2 and 3 should be attributed to the association of R6G on LapB.

At these loadings (<15% CEC), the observed isosbestic point in Figs. 2 and 3 suggests the existence of only one aggregate. If the dimer formation is considered as the only reaction, the association constant and the absorption spectrum of the dimer can be calculated (López Arbeloa, 1981) from the observed evolution of the absorption spectra with the relative dye/clay concentration in Fig. 3. The calculated dimer spectrum is similar for several suspensions between 3 and

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**Fig. 2.** Evolution of absorption spectra of Rhodamine 6G with stirring time for a Rhodamine 6G/Laponite suspension of 10% CEC ([R6G] = 10⁻⁶ M and [Lap] = 0.0136 g/l): (a) 10 min, (b) 1.5 h, (c) 5 h, (d) 8 h, (e) 1 day, (f) 2 days, (g) 1 week.

**Fig. 3.** Absorption spectra of Rhodamine 6G (10⁻⁶ M) in aqueous solution (dashed curve) and adsorbed in Laponite suspensions. (a) 0.23% CEC ([Lap] = 0.5932 g/l); (b) 1% CEC ([Lap] = 0.1363 g/l); (c) 3% CEC ([Lap] = 0.0455 g/l); (d) 5% CEC ([Lap] = 0.0273 g/l); (e) 12% CEC ([Lap] = 0.0114 g/l); (f) 15% CEC ([Lap] = 0.0091 g/l).
15% CEC, indicating the suitability of the calculation method and confirming the dimer as the unique aggregate formed in this CEC interval. For loadings >15% CEC, a loss of the isosbestic point of Fig. 3 is observed and the shape of the calculated absorption spectrum of the aggregate changes with the loading. This should be attributed to the formation of a different dimer and/or higher aggregate as has been suggested for another dye-clay systems (Cenens & Schoonheydt, 1988; Cenens, 1988; Yariv & Nasser, 1990). In this work, only the R6G/LapB adsorption for suspensions with loadings <15% CEC was studied.

The increase in the relative concentration of R6G on LapB produced an increase of the dimerization constant, $K_d$. For instance, $K_d$ values 1.4 x 10^4, 1.3 x 10^6, 1.5 x 10^6, 2.5 x 10^6 and 3 x 10^6 (standard concentration: 1M) at 20°C for 0.8, 1, 5, 10 and 15% CEC loadings, respectively, were obtained. These $K_d$ values are higher than those obtained for the dimerization of R6G in aqueous solution, i.e. $K_d = 4700 \pm 300$ (standard concentration 1M) at 20°C. Therefore, the tendency to the association is much more important on LapB than in aqueous solution. This can be attributed to different causes: an increase of the local dye concentration on the clay (Cenens, 1988), a restriction of the thermal motion of the dye when it is adsorbed at the clay surface, which decreases the tendency of the aggregate to dissociate and so on.

Figure 4 shows the average absorption spectrum of the R6G dimer adsorbed on LapB for loading <15% CEC. This spectrum has two bands at 478 and 528 nm, the higher energy band being more intense.

In order to study the geometric structure of the dimer, the Exciton Theory (McRae & Kasha, 1964; Kasha et al., 1965), summarized in the Appendix, was applied. This theory predicts a sandwich structure for a dimer with two allowed transitions in its absorption spectrum, the band at higher energies being more intense (Monahan et al., 1971). Figure 4 suggests a sandwich dimer for R6G adsorbed on LapB in which the planar xanthene rings of the dye are parallel to each other. The excitonic and geometric parameters that characterize the aggregate are calculated in the following way. The resonance energy, $U$, between the chromophore (xanthene ring for R6G) of the monomers is half of the difference between the wavenumber of dimer absorption spectrum maxima ($\bar{\nu}_1$, $\bar{\nu}_2$):

$$U = \frac{(\bar{\nu}_1 - \bar{\nu}_2)}{2}$$  \hspace{1cm} (1)

where $\bar{\nu}_1$ and $\bar{\nu}_2$ are the wavenumbers of the long-wave and the short-wave dimer bands, respectively.

