

Molecular Aggregation of Rhodamine Dyes in Dispersions of Layered Silicates: Influence of Dye Molecular Structure and Silicate Properties

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The molecular aggregation of six rhodamine dyes (rhodamine 560, B, 3B, 19, 6G, 123) in layered silicate (saponite and fluorohectorite) dispersions was investigated by using visible (vis) spectroscopy. The dye molecular aggregation was influenced by the properties of both the silicates and the dyes themselves. The layer charge of the silicates enhanced the molecular aggregation of the hydrophilic, cationic dyes. The presence of a carboxyl acid group in the dye molecules inhibited adsorption of the dyes on the surface of fluorohectorite, a silicate with a high charge density. A lower or no adsorption could be observed by vis spectroscopy. Strong association of the dyes to the silicate surface led to remarkable changes in the dye spectra, mainly due to the molecular aggregation. Dye assemblies initially formed after mixing the dye solutions with silicate dispersions were unstable. Decomposition of the dye molecular assemblies, and the formation of new species or molecular aggregate rearrangements, were studied on the bases of time-difference spectra. The reaction pathways were specific, not only for the dyes, depending upon their molecular structure and properties, but also on the silicate substrates.

Introduction

The formation and properties of organic dye molecular aggregates have been the subject of numerous papers and books. The most important features of molecular aggregation are the significant changes in the chemical, but mainly, the optical properties of the interacting chromophore units.¹ Principally, there are two main types of molecular aggregates: The first type, called the H-aggregates, is based on a sandwich-type association. The H-aggregates are characterized by light absorption at higher energies.² Less-frequently-occurring J-aggregates are composed of molecular assemblies with a head-to-tail intermolecular association and absorb light of relatively low energies.³ Molecular aggregates, with significantly altered optical properties, are formed only under certain conditions.⁴ In general, the distances and angles between interacting electronic transition moments and the number of interacting molecules in a molecular aggregate are key parameters that determine the resulting spectral properties.⁵ These parameters significantly depend on the structure of the interacting dye molecules as well as on the reaction conditions.⁶

The aggregation of rhodamine dyes has been described in numerous papers. The interaction with some layered silicates in dispersions, e.g., clay minerals, has been investigated, e.g., for rhodamine 6G,⁷ rhodamine B,⁸ and rhodamine 3B.⁹ The molecular aggregation of cationic dyes has been used for characterization of the silicate surface properties such as swelling¹⁰ and layer charge distribution.¹¹ The effect of the dye structure on the molecular aggregation has not been studied in detail and is not yet fully understood. Moreover, there are controversial interpretations of some phenomena concerning the

interaction of dyes with layered silicates.¹² Recently, the study on the molecular orientation of rhodamine dyes on layered silicates has been published. The relationship between the formation of the molecular assemblies in the silicate film and the dye orientation with respect to the silicate surface was observed.¹³ The objective of this paper was to investigate rhodamine dye aggregation in layered silicate dispersions, namely, to study the relationship between the optical properties, molecular aggregation of rhodamine dyes, and their molecular structure. A further objective was to investigate the effect of the silicate properties on the molecular aggregation of structurally different rhodamine dyes. Understanding the roles of both the dye and the silicate properties on the dye aggregation (adsorption) will help to identify the basic aspects of the interaction between the rhodamine dyes and layered silicates or charged solid surfaces in general. The spectral properties of six representative rhodamine dyes in layered silicate dispersions were investigated. The structure of the dyes varied in several ways, such as in the presence of a carboxyl acid or a primary, secondary, or tertiary ammonium group in molecules, in hydrophilicity, and the size of the molecule. Two samples representing layered silicates were used, i.e., synthetic fluorohectorite and natural saponite. These two silicates represented samples of high- and low-layer charge densities, respectively.

Experimental Section

Materials. Two layered silicates, Li⁺-saturated synthetic fluorohectorite (FH, Corning) and natural saponite (Sap, SapCa-1),¹⁴ were used. FH was used as obtained without any further purification.¹⁵ Sap was purified by suspension sedimentation in order to remove the mineral admixtures. The Na⁺ form of saponite (Sap) was prepared by the ion-exchange reaction performed as a repeated saturation with NaCl solution (1 mol dm⁻³). The cation exchange capacities of FH and Sap, which

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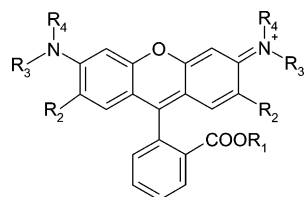


