Adsorption of Rhodamine 3B Dye on Saponite Colloidal Particles in Aqueous Suspensions

ARTICLE *in* LANGMUIR · FEBRUARY 2002

Impact Factor: 4.46

3 AUTHORS, INCLUDING:

Fernando López Arbeloa
Universidad del País Vasco / Euskal Herriko U…
110 PUBLICATIONS   **2,912** CITATIONS

SEE PROFILE

Virginia Martínez Martínez
Universidad del País Vasco / Euskal Herriko U…
45 PUBLICATIONS   **1,176** CITATIONS

SEE PROFILE

Adsorption of Rhodamine 3B Dye on Saponite Colloidal Particles in Aqueous Suspensions

F. López Arbeloa,* V. Martínez Martínez, J. Bañuelos Prieto, and
I. López Arbeloa

*Departamento Química Física, Universidad del País Vasco EHU, Apartado 644,
68080-Bilbao, Spain*

Absorption and fluorescence spectroscopies were used to study the adsorption of Rhodamine 3B (R3B) dye on Saponite (Sap) particles in aqueous suspensions. Fluorescence data confirmed that the R3B monomer can be adsorbed in the interlayer space and at the water/clay interface of the Sap tactoids. From the evolution of the fluorescence band with the loading and the aging, it was concluded that the internally adsorbed R3B molecules were obtained by the migration of externally adsorbed species. The aggregation of the dye at the clay surfaces was studied by the metachromasy observed in the R3B absorption spectrum, and head-to-tail R3B dimers and trimers were identified. The molecular arrangement for the head-to-tail J-type R3B allows the incorporation of more monomeric units to reach trimers (and higher aggregates), even in the restricted interlayer space of Sap tactoids.

Introduction

The incorporation of aromatic compounds in general and organic dyes in particular into organized assemblies[1-7] has important technological applications in the development of new photonic and optoelectronic devices,[8,9] even in the nanometer spatial domain. Solid host materials can improve the photophysical, lasing, and photostability properties of the guest molecules or can induce the arrangement of photonic materials in a spatial distribution of interest. One-, two-, and three-dimensional dispositions can be obtained by appropriately organized assemblies such as nanotubes, nanolayered (clay and metal oxides) materials and films, and zeolite-like and nanosphere materials, respectively.[10-12] Moreover, the use of the aromatic compounds as molecule probes allows the applications of electronic absorption and fluorescence spectroscopies to study the adsorption characteristics and the physicochemical properties of the host surfaces.

Smectite type clays are TOT aluminosillicate lamellar materials formed by the condensation of an octahedral Al_2O_3 (or MgO) between two tetrahedral (SiO_2) sheets.[13] The negative charges of smectite layers, due to the isomorphic substitution in the octahedral and/or tetrahedral cations by lower valence ions, are compensated by exchangeable hydrated inorganic cations at the layer surface. The tactoidal structure is a consequence of the stacking of several clay layers in parallel planes induced by the inorganic cation giving rise to two different adsorption surfaces of smectites: the interlayer space and the water/clay interface. The extent (charge density) and the type (tetrahedral or octahedral) of the isomorphic substitution are important factors affecting the adsorption capacity and the physicochemical properties (polarity, acidity, etc.) of the clay surfaces as well as the swelling characteristics of the interlayer space.[13,14] Smectites are colloidal in nature and form stable colloidal suspensions in water: octahedral smectites, such as Laponite, present well-dispersed aqueous suspensions, whereas tetrahedral smectites, such us Saponite, form compact tactoids in water.

The adsorption of dye molecules on clay surfaces leads to a metachromasy effect in the absorption spectrum of the dye. This effect has been ascribed to (i) the dye aggregation, due to an increase in the local dye concentration,[15-17] or (ii) an interaction between the π-system of the dye and the electron lone pairs of the O atoms of the clay layer.[18] This interaction is not possible in rhodamine dyes due to steric hindrance of the o-carboxyphenyl group (see molecular structure).[19] Rhodamines are laser dyes with important applications not only in photonics (probably the most used active medium in the visible region of syntonizable lasers[20]) but also as molecular probes to study a multitude of systems.[21-23]

* Corresponding author. E-mail: QFPLOARF@LG.EHU.ES.
(1) Thomas, J. K. *The Chemistry of Excitation Chemistry*; ACS Monograph 181; American Chemical Society: Washington, DC, 1984.
(2) Kalyanasundaram, K. *Photochemistry in Microheterogeneous Systems*; Academic Press: New York, 1987.
(3) Ramamurthy, V., Ed. *Photochemistry in Organized and Constrained Media*; VCH: New York, 1991.
(4) Thomas, J. K. *Chem. Rev.* **1993,** *93,* 301–320.
(5) Karmat, P. V. *Chem. Rev.* **1993,** *93,* 267–300.
(6) Ramamurthy, V.; Eaton, D. F. *Chem. Mater.* **1994,** *6,* 1128–1136.
(7) Avnir, D. *Acc. Chem. Res.* **1995,** *28,* 328–334.
(8) Nalwa, H. R., Ed. *Handbook of Advanced Electronic and Photonic Materials and Devices*; Academic Press: San Diego, CA, 2001.
(9) Davies, R.; Schurr, G. A.; Meenan, P.; Nelson, R. D.; Bergna, H. E.; Brevett, C. A. S.; Goldbaun, R. H. *Adv. Mater.* **1998,** *10,* 1264–1270.
(10) Ogawa, M.; Kuroda, K. *Chem. Rev.* **1995,** *95,* 399–438.
(11) Lourie, O. R.; Jones, C. R.; Bartlett, B. M.; Gibbons, P.; Ruoff, R. S.; Buhro, W. E. *Chem. Mater.* **2000,** *12,* 1808–1810.
(12) Ganesan, V.; Ramaraj, R. *J. Lumin.* **2001,** *92,* 167–173.
(13) Newmann, A. C. D. *Chemistry of Clays and Clay Minerals*; Longman Science Technology Mineral Society: London, 1987.