The $\theta$ angle between polarization axes of the chromophores in the dimer can be approximately obtained by the relation:

$$\tan^2 \frac{\theta}{2} = \frac{A_1}{A_2}$$  \hspace{1cm} (2)

where $A_1$ and $A_2$ are the areas of the long-wavelength and the short-wavelength dimer bands, respectively.

These two parameters, $U$ (cm⁻¹) and $\theta$ (⁰), allow the determination of the distance $R$ between the chromophores in the sandwiched aggregate by the equation

$$U = \frac{-|\vec{M}|^2 \cos\theta}{R^3}$$  \hspace{1cm} (3)

where $|\vec{M}|$ is the transition moment of the monomer that can be calculated from the maxi-
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The adsorption of Rhodamine 6G (R6G) on Laponite B was studied. The monomer wavenumber ($\tilde{\nu}_m$) and the area of the monomer absorption band (Sandorfy, 1964):

$$|M| = e^2 \frac{3.98 \times 10^{-20}}{\tilde{\nu}_m} \int \varepsilon(\tilde{\nu}) \, d\tilde{\nu} \quad (4)$$

The results obtained for the dimer of R6G adsorbed at LapB surface and those in aqueous solution are given in Table 1.

A sandwich aggregate with the planar xanthene ring of the chromophores in parallel planes twisted an angle of 86° and at a distance of 3.5 Å was obtained for R6G-LapB suspensions with loadings <15% CEC. Figure 5 shows the geometric disposition of the R6G monomers in the dimer on the clay surface.

This R6G dimer adsorbed on clay has a similar structure to that of R6G in aqueous solution (Table 1, as discussed by López Arbeloa et al., 1982). However, the shorter distance between monomers in the adsorbed dimer (3.5 Å) than for the aggregate in aqueous solution (6.2 Å) indicates that the former is a more constrained aggregate which could suggest the location of the dimer at the interlamellar space of the clay. This possibility is apparently corroborated by XRD measurements. The interlayer space obtained for LapB (4.9 Å) and for R6G-LapB with 0.10% CEC loading (5.0 Å) is lower than that obtained for a loading of 2% CEC (8.9 Å). These results should not be taken as the actual interlamellar space with intercalated dye as they are affected by the presence of dye-free clay particles, mainly for the 0.10% CEC suspension value. In any case, it can be confidently stated that the dimer in the 2% CEC suspension seems to increase the interlayer distance.

Figures 2 and 3 show that increasing the loading of dye and the suspension stirring time have the same effect: both cause the dimerization of the dye. For a long stirring time, i.e. one week for a 10% CEC suspension (Fig. 2g), the absorption spectrum of the sample is similar to the calculated absorption spectrum of the R6G dimer on LapB (Fig. 4), indicating that the same aggregate is formed by both procedures. The storage time can cause association of the clay platelets e.g. the formation of tactoids (Grauer et al., 1984). This fact can be considered as confirmation of the interlamellar location of the dimer at loadings <15% CEC.

**Fluorescence spectra**

Fluorescence spectroscopy can generate additional information on the adsorption of fluorescence probes in clay minerals. The shape of the fluorescence spectrum of R6G adsorbed on LapB does not change with the clay concentration at room temperature and is similar to that of R6G in aqueous solution. These observations suggest that the emission of the R6G dimer on LapB is negligible at room temperature, which is similar to solution behaviour (López Arbeloa et al., 1988). For this reason, fluorescence can be a useful tool to study the adsorption of R6G in the monomeric state on clays without fluorescence quenchers.