Figure 1. General structural formula and differences between the rhodamine dye cations. Rhodamine 19 ($R_1=R_3=H$, $R_2=CH_3$, $R_4=C_2H_5$). Rhodamine B ($R_1=R_2=H$, $R_3=R_4=C_2H_5$). Rhodamine 560 ($R_1=R_2=R_3=R_4=H$). Rhodamine 3B ($R_1=R_3=R_4=C_2H_5$, $R_2=H$). Rhodamine 123 ($R_1=CH_3$, $R_2=R_3=R_4=H$). Rhodamine 6G ($R_1=R_4=C_2H_5$, $R_2=CH_3$, $R_3=H$).

reflect the layer charge densities, were 1.50 and 0.95 mmol g⁻¹, respectively.

Rhodamine dyes of high purities were purchased from Lambda Physik and used without further purification. The dyes include three cationic dyes (rhodamine 6G¹⁶ (benzoic acid, 2-[6-(ethylamino)-3-(ethylimino)-2,7-dimethyl-3H-xanthen-9-yl]-ethyl ester, monohydrochloride), rhodamine 3B (R3B) (benzoic acid, 2-[6-(diethylamino)-3-(diethylimino)-3H-xanthen-9-yl]-ethyl ester, monohydrochloride), and rhodamine 123¹⁷ (benzoic acid, 2-(6-amino-3-imino-3H-xanthen-9-yl)-methyl ester monochloride)) and three zwitterionic dyes (rhodamine B¹⁸ (RB) (2-[6-(diethylamino)-3-(diethylimino)-3H-xanthen-9-yl] benzoic acid), rhodamine 19¹⁹ (R19) (benzoic acid, 2-[6-(ethylamino)-3-(ethylimino)-2,7-dimethyl-3H-xanthen-9-yl], perchlorate), and rhodamine 560 (R560) (*o*-(6-amino-3-imino-3H-xanthen-9-yl)-benzoic acid). The general structural formula and structural differences of the dyes are shown in Figure 1.

Methods. The visible spectra of the rhodamine/silicate dispersions were measured. The concentration and loading of the dye in the dispersion were always 2.5×10^{-6} mol dm⁻³ and 0.05 mmol g⁻¹, respectively. The spectra were measured with a V-550 UV-vis spectrophotometer (Jasco Co., Ltd.) at room temperature for 1 min after mixing the dye solution with the silicate dispersion. The adsorption of the dyes was then estimated. It was performed under the conditions used for the measurements of the UV-vis spectra. The dye/silicate dispersions were filtered through a 0.2 μ m filter, and the supernatant spectra were recorded. Filtration of the dye solution was performed as well to determine whether the dyes interacted with the filter membrane material in significant amounts.

The spectra of dye/silicate dispersions changed with time due to the processes of rearrangement and reorganization of the formed molecular aggregates. The dispersions were shaken for 24 h so as to achieve chemical equilibrium, and another series of spectra was taken. The spectra of the clay dispersions without the dye, which mainly included light scattering from solid particles, were subtracted from the dye/silicate spectra. The evolution of the dye species with the aging time was checked by the difference spectra. The time-difference spectra (TDS) were calculated by subtracting the absorbance values measured at different reaction times for each wavelength according to the following equation:

$$A(\lambda_i) = A(\lambda_i, t = 1 \text{ min}) - A(\lambda_i, t = 5, 10, 15, 20, \text{ or } 25 \text{ min})$$

TDS helped to identify the species that decomposed or were formed with aging. The spectral bands' positions were calculated by using the second derivatization method.