(14) Van Olphen, H. *An Introduction to Clay Colloid Chemistry*; Wiley: New York, 1977.
(15) Tapia Estévez, M. J.; López Arbeloa, F.; López Arbeloa, T.; López Arbeloa, I.; Schoonheydt, R. A. *Clay Miner.* **1994,** *29,* 105–113.
(16) Cione, A. P.; Neumann; M. G.; Gessner, F. *J. Colloid Interface Sci.* **1998,** *198,* 107–112.
(17) Jacobs, K. Y.; Schoonheydt, R. A *J. Colloid Interface Sci.* **1999,** *220,* 103–111.
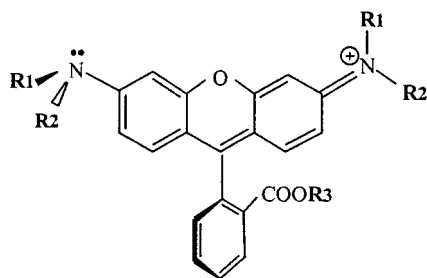(18) Gauer, Z.; Avnir, D.; Yariv, S. *Can. J. Chem.* **1984,** *62,* 1889–1894.
(19) Cohen, R.; Yariv, S. *J. Chem. Soc., Faraday Trans. 1* **1984,** *80,* 1705–1715.
(20) Drexhage, K. M. In *Dye Laser*; Schäfer, F. P., Ed.; Springer-Verlag: Berlin, 1990; Vol. 1, p 187.
(21) Verschuere, B.; Van der Auweraer, M.; De Schryver, F. C. *Chem. Phys.* **1991,** *149,* 385–400.
(22) Nasr, C.; Liu, D.; Hotchandani, S.; Karmat, P. V. *J. Phys. Chem.* **1996,** *100,* 11054–11061.

general molecular structure of rhodamines
(R3B: $R_1 = R_2 = R_3 = C_2H_5$)

Previous results suggested that the hydrophobicity of rhodamines plays an important role in the dye aggregation at smectites surfaces. Indeed, a sandwich H-type dimer of Rhodamine 6G (R6G) has been characterized in both the external and the internal surfaces of several smectites,[24] including octahedral (Laponite and Hectorite), partial tetrahedral (Montmorillonite), and total tetrahedral (Saponite) substituted smectites. Instead, the aggregation of Rhodamine 3B (R3B), a more hydrophobic dye, in octahedral (Laponite[25] and Hectorite[26]) and partial tetrahedral (Montmorillonite[27]) smectites leads to head-to-tail aggregates (dimer, trimer, and higher aggregates) on the external surface and in the interlayer space. The hydrophobicity of rhodamines also affects the extent of the aggregation and the type of aggregates in liquid solution.[28,29] Thus, R6G dimer was observed in diluted dye concentration of 10^{-5} M in water, whereas R6G aggregates were not detected for concentrated solutions up to 10^{-3} M in ethanol. Besides, a sandwich dimer was characterized for the aggregation of R6G in water, while a head-to-tail dimer and trimer were identified in ethanol.

This paper is oriented to complete the study of the adsorption of rhodamine 3B in smectites, considering a total tetrahedral substituted smectite such as Saponite (Sap). Two aspects are specially considered: the type and extent of the R3B aggregation; the mechanism for the adsorption of R3B species in the interlayer space of Sap. In fact, R3B molecules are adsorbed in the interlayer space of Laponite by the stacking of well-dispersed layers in water suspensions.[25] This stacking process is induced by the presence of R3B molecules in the external surface of the layers. However, the adsorption of R3B molecules in the internal surface of a partial tetrahedral smectite such as Montmorillonite[27] is attributed to a migration of the R3B molecules from the external surface of the tactoids.

Experimental Section

Rhodamine 3B (R3B, laser grade) was supplied by Kodak and was used without further purification. Saponite (Sap) was supplied by the Clay Minerals Society (Boulder, CO). To get stable colloidal Sap/water suspensions and to reduce the scattering of the incident light in the spectroscopic studies, the sodium form

of the clay with a particle size lower than 0.2 μm was obtained by conventional methods as described elsewhere.[30]

The R3B/Sap samples were prepared by adding an adequate amount of a R3B/water stock solution (2×10^{-5} M, stirred overnight) into a previously diluted clay suspension with a prefixed amount of a Sap stock suspension (8.0 g L^{-1}, stirred overnight). R3B molecules do not self-aggregate in the stock solution, since the shape of the absorption spectrum of the dye does not change with the dye concentration in the 10^{-6}–2×10^{-5} M range. Samples with different loadings of dye on clay were prepared by changing the final clay concentration for a fixed final dye concentration of 2×10^{-6} M. The relative dye/clay concentration was monitored by the % CEC value, defined as the percentage of the cationic dye exchanged over the total cation exchange capacity of the clay (56.8 mequiv/100 g of clay[31]). To scan the 0.05–100% CEC loading range, the final clay concentration was changed from 7.04 down to 3.52×10^{-3} g L^{-1}. The dye/clay suspensions were aged by magnetic stirring, and the time from sample preparation and sample registration was taken into account in all recorded spectra. The stirring time does not affect the photophysics of a diluted solution of R3B in water, at least during 1 month of aging.

Absorption and fluorescence spectra were recorded, respectively, on a double-beam Varian UV/vis spectrophotometer model Cary 4E and a Shimadzu spectrofluorometer model RF-5000 with 1-cm optical pathway polystyrene cuvettes. The same clay suspensions but without dye were used in the reference beam in the absorption recording. Absorption spectra at very short stirring times (lower than 15 min) were registered by directly mixing the stock dye solution and clay suspension in the absorption cuvette with the help of an internal magnetic stirrer incorporated into the spectrophotometer. Fluorescence spectra were recorded after excitation at 525 nm, and the scattering of the excitation light by the clay particles was also recorded.