The emission maximum of R6G on LapB is at 554 nm for loadings <3% CEC. This maximum shifts progressively to higher energies by increasing the loading, as shown in Fig. 6. A constant value of 544 nm is reached for loadings >12%
CEC. These results suggest the existence of two monomers of R6G on LapB, which should be assigned to the adsorption of the R6G monomer at sites on the external and internal surfaces. Because the emission of the monomer for loadings >12% CEC is at 544 nm, close to that of the R6G in aqueous solution (546 nm), this monomer is considered to be adsorbed at the water/solid interface. Consequently, the monomer for loadings <3% CEC is located at the internal surface. This conclusion has been obtained previously for other dye/clay systems (Yariv & Nasser, 1990).

The existence of the internal monomer at loadings <3% CEC can be explained by the high proportion of the interlamellar surface due to tactoid formation in very concentrated clay suspensions (>0.50 g/dm³). This monomer is supposed to be adsorbed in the same way as Rhodamines are on montmorillonite, i.e. the xanthene ring is parallel to the clay layer. The interlamellar distance observed for very small R6G/LapB loadings (ca. 0.1% CEC) seems to confirm this suggestion. An increase in external/internal surface ratio is expected when the clay concentration is diminished (for instance, to obtain higher loadings for a constant dye concentration), explaining the presence of monomers at the external clay surface.

The absorption spectrum obtained with loadings <0.50% CEC should be attributed to the interlayer monomer. The absorption spectrum for the externally adsorbed R6G monomer could not be obtained due to the high participation of the dimer in the spectra for loadings between 3 and 15% CEC.

In the 1–15% CEC interval, most of the R6G is in the dimeric state as the high dimerization constant implies and the aggregate seems to be localized at the interlamellar space. This conclusion could be explained if the externally adsorbed monomer had a strong tendency to associate another monomer adsorbed at the clay/water interface. Two phenomena could contribute to the formation of this internal dimer: (i) the tendency of the dye to self-associate, (ii) the higher facility for the stacking of clay platelets due to the adsorption of the cationic dye. A similar conclusion has been reported for the adsorption of Crystal Violet (CV) on Laponite XLG (Yariv & Nasser, 1990). For low/high % CEC values the adsorption of CV monomer is in the internal/external surface. The methachromasy observed at intermediate dye/clay concentrations is explained by the adsorption of CV as dimeric state at the interparticle space of the clay.

A decrease in the fluorescence intensity of R6G adsorbed on LapB with respect to that in aqueous solution is observed. This emission diminution depends on the relative dye/clay concentration. The fluorescence quantum yield is calculated from eqn. (5), where the factor $\varepsilon_m\varepsilon$ is introduced to correct for the absorption of the dimer at the excitation wavelength (López Arbeloa, 1980).

$$\phi = \phi(r) \frac{F}{F(r)} \frac{1 - 10^{-A(r)}}{1 - 10^{-A}} \varepsilon m x$$

where $\phi(r)$, $F(r)$, $A(r)$ are the fluorescence yield, emission intensity and the absorbance at the excitation wavelength (495 nm) of the R6G (10^{-6} M) in aqueous solution used as reference ($\phi(r) = 0.59$, López Arbeloa et al., 1991a,b); $\phi$, $F$ and $A$ are the same parameters for the dye-clay suspension; $\varepsilon$, $\varepsilon_m$ are the experimental sample and the monomer molar absorbity at the excitation wavelength, and $x$ is the monomer mole fraction of the sample. The value $\varepsilon_m$ is taken as the average of the molar absorbity for low loadings (between 0.10 and 0.50% CEC), where the dimer formation is negligible. The fluorescence quantum yield obtained by eqn. (5) does not consider the existence of two fluorescent monomers. As the relative excitation of both species cannot be adequately evaluated, the results have to be considered as average values of both R6G monomers.