Results and Discussion

Dye Adsorption. FH, a layered silicate of high charge density, exhibits a low affinity to RB and R560. No adsorption of either dye was detected. Only a low adsorption (around 20%) on the FH surface was also found for the R19 dye. The low or absent adsorption could be explained in terms of the molecular structure of the dyes. RB, R560, and R19 contain a carboxyl acid group in their molecules. Lower adsorption of acidic rhodamine dyes has been observed in the experiments of dye adsorption into solid silicate films.¹³ For example, no intercalation of RB and R19 dyes into FH film occurred. However, the intercalation of R560 in FH film was achieved. This exception can be assigned to the conditions used for the preparation of dye/silicate films. Whereas the intercalation proceeded from rather concentrated solutions,¹³ the dispersions studied in this work contained dyes in much lower concentration. R560 is structurally simple without any hydrophobic groups (Figure 1). Therefore, it is expected to more easily penetrate into the interlayer spaces of the inorganic host. On the other hand, low adsorption of R560 in the FH dispersion can be assigned to a much lower concentration of the dye in this reaction system. The aggregation of R560 at high concentration in solution compared to R19 and RB can contribute to favored intercalation in FH by contrast to acid forms dissociation into zwitterions and a proton at low concentration that synergistically inhibits adsorption on FH surface. The dyes with esterified groups were fully adsorbed on the FH surface under the present reaction conditions. The adsorption of all dyes, including those with a carboxyl acid group in their molecules, readily proceeded on the surface of Sap. This indicates that both the properties of the dyes, such as hydrophobicity, polarity, and molecular charge, and the parameters of the silicate substrate affect the dye adsorption process. Similar observations have been published elsewhere: the effect of the molecular structure on the rhodamine dye absorption in porous AlPO₄₋₅ has been reported.²⁰ In this case, the absorption in the pores increased for the dye derivatives with aliphatic amino groups. The lower adsorption of the zwitterionic, anionic, or neutral forms of the acridine dyes and higher retention of cationic dyes on phyllosilicates was proved.²¹ The adsorption of the acridine derivatives with acidic carboxyl groups dramatically decreased with the increasing pH. This was explained in terms of the repulsive electrostatic forces, which occurred with a number of anions formed under the high pH conditions.²¹ This trend could be used for the interpretation of our results; hydrolysis of the FH octahedrons with Mg(II) and Li(I) central atoms, located at the edges of the silicate particles, results in a strongly basic reaction, mainly due to the hydrolysis of the Li⁺ (O, OH) polyhedrons. The basicity of the FH dispersions was, therefore, higher than that of Sap, whose octahedral sheets are composed of Mg(II) polyhedrons (without Li(I)). Hydrolysis of the rhodamine dyes with carboxyl acid groups may turn dye molecules in a zwitterionic form,²² which could reduce the dye adsorption. Another property of FH, which might contribute to the low adsorption of the acidic rhodamine dyes, is a high negative charge density.¹⁵ Rhodamine molecules with a negatively charged COO⁻ group would be electrostatically repulsed more from the FH surface.

Dye Aggregation. Figures 2–4 show the vis spectra of fresh and aged rhodamine dye/layered silicate dispersions, which are compared with a respective dye solution (lines E). The spectra in Figure 2a indicate negligible changes in the properties of the R560 chromophores in the presence of the silicates. Apparently no aggregation proceeded in this case. Moreover,

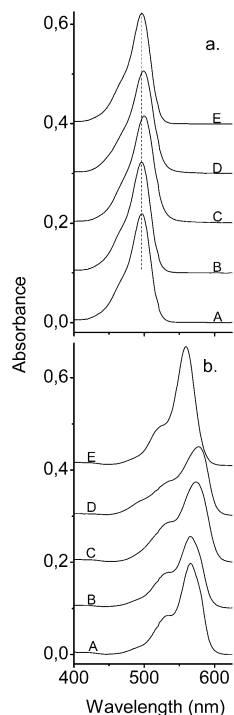


Figure 2. Spectra of rhodamine 560 (a) and rhodamine 3B (b) in the presence of fluorohectorite (A, B), saponite (C, D), and for an aqueous solution (E). Spectra were measured 1 min (A, C) and 24 h (B, D) after mixing the silicate dispersion with the dye solution.

no adsorption on FH supports this assumption. All the spectra are dominated by the band near 500 nm. Only for the R560/Sap dispersion (lines C, D), a slight but reproducible 3 nm shift in the main band to higher wavelengths was observed. This indicates the weak association of this dye to the Sap surface. This shift is due to polarization of the π -electron system of the chromophores by the framework dipoles on the silicate surface. The molecular aggregation, which usually brings about significant spectral changes, was not observed. Adsorption and formation of the molecular aggregates of this dye was observed for the solid films of layered silicates. This exception can be explained in the same way as discussed above for the R560/FH system. Slight molecular aggregation in R560/Sap intercalation film was concluded on the basis of the comparisons of linearly polarized spectra.¹³ In this case, intercalation of the dye was achieved due to the adsorption from more concentrated solutions. High concentration may be the main condition which promotes dye molecular aggregation in the film.