Results and Discussion

The extent of the adsorption of the Rhodamine 3B (R3B) dye at the Saponite (Sap) particles in aqueous suspension is determined by the flocculation method.[24] High loading R3B/Sap samples (>30% CEC) flocculated after 1 h of sample preparation. The supernatant from the flocculated 100% CEC samples (settling for at least 2 days) did not present any absorption or emission bands in the vis region, indicating the absence of free dye molecules dissolved in the supernatant. Consequently, it is concluded that the adsorption of R3B in Sap particles is complete in the loading range used in this work.

The absorption and fluorescence characteristics of the R3B dye adsorbed in Sap clay particles are different from those in water solution. Figure 1 shows a spectral shift to lower energies in both absorption and emission bands of the R3B/Sap system with respect to the R3B/water system. These differences are observed after a few seconds of sample preparation, suggesting an instantaneous adsorption of R3B molecules in Sap surfaces. Since the carboxyphenyl group avoids the interaction between the electron π-system of the xanthene ring and the electron lone pair of the clay oxygen atoms,[19] the bathochromic shifts are ascribed to the different micropolarity/microacidity of the clay surface with respect to the hydration properties of the liquid water, as is discussed below.

For very diluted R3B/Sap samples (<0.1% CEC) and short stirring times (<0.5 h), the shape of the absorption spectrum (Figure 1b) does not change with either the loading and the aging of the samples and is similar to that of R3B in diluted solutions of water (Figure 1a). These results suggest that, at this stage of adsorption, R3B is adsorbed in the monomer form. The slight broadening of

(23) Sathy, P.; Penzkofer, A. *J. Photochem. Photobiol., A* **1997**, *109*, 53–57.

(24) López Arbeloa, F.; López Arbeloa, T.; López Arbeloa, I. *Trends Chem. Phys.* **1996**, *4*, 191–213.

(25) López Arbeloa, F.; Herrán Martínez, J. M.; López Arbeloa, T.; López Arbeloa, I. *Langmuir* **1998**, *14*, 4566–4573.

(26) Chaudhuri, R.; López Arbeloa, F.; López Arbeloa, I. *Langmuir* **2000**, *16*, 1285–1291.

(27) López Arbeloa, F.; Chaudhuri, R.; Arbeloa López, T.; López Arbeloa, I. *J. Colloid Interface Sci.*, in press.

(28) López Arbeloa, F.; Ruiz Ojeda, P.; López Arbeloa, I. *Chem. Phys. Lett.* **1988**, *48*, 253–258.

(29) López Arbeloa, F.; Ruiz Ojeda, P.; López Arbeloa, I. *J. Chem. Soc., Faraday Trans. 2* **1988**, *84*, 1903–1912.

(30) Tapia Estévez, M. J.; López Arbeloa, F.; López Arbeloa, T.; López Arbeloa, I. *Langmuir* **1993**, *9*, 3629–3634.

(31) Van Olphen, H.; Fripiat, J. J. *Data Handbook for Clay Minerals and other Non-Metallic Minerals*; Pergamon Press: London, 1979.
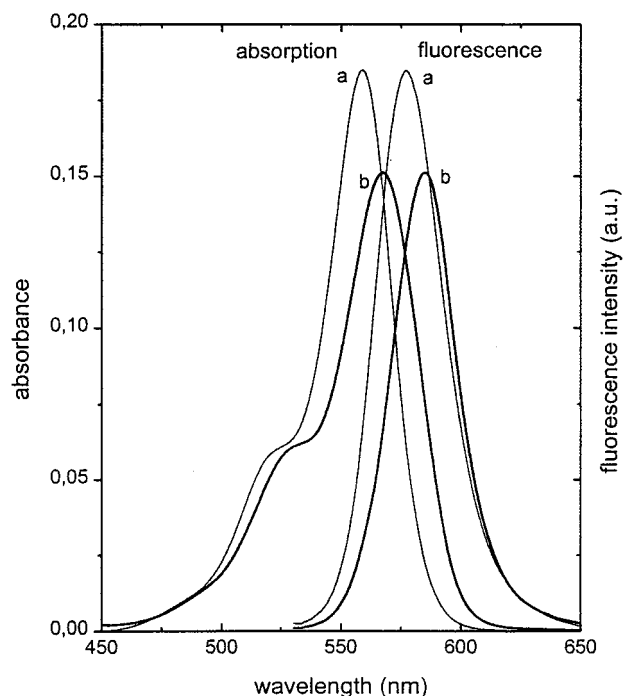
Figure 1. Absorption and normalized fluorescence spectra of R3B (2×10^{-6} M) in water (a) and in 3.52 g/L Sap suspension (0.1% CEC) recorded immediately after sample preparation (b).

Figure 2. Evolution of the absorption spectrum of the 0.2% CEC R3B/Sap suspension with the following stirring times: (a) 0 min; (b) 0.5 h; (c) 3 h; (d) 8 h; (e) 1 day; (f) 3 days; (g) 7 days. The absorption spectrum of the externally adsorbed R3B monomer (dashed curve) is also shown for comparison.

the absorption band for the R3B/Sap system with respect to R3B/water system could be attributed to modifications of the vibrational levels of the dye when it is adsorbed at the clay surface or to an inhomogeneity in the adsorption sites.