The fluorescence quantum yield is 0.25 for loadings <0.50% CEC, with R6G in monomeric form. It decreases continuously with increase in the relative dye/clay concentration to reach a value of 0.11 for the 15% CEC suspension. This
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fluorescence quenching is supposed to be due to energy transfer from the monomer to the dimer, as it is observed in homogeneous solution (López Arbeloa et al., 1988). A Stern-Volmer plot (Turro, 1978) does not show a linear correlation of $\phi_0/\phi$ vs. the dimer concentration (where $\phi_0 = 0.25$ is the fluorescence quantum yield for a suspension without quencher, i.e. $<0.50\%$ CEC). This seems to be a reasonable observation as the Stern-Volmer formulation is no longer valid for systems where the statistical mixing of donor and acceptor is not obtained. Perrin’s model of energy transfer (Turro, 1978) assumes that the donor and acceptor cannot undergo displacement in space during the fluorescence lifetime of the donor. Quenching molecules that are inside a ‘quenching sphere’ around a donor molecule produce fluorescence deactivation with 100% efficiency. This model predicts the following relationship:

$$\ln \left( \frac{\phi_0}{\phi} \right) = V N [Q]$$

(6)

where $V$ is the volume of the active sphere of quenching (in cm$^3$), $N$ is Avogadro’s number and $[Q]$ is the quencher (dimer) concentration in mol/dm$^3$.

A plot of $\ln \left( \frac{\phi_0}{\phi} \right)$ vs. dimer concentration gives a straight line for loadings between 3% and 15% CEC, as shown in Fig. 7. This result implies that the fluorescence quantum yield of the externally and the internally R6G adsorbed monomer is of the same order. Perrin’s radius, calculated from the slope of Fig. 7, is 77 Å.

Therefore, the fluorescence quenching of R6G adsorbed on LapB for loadings between 3 and 15% CEC seems to be due to an efficient energy transfer from the monomer to the dimer of the dye, following the Perrin formulation. This conclusion is reasonable as the displacement of the species involved is very restricted at the clay surface.

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Fig. 7. Perrin plot for the fluorescence quenching by the dimer of Rhodamine 6G/Laponite suspensions for loadings between 3 and 15% CEC.


APPENDIX

Exciton theory for dimers

The Exciton model was first developed in the field of molecular crystals, extending later to the study of non-crystalline molecular composite systems, e.g. the aggregation of dyes (Kasha et al., 1965).

The molecular Exciton model offers a satisfactory approximation for the treatment of excited states in weakly coupled associate systems, meaning that the molecular units preserve their individual characteristic in the aggregate system when the orbital overlap between these partners is negligible (McRae & Kasha, 1964; Förster, 1965). In this case, the interaction potential is taken as a perturbation term in the Hamiltonian of the system.

When the Schrödinger equation is solved for a dimer, two excited states are obtained. The energy difference
between these two states is twice the resonance energy ($U$). When the monomer has allowed the first electric dipole transition, the R6G case, the interaction potential is approximately described by a dipole-dipole potential and the resonance energy is given by:

$$U = -\frac{M^2}{R^3} (\cos \theta + 3 \cos^3 \phi)$$  \hspace{1cm} (I)

where $M$ is the transition moment of the monomer, $\theta$ is the angle between polarization axes for the chromophores and $\phi$ is the angle between the monomer polarization axes and the line of molecular centres. The transition moment between the ground and the two excited states of the dimer depends on the relative disposition of both chromophores, following the relation:

$$\tan^2 \frac{\theta}{2} = \frac{f_1}{f_2}$$  \hspace{1cm} (II)

where $f_1$ and $f_2$ are the oscillator strengths of the long-wavelength and the short-wavelength dimer band. Two geometric models allow two transitions in the dimer absorption spectrum (Monahan et al., 1971): (i) the monomers are in parallel planes (sandwich structure) with a twist angle $\theta$, which implies a higher intensity for the shorter wavelength band; and (ii) the monomers are in the same plane, forming an angle $\theta$, which produces a more intense band at lower resonance energy. Versions of eqn. (I), for these two models are, respectively:

$$U = -\frac{M^2}{R^3} \cos \theta$$  \hspace{1cm} (III)

$$U = -\frac{M^2}{R^3} \left( \cos \theta + 3 \sin^2 \frac{\theta}{2} \right)$$  \hspace{1cm} (IV)