RB and R19 behaved differently in dispersions of Sap and FH (Figure 3). Whereas the presence of Sap significantly changed the shape of the spectra (lines C, D), the dispersions with FH produced spectra (lines A, B) very similar to those of solutions (line E). Also, for these dyes, no adsorption or reduced retention on the FH surface was observed, and hence, the absence of dye aggregation is expected. Neither of these dyes was able to be adsorbed on the solid film of FH,¹³ which is in accordance with the results presented here. On the other hand, the adsorption readily proceeded, and rather complex types of dye aggregates were identified for the reaction with Sap. Light absorption was in a broad range including both the higher and lower wavelengths. This indicates the formation of molecular aggregates of both the H- and J-aggregate types, or the species having features of both the forms. For example, the adsorption of RB on saponite leads to a spectral shift in a main band from 556 nm (solution, line E) to significantly higher wavelengths (580–584 nm) and the formation of a broad shoulder at low

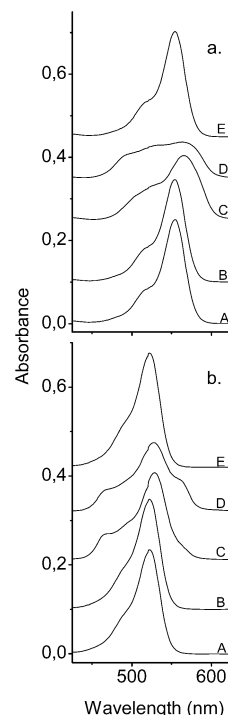


Figure 3. Spectra of rhodamine B (a) and rhodamine 19 (b) in the presence of fluorohectorite (A, B), saponite (C, D), and for an aqueous solution (E). Spectra were measured 1 min (A, C) and 24 h (B, D) after mixing the silicate dispersion with the dye solution.

wavelengths (500 nm) (Figure 3a, lines C, D). The light absorption at higher wavelengths (584 nm) may be assigned to the formation of the RB J-aggregates. Similar conclusions have been done for RB in other reaction systems by using montmorillonite²³ and silica.⁵ Similar forms were identified in a RB/FH-oriented film.¹³ However, the amounts of molecular aggregates were much smaller in the film¹³ than that formed in the dispersion. It can be assigned to different reaction conditions. The presence of water often significantly supports the molecular aggregation of some cationic dyes in the silicate dispersions.²⁴

In a similar way, a slight shift in the main band and the presence of shoulders at both the higher and lower wavelengths were observed for a fresh R19/Sap dispersion (Figure 3b). The position of the band of monomers changed from 525 nm (line E) to 543 nm. The shoulders at both the lower (460–472 nm) and higher wavelengths (565–571 nm) are due to the presence of molecular aggregates.

According to a previously published theory, the dye assemblies, observable in the beginning of the reaction, are formed in zones of the electric double layer of colloid particles.²⁵ After dye molecular assemblies reach the silicate surface, a new reaction often starts to adopt new conditions, either the formation or decomposition or rearrangement of the molecular assemblies.²⁵ This phenomenon was also observed for rhodamine dye/clay reaction systems.²⁶ For the mentioned reaction systems including Sap with RB or R19, more aggregates formed as the reaction progressed: H-aggregates were formed for the RB/Sap dispersions (Figure 3a), but the amounts of both the H- and J-aggregates increased only slightly for R19/Sap (Figure 3b). More J-aggregates were formed in the latter case.

Slight differences in the spectra were observed for R3B (Figure 2b). R3B is structurally similar to RB (Figure 1), but with an esterified carboxyl group. This slight change makes this dye to interact with FH (Figure 2b, lines A, B), which leads to the spectral changes with respect to the spectrum of the dye solution (line E). The main band shifted from 561 to 566 nm.

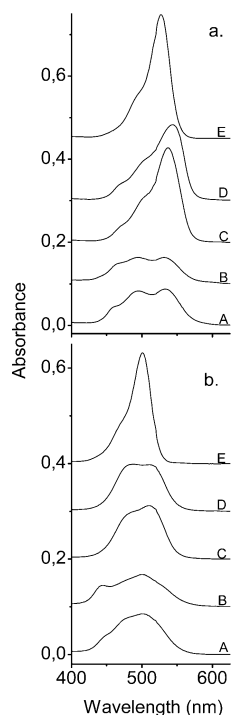


Figure 4. Spectra of rhodamine 6G (a) and rhodamine 123 (b) in the presence of fluorohectorite (A, B), saponite (C, D), and for an aqueous solution (E). Spectra were measured 1 min (A, C) and 24 h (B, D) after mixing the silicate dispersion with the dye solution.