Loadings higher than 0.1% CEC or stirring times longer than 0.5 h lead to changes in the absorption spectrum of R3B in Sap. The evolution of the absorption spectrum of the 0.2% CEC sample with the aging (Figure 2) indicates the substitution of the main absorption band by a new band centered at longer wavelengths and a slight increase in the absorbance at the 535 nm shoulder with isosbestic points around 525 and 565 nm for moderated stirring times (<2 days). Further increase in the aging leads to an important diminution of the main absorption band and a new absorption band at 495 nm with an isosbestic point around 525. The isosbestic points suggest the presence of, at least, three adsorbed R3B species. The presence of two or more molecular forms for R3B monomers (controlled by the pH) with different spectroscopic properties can be ruled out because of the presence of an ester group at the carboxyphenyl moiety. Therefore, the changes in the R3B/Sap absorption spectrum could be due to the dye aggregation at the clay surfaces and/or to the adsorption of R3B monomers at two Sap surfaces with different physicochemistry properties, i.e., at the external surface and in the interlayer space.

Spectroscopic Characterization of the Adsorbed Species. The metachromic effect observed in the absorption spectrum of rhodamines adsorbed in smectites particles has been assigned to the aggregation of the dye.[24] However, changes in the absorption spectrum can also be ascribed to the adsorption of R3B monomers in the two surfaces of smectite tactoids.[30] Since the rhodamine aggregates do not emit at room temperature,[28,29] fluorescence spectroscopy is a more adequate technique to characterize the monomer of rhodamines in the interlayer space and in the water/clay interface.
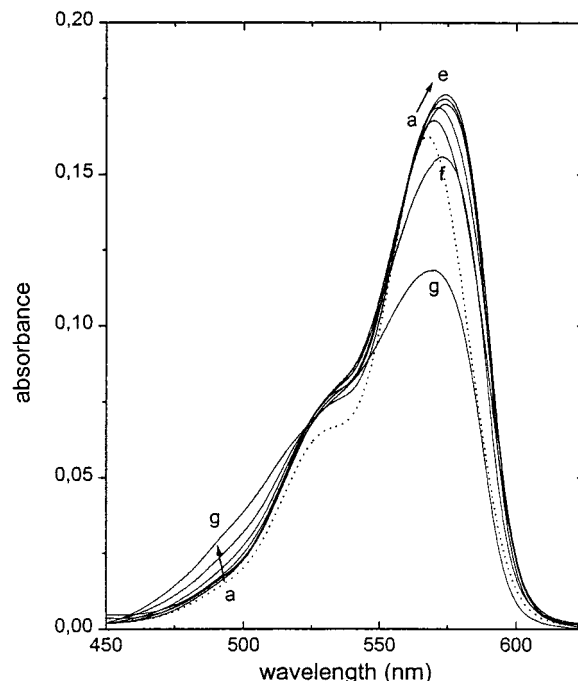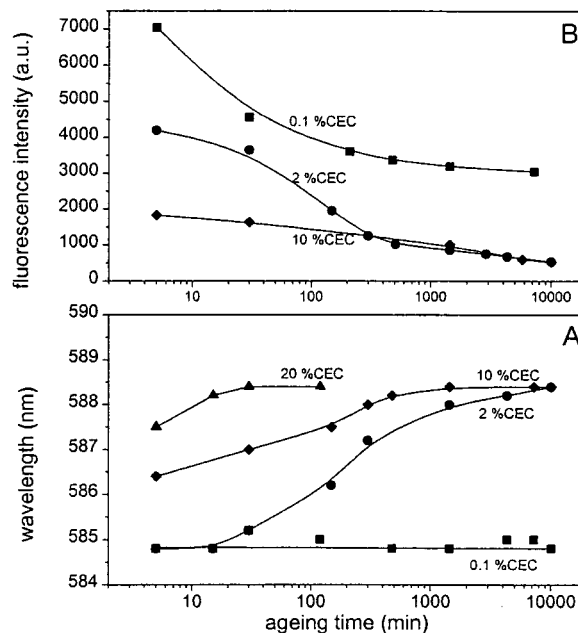
Figure 3. Evolution of the fluorescence wavelength (A) and intensity (B) for four R3B/Sap loadings (0.1, 2, 10, and 20% CEC) with the stirring time. Note the logarithm scale in the aging time axis.

Figure 3 shows the evolution of the emission wavelength and intensity with the aging for four R3B/Sap samples with different loadings: 0.1, 2, 10, and 20% CEC. The fluorescence wavelength for very diluted R3B/Sap loadings (<0.1% CEC) does not change with the aging, suggesting the adsorption of the R3B monomer in one of the two available surfaces of Sap tactoids. It emission band, centered at 585 nm, is that shown in Figure 1, and it is placed 230 cm^{-1} at longer wavelengths with respect to that in water ($\lambda_{fl} = 577$ nm), similar to the bathochromic shift in the absorption band previously described. The

intensity of this fluorescence band decreases with the aging (Figure 3B) due to the dye aggregation. Rhodamine aggregates are potential quenchers for the monomeric emissions and cause inactive absorption of the excitation light.

This emission band is also observed for loadings in the 0.1−2% CEC range immediately after sample preparation. Nevertheless, the emission band progressively shifts to lower energies by aging of the samples, to reach a new emission band placed at 588.5 nm for aging longer than several days. This new 588.5-nm emission band indicates the adsorption of the R3B monomer in the other surface of Sap tactoids. The bathochromic shift of this emission band (340 cm^{-1}, with respect to that in water) is higher than that observed at very low loadings, indicating more drastic changes in the physicochemical properties of the Sap surface for the former emission band. Consequently, the 585- and 588.5-nm emission bands are assigned to the R3B monomer adsorbed at the water/Sap interface and in the interlayer space of Sap tactoids, respectively. Moreover, the fact that the former emission band is observed at short stirring times confirms this assignment because of the higher accessibility of the external surface for the adsorption than the interlayer space.