A larger shift was observed due to the presence of Sap (up to 580 nm). Nevertheless, the presence of a layered silicate, either FH or Sap, causes relatively small changes in the spectra of this dye. Also, the changes with time were rather negligible. This can be explained in terms of the rather weak sensitivity of the optical properties of R3B to the molecular environment.²⁷ This is in contrast to RB, whose optical properties in solutions exhibit a higher variability,²⁸ which was observed for the Sap dispersions (Figure 3a).

Large spectral changes due to the presence of FH were observed for R6G and R123 (Figure 4). A detailed characterization of the species of these dyes is problematic, even for dye solutions. Concentrated solutions of R6G, for example, contain not only monomers and dimers, but also tri- and tetramers;²⁹ the spectra of the dye in silicate dispersions are even more complicated. Dye aggregates may exhibit different optical properties depending on the adsorption site (internal and external silicate surfaces) and their structure.³⁰ Aggregates on the surfaces of layered silicates may include large-size assemblies and with more variable types of associations and structures. For both R6G and R123, the H-dimers and large-size H-aggregates (lower wavelengths) were probably formed in the silicate dispersions. Fewer H-aggregates for either dye were present in the dispersions of Sap. This is for the R6G case, which agrees with trends reported in our previous study,¹ in which the relationship between the R6G aggregation and the silicate layer charge was proven. The amount of R6G H-aggregates (455–470 nm) formed in both dispersions¹ as well as on the composite films¹⁶ increased with the layer charge of the silicate. This trend is in accordance with the spectra of R6G/Sap and R6G/FH films, published recently.¹³ In a similar way, the layer charge may affect the aggregation of R123 (Figure 4b). The number of large-size R123 H-aggregates, which absorbed light at low wavelengths (440–450 nm), increased with the reaction time mainly for the FH dispersions (lines A, B). The results are consistent with those published for rhodamine dyes/silicate films.¹³ An

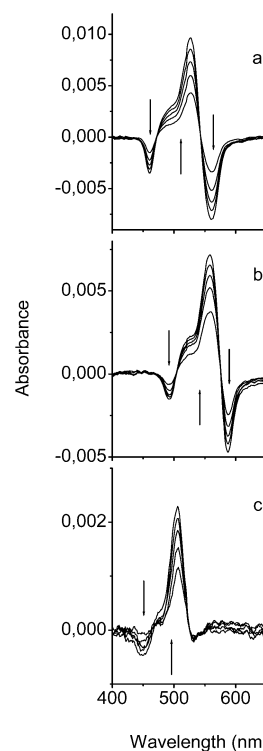


Figure 5. Time-difference spectra for the reaction systems in saponite dispersions with rhodamine 19 (a), rhodamine B (b), and rhodamine 560 (c).

H-type of molecular aggregates was formed after the intercalation of the R123 dye into a FH film. The amount of the aggregates was larger than that formed in a R123/Sap film.¹³

Time-Difference Spectra. The spectra of the dye/silicate dispersions were measured 1, 5, 10, 15, 20, and 25 min after mixing the clay dispersions with the dye solutions. Small changes were indicated by the absorption differences, which were below 5% of the initial absorption values. No detectable spectral changes were observed for dispersions of FH with the dyes, having carboxyl acid groups in their molecules (R19, RB, R560). The changes in the other reaction systems were also very slight to be clearly observable in the original spectra. Therefore, the time-difference spectra (TDS) were calculated by subtraction of the spectra measured at different reaction times, as already described. This method eliminated the light absorption of the species, which did not change in amount with time. The TDS show both the positive and negative absorption bands identifying only such dye species, which were either formed or decomposed during aging (Figures 5–8). A positive absorption identifies the species formed in the system of the fresh dispersions, which decomposed with time (reaction adducts). The negative absorption bands are due to the absorption of new species, which formed as the reaction progressed (reaction products).

A relatively simple reaction proceeded in the Sap dispersion containing a dye with the simplest molecule, R560 (Figure 5c). Monomers, which absorbed at 505 nm, changed into H-aggregates (450 nm). The formation of the species absorbing light of higher energies is questionable, and if trace amounts were formed, it was within the sensitivity limit of the method. One could compare the much lower absorptivity of the H-aggregates with the monomeric species. As mentioned above, no changes occurred in the reaction system of R560/FH (not shown).