The emission band observed for high loadings (>2% CEC) and short-stirring times is centered between both emission wavelengths above characterized (Figure 3A), suggesting the adsorption of R3B monomers in both the external and the internal surfaces of Sap tactoids, as is discussed above. The aging of these samples leads to internally adsorbed monomers, which is observed at shorter stirring times as the loading of the sample is increased. For a fixed R3B concentration, high loadings mean diluted Sap suspensions in which less compact tactoids are expected. Consequently, the accessibility of the interlayer space to adsorb R3B molecules should be more important for diluted Sap suspensions (high-loading samples), corroborating the above assignment.

The absorption band of the externally and internally adsorbed R3B monomer is not so easily characterized due to the metachromasy, which masks the absorption band of pure monomers. Taking into account the above discussion, the 567.5-nm absorption band of Figure 1, which is independent of the loading and aging in the <0.1% CEC and <0.5 h ranges, is ascribed to the externally adsorbed monomer. On the other hand, fluorescence data (Figure 3A) suggest that there is no adsorption of the R3B monomer in external surface for the 20% CEC sample after 10 min of aging. The shape of its absorption spectrum is similar to that externally adsorbed R3B monomer (Figure 1a) but centered at 570.5 nm. This 3-nm bathochromic shift respect to the externally adsorbed monomer is consistent with the 3.5-nm spectral shift observed between the emission bands of the externally and the internally adsorbed monomers. Consequently the 570.5-nm absorption band for the 20% CEC sample recorded immediately after sample preparation is ascribed to the absorption spectrum of R3B monomer adsorbed in the interlayer space of Sap.

Conversion from externally to internally adsorbed monomers can also be followed by absorption spectroscopy. The time evolution of the absorption spectrum for the 1% CEC sample (Figure 4) suggests the replacement of the 567.5-nm by the 570.5-nm monomeric absorption band the first day of aging, with an isosbestic point around 576 nm. Longer stirring times (>1 day) of the 1% CEC sample produce an important diminution of the main absorption band and a slight increase at the 495-nm shoulder, ascribed to the dye aggregation. Table 1 summarizes the
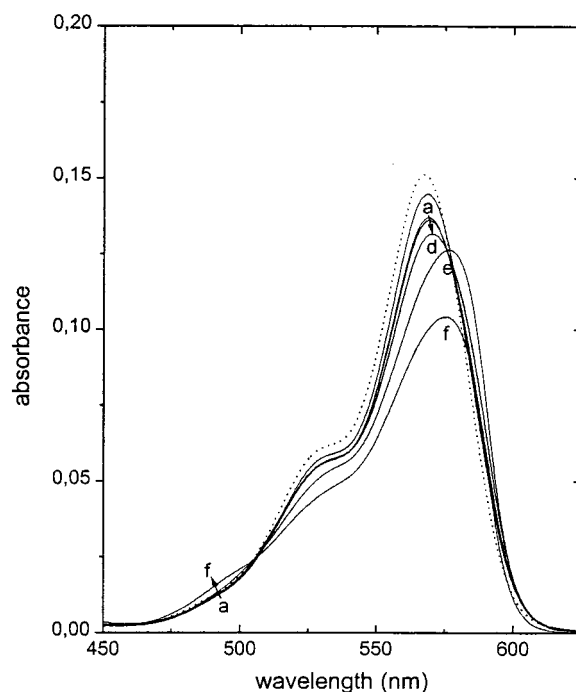

Figure 4. Evolution of the absorption spectrum of the 1% CEC R3B/Sap suspension with the following stirring times: (a) 0 min; (b) 0.5 h; (c) 3 h; (d) 8 h; (e) 1 day; (f) 7 days. The absorption spectrum of the externally adsorbed R3B monomer (dashed curve) is also inserted.

Table 1. Spectroscopic (Absorption, λ_{ab}, and Fluorescence, λ_{fl}) Wavelengths of the Characterized Rhodamine 3B Species (Monomer, M, Dimer, D, and Trimer, T) Adsorbed at the External, Ext, and Internal, Int, Surfaces of Saponite Tactoids, within the Loading and Aging Intervals in Which They Are Characterized[a]

species	λ_{ab} (±0.2 nm)	λ_{fl} (±0.5 nm)	loading interval	aging interval
M (water)	559.0	577.0		
M (ext)	567.0	585.0	< 0.1% CEC	<1/2 h
M (int)	570.5	588.5	1% CEC	>1 day
			10−20% CEC	<10 min
D (ext)	537.5/584.5		< 0.1% CEC	>1/2 h
	$R = 9.3$ Å, $\theta = 95°$, $U = 752$ cm^{-1}		0.2−0.5% CEC	<1 day
T (ext)	515/543/582.5		0.2−1% CEC	>2 days
D (int)			2−10% CEC	low aging
T (int)			2−10% CEC	high aging

[a] The geometric parameters (intermonomeric distance, R, and twisted angle, θ) and the interaction energy, U, of the well-characterized externally adsorbed dimer are also listed.

absorption and emission wavelengths of R3B monomers adsorbed in the interlayer space and at the water/clay interface of Sap tactoids.

The aggregation of R3B at the Sap surfaces can be spectroscopically confirmed by (i) changes in the shape of the absorption spectra and (ii) diminution in the emission intensity of the fluorescence band of R3B monomers. The observed metachromasy in the absorption spectrum for the 0.2% CEC sample (Figure 2) is associated with a drastic diminution in the fluorescence intensity (similar to that shown in Figure 3B for the 0.1% CEC sample), indicating that the R3B aggregation in Sap surfaces is already present for very diluted dye/clay suspensions. The isosbestic points at 525 and 565 nm of Figure 2, observed for moderated aging (<2 days), suggest the formation of an aggregate species. On the other hand, the loss of the 565-nm isosbestic point and the increase in the absorbance at 495 nm for high stirring times (>2 days) indicate the
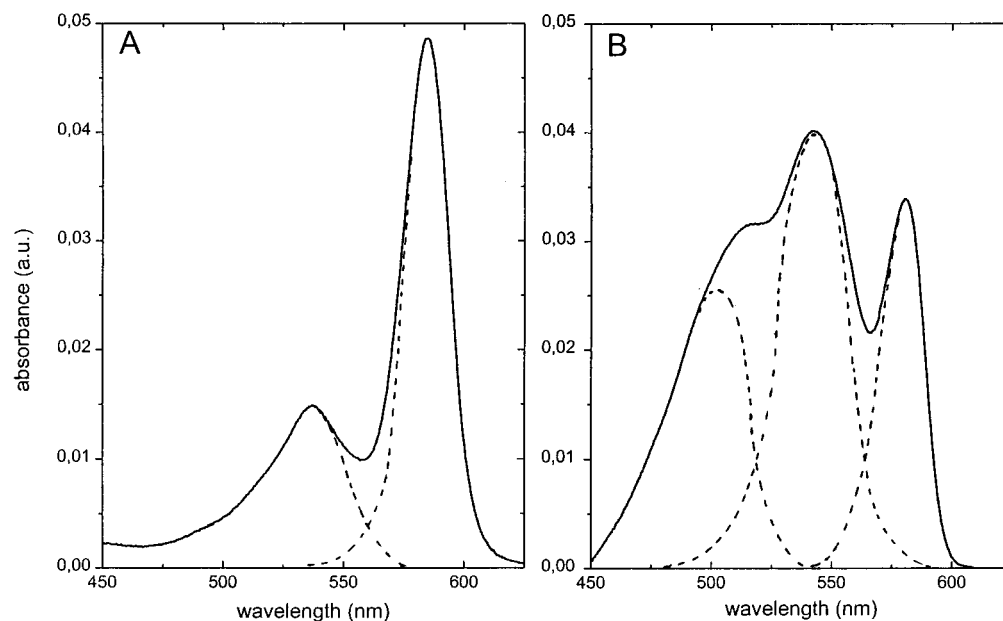
Figure 5. Average absorption spectrum for the externally adsorbed dimer (A) and trimer (B) of R3B in Sap tactoids: (A) calculated for samples in the <0.1% CEC loading interval at any stirring time and for aging lower than 1 day in the 0.2−0.5% CEC loading range; (B) obtained in the 0.2−1% CEC loading and >2 days aging intervals.

presence of a new aggregate species with the aging. These aggregates are in equilibrium with the externally adsorbed R3B monomers since the observed fluorescence band centered at 585 nm does not change with the aging and correspond to the emission of this monomer (Figure 3A).

To characterize the aggregates of R3B in Sap, the contribution of the monomeric absorption band has to be subtracted from the recorded absorption spectra. The molar fraction of the monomers in equilibrium with the aggregates can be estimated by an iterative method, described elsewhere.[32] This method considers the proportion of monomers in equilibrium with the aggregates as the ratio of the H value (defined as the absorbance at the absorption maximum over that at the shoulder, $H \equiv A_{max}/A_{sho}$) of a metachromasy absorption spectrum and the corresponding H_0 value of the monomeric absorption spectrum.

As fluorescence results suggest (Figure 3), the R3B aggregates are in equilibrium with the externally and internally adsorbed R3B monomer, respectively, for low (<1% CEC) and for high (>2% CEC) loading samples. Therefore, the contribution for the monomeric absorption spectrum centered at 567.5 and 570.5 nm has to be subtracted from the recorded absorption spectra for low- and high-loading samples, respectively.

For loadings <0.1% CEC, the shape of the calculated absorption spectrum for the aggregate is independent of the aging (Figure 5A) and consists of two absorption bands centered at 537.5 and 584.5 nm (Table 1), the band placed at lower wavenumbers being more intense. Exciton theory[33,34] proposes a head-to-tail J-type dimer for such a kind of absorption spectrum, in which the xanthene rings are disposed in the same plane at an intermolecular distance R and twisted at an angle θ. These geometric parameters can be obtained from the ratio between the area under the curve ($f = \int \epsilon \, d\nu$) of the two absorption

bands of the dimer and from both the intermonomeric interaction energy (U), calculated from the energy difference between the absorption maximum of both bands, and the transition dipole moment of the monomer ($|\vec{M}_M|$), by means of equations[34,35]

$$U = \frac{\nu_1 - \nu_2}{2} \tag{1}$$

$$\tan^2(\theta/2) = \frac{f_1}{f_2} \tag{2}$$

$$U = -\frac{|\vec{M}_M|^2}{R^3} [\cos(\theta) + 3 \sin^2(\theta/2)] \tag{3}$$

$$|\vec{M}_M|^2 = \frac{9.19 \times 10^{-39}}{\nu_M} \int \epsilon_M \, d\nu \tag{4}$$

where ν and ϵ are respectively the wavenumber and the molar absorption coefficient and subscripts 1, 2, and M represent respectively the long-wavelength and the short-wavelength absorption bands of the dimer and the monomer absorption band. From the absorption spectrum of Figure 5A, a head-to-tail dimer with an interaction energy between monomer of 750 cm^{-1}, an intermonomeric distance of 9.3 Å and a twisted angle of 95° are obtained in the first stage (loading <0.1% CEC and any stirring time and loading in the 0.2−0.5% CEC range for stirring times <1 day) of the R3B aggregation in Sap particles. The absorption spectrum of this dimer is the responsible for the isosbestic points at 525 and 565 nm observed in the recorded spectra of Figure 2.

Longer stirring times for loading in the 0.2−0.5% CEC range give rise to a nearly constant absorption spectrum for the aggregate with three absorption bands (Figure 5B) centered at 515, 543, and 582.5 nm (Table 1) after deconvolution in three Gaussians. The three-band absorption spectrum is consistent with exciton theory for an

(32) López Arbeloa, I. *J. Chem. Soc., Faraday Trans. 2* **1981**, *77*, 1725−1734.
(33) McRae, E. G.; Kasha, M. *Physical Processes in Radiation Biology*; Academic Press: New York, 1964.
(34) Kasha, M.; Rawls, H. R.; El-Bayoumi, M. A. *Pure Appl. Chem.* **1965**, *11*, 371−392.

(35) Birks, J. B. *Photophysics of Aromatic Molecules*; Wiley-Interscience: London, 1970.

open linear head-to-tail trimer. Indeed, if a third monomer unit is added to the previously characterized dimer with the same geometric parameters, then the interaction energy between the two extreme monomers would be U, given by[34]

$$U = -\frac{|\vec{M}_M|^2}{(2R)^3}[1 - 3\sin^2(\theta)] \qquad (5)$$

A U value of 40 cm^{-1} is obtained for the R3B/Sap trimer. The excited-state splitting for such a trimer would give rise to three-energy levels with energetic terms $H - E = -1080, 40,$ and 1040 cm^{-1}: two consecutives energy levels would be energetically separated by 1000 and 1120 cm^{-1}, and the energy difference between the two extreme levels would be 2120 cm^{-1}. These values agree with the energy difference between the three bands of the absorption spectrum of Figure 5B: two adjacent bands are separated 1000 and 1250 cm^{-1}, and the separation energy between the two extreme absorption bands is 2250 cm^{-1}. This trimer can be identified in the recorded spectra by the absorbance at the 495-nm shoulder (Figure 2).

The R3B dimer and trimer characterized above are in equilibrium with the externally adsorbed monomers and are assigned to R3B aggregates adsorbed at the water/Sap interface. The absorption spectrum calculated by subtracting the monomer contribution for the aggregate observed for the 0.5% CEC sample after 7 days of aging is similar to that shown in Figure 5B, but the presence of a shoulder at the 515-nm band could imply the formation of higher aggregates of R3B at the external surface of Sap.

The aggregation of R3B for loadings >1% CEC cannot be studied in detail because (i) at short stirring times the R3B monomer is absorbed in both the external and the internal surface and their proportions cannot be estimated from the position of the recorded fluorescence band since the emission intensity of the monomer bands are quenched by the aggregates and (ii) at long stirring times the samples flocculate. The shape of the absorption spectrum for the aggregates observed in the 5% CEC sample at different stirring times (Figure 6) is not constant and would hint at the conversion from a two-band to a three-band absorption spectrum. However, there are no available experimental data to deconvolute these spectra in two different absorption spectra. None of the absorption spectra calculated by subtracting the monomer contribution in the >1% CEC loading range can be considered as that of a pure aggregate, since they depend on the aging and loading. Consequently the spectroscopic characterization of these aggregates was not possible. These aggregates are in equilibrium with the internally adsorbed monomer and are ascribed to the R3B aggregates in the interlayer space of Sap. The fact that the absorption band placed at longer wavelengths is the most intense could be indicative of head-to-tail aggregates, as were characterized for the R3B aggregates at the interlayer space of Laponite[25] and Hectorite.[26]

Mechanism for the Adsorption. Sap is a tetrahedral smectite with a high tendency to stack clay layers to form the tactoidal structure, even in diluted clay suspensions.[13,36] The present experimental results suggest that R3B molecules are adsorbed at the external surface of Sap tactoids for low-loading samples. For a fixed dye concentration, low loadings require high concentrated clay
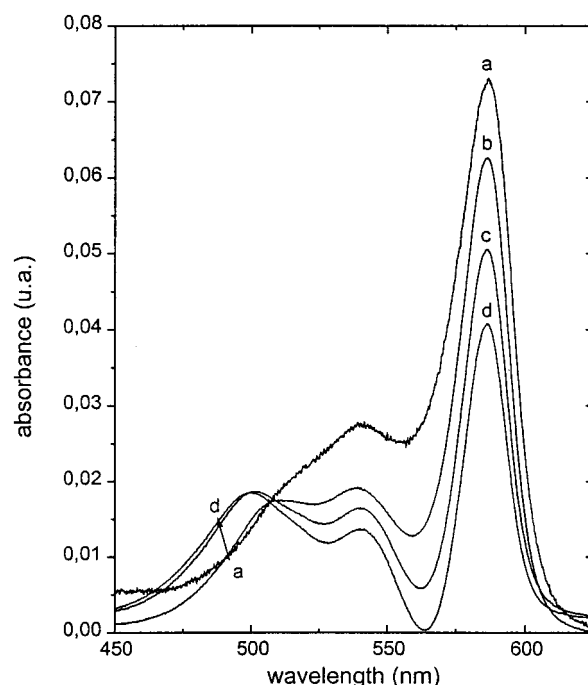

Figure 6. Calculated absorption spectra of the aggregates formed for the 5% CEC R3B/Sap samples at different aging times: (a) 0.5 h; (b) 1 day; (c) 3 days; (d) 7 days.

suspensions, where high and compact tactoids are expected. The incorporation of R3B molecules leads to the adsorption of the dye at the external surface of tactoids, which is the most accessible surface for the adsorption.

High and compact tactoids reduce the proportion of the external over the total surface area of Sap tactoids, favoring the dye aggregation at the external surface. Even for a very low loading sample of 0.1% CEC, the R3B molecules self-associate. The dye aggregation at the external surface is favored with the aging of the samples; for instance, the dimerization constant evaluated for the 0.1% CEC sample is estimated to be 3.39×10^4, 4.24×10^4, and 5.28×10^4 (standard concentration 1 M) for stirring times of 30 min, 8 h, and 1 day, respectively. These results rule out the direct self-association of R3B molecules in particular sites of the external surface. At the first stage, the adsorption of R3B monomers would be extended over all the available external surface of tactoids and with the aging the adsorbed monomers migrate through the external surface to form aggregates. The driving force for this aggregation could be hydrophobic in nature (i.e., to avoid water molecules, the dye molecules tend to agglomerate in particular sites of the external surface). By an increase of the aging and the loading of R3B in Sap (but for low-loading samples <1% CEC), the extension of the dye aggregation at the external surface augments. Both processes would favor the agglomeration of the dye molecules in the water clay/clay interface. The R3B dimer in the external surface is observed for relative low-loading and -aging samples. Long aging leads to the formation of trimer or higher aggregates.

The dilution of the Sap suspensions to increase the R3B/Sap loadings above the 1% CEC value leads to the adsorption of R3B species in the interlayer space of Sap. This adsorption can take place by[24,37] (i) the stacking of well-dispersed smectite layers (i.e. in rhodamine/Laponite systems[14,25]) or compact tactoids (i.e. in the R6G/Sap

(36) Yariv, S. In *Modern Approaches to Wettability: Theory and Applications*; Malcolm, E., Schrader, E., Loeb, G., Eds.; Plenum Press: New York, 1992; p 279.

(37) Cione, A. P.; Schmitt, C. C.; Neumann, M. G.; Gessner, F. *J. Colloid Interface Sci.* **2000**, *226*, 205−209.

system[38]), both processes induced by the presence of dye molecules in the water/clay interface, and (ii) by the migration of the externally adsorbed molecules toward the interlayer space (i.e. in rhodamine/Montmorillonite systems[26,30]). Both mechanisms can be experimentally discerned by the loading and the aging conditions in which internally adsorbed species are observed. The stacking is a relatively fast process favored in concentrated clay suspensions, and internally adsorbed species are then observed immediately after sample preparation and for low loadings.[14] On the other hand, the external-to-internal migration can take place on a time scale of hours/days, depending on the compactness of the tactoids, and it is favored in diluted clay suspensions.[30]

Fluorescence data indicate that the proportion of internally adsorbed species of R3B in Sap increases with the loading and the aging (Figure 3), suggesting a migrational mechanism of the R3B molecules from the external surface to the interlayer space of Sap. Moreover, the scattering of the excitation light of the R3B/Sap samples is similar to that of the corresponding Sap suspensions (without dye) indicating a similar distribution of the Sap particles in aqueous suspensions in the presence and absence of dye. On the other hand, tactoids with a more accessible interlayer space (less compact) are obtained in diluted Sap suspensions, since the internally adsorbed species are observed for shorter aging as the relative R3B/Sap concentration is increased (Figure 3).

This mechanism contrasts with that previously proposed for the R6G/Sap system, in which internally adsorbed species were observed in diluted dye/clay suspensions and short stirring times.[38] In this case, the adsorption of R6G species in the interlayer space was obtained by the stacking of compact tactoids, induced by the presence of R6G molecules adsorbed at the external surface.[38] It is possible that the hydrophobicity of the adsorbed dye also plays an important role in the interaction between clay particles. Indeed, R3B/Sap samples with loadings >30% CEC flocculate after 1 h of sample preparation, whereas R6G/Sap colloidal suspensions were stable at least during 1 day, even for the 100% CEC sample.[38]

R3B aggregation also occurs in the interlayer space of Sap tactoids. Although not well-characterized, head-to-tail R3B dimers and trimers or higher aggregates could be present in the interlayer space of Sap. The trimer or higher aggregate would be formed in detriment of the dimer by increasing the loading (from 2% CEC) and the

aging. Both factors increase the presence of R3B molecules in the interlayer space. These results contrast with those of the R6G/Sap system where only sandwich R6G dimers were observed in the interlayer space of Sap tactoids.[38] The monomer arrangement in head-to-tail R3B dimers, parallelly disposed to the clay layers, assists the incorporation of a third monomeric unit to form the head-to-tail trimer in the restricted bidimensional space of the interlayer surface. This is not the case for sandwich dimers (i.e., in the R6G/Sap system), in which the limitation of the interlayer space does not permit the addition of a third monomer unit to the dimer. Consequently, R6G dimers were the only aggregate species observed in the interlayer space of Sap. Parallel dispositions of the aromatic plane of dyes in the interlayer space of clays in general and of saponite in particular have been also proposed by other authors.[39,40]

Conclusions

The adsorption of Rhodamine 3B in concentrated Saponite suspensions is performed at the external surface of compact tactoids. The dilution of the clay suspensions increases the accessibility of the interlayer space (less compact tactoids) for the adsorption of dye molecules in the internal surface. These internally adsorbed species are obtained by the migration of dye molecules adsorbed in the external surface, which is the most accessible surface for the adsorption. Increasing the loading of dye molecules leads to the formation of head-to-tail aggregates, which are favored with the aging of the samples. The disposition of monomeric units in head-to-tail dimers assists the formation of higher aggregates, even in the restricted space of the internal surface. The hydrophobicity of the dye not only affects the type and extent of the dye aggregation but also influences the interparticle clay interaction affecting the stability of colloidal clay particles in aqueous suspensions.

(38) López Arbeloa, F.; Tapia Estévez, M. J.; López Arbeloa, T.; López Arbeloa, I. *Langmuir* **1995**, *11*, 3211−3217.

(39) Yu, L. S.; Newton, S. Q.; Norman, M. A.; Miller, D. M.; Schäfer, L.; Teppen, B. J. *Clays Clay Miner.* **2000**, *48*, 665−681.
(40) Iwasaki, M.; Kita, M.; Ito, K.; Cono, A.; Fukunishi, K. *Clays Clay Miner.* **2000**, *48*, 392−399.