Very similar spectral changes occurred for reaction systems containing Sap with either R19 or RB (Figure 5a, b). The

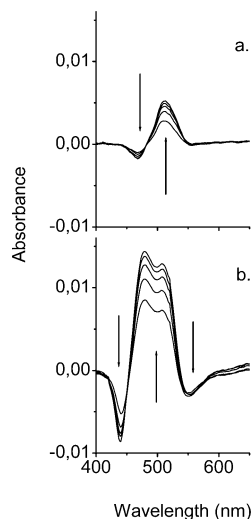


Figure 6. Time-difference spectra for the reaction systems in saponite (a) and fluorohectorite (b) dispersions with rhodamine 123.

molecules of these dyes contain more hydrophobic groups (Figure 1), which might contribute to an extensive aggregation of these dyes (Figure 2b), followed by a rapid molecular reorganization and rearrangement.³¹ The spectral changes include transformation of the monomers and possibly also H-dimers into aggregates of a larger size. These aggregates absorb light at both the higher and lower energies. For example, R19 (Figure 5a), whose solution absorbs light at 525 nm, formed new species characterized by the bands at 460 and 560 nm, respectively. Typical for these dyes, the aggregates include features of both the H- and J-type associations;³² however, the mixture of various types of aggregates, including both the mixed-type and also the pure H- and J-types, cannot be neglected. A very similar trend was observed for the RB/Sap reaction (Figure 5b), in which monomers (558 nm) and dimers (525 nm) changed to the larger-size H-aggregates (493 nm) and J-aggregates (587 nm).

The modification of the carboxyl acid groups in rhodamine dye molecules into that of an ester-type significantly changed the interaction with layered silicates in the dispersions (Figure 6, 7). The first example is the simplest dye used in this study, with a methyl ester group in its molecule, R123 (Figure 6). In contrast to the dyes with carboxyl groups, R123 more extensively changed its optical properties with time in the dispersion of FH (Figure 6b). Monomers (509 nm), but mainly the H-dimers (479 nm), were rearranged into the large-size H-aggregates (439 nm). Also, the J-aggregates (552 nm) were probably formed at the beginning of the reaction, but their concentration did not significantly change after 5 min. J-aggregates were often observed for the rhodamine dyes.³³ Lower spectral changes occurred for R123/Sap (Figure 6a). Monomers (512 nm) changed to H-dimers or larger-size H-aggregates (468 nm). The size of the R123 H-aggregates formed in the presence of Sap did not achieve the one present on the FH surface, as indicated by the bands' positions. Occurrence of the species absorbing light of lower energy was not detected in the reaction with Sap. Interestingly, the spectral changes are very similar to those observed for a R560/Sap dispersion (Figure 5c). There could be some relationship between the type of the changes and similar structure (and relatively low hydrophobicity) of both the R123 and R560 dyes.

The interaction of R6G with layered silicates in dispersions has been extensively studied.^{7,34} Furthermore, the TDS have been studied for a series of dispersions with reduced-charge

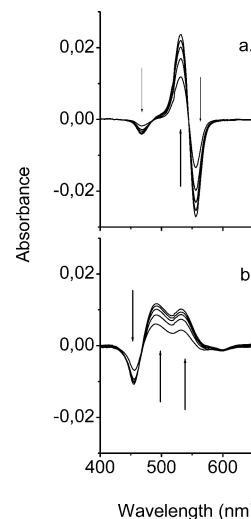


Figure 7. Time-difference spectra for the reaction systems in saponite (a) and fluorohectorite (b) dispersions with rhodamine 6G.

montmorillonites (RCMs).¹ The RCMs are semisynthetic layered silicates prepared from one parent, natural sample (Li⁺-saturated montmorillonite) and differ only in the layer charge and related properties. It would be interesting here to compare the TDS obtained for FH and SAP, typical representative layered silicates of high and low charges, respectively, with those obtained for the RCMs. In the FH dispersions, the R6G H-dimers (491 nm) and monomers (531 nm) rearrange into large-size H-aggregates (456 nm), (Figure 7b). The spectral changes are very similar to those observed for the same dye in dispersions with high-charge RCMs.¹ For FH, relatively more H-dimers decompose than those observed for the RCMs. This difference may be due to the higher initial formation of the H-dimers during an early stage of the reaction. The lower swelling ability of FH (due to very high charge) and higher concentration of the ions at the electric double layer would support the formation of the H-aggregates. The TDS for the R6G/Sap reaction are similar to those observed for the RCMs with a low layer charge in some important features. For example, only a low amount of H-aggregates (468 nm) is formed. Nevertheless, the amount of monomers absorbing at 532 nm significantly decreased in favor of the species absorbing at 556 nm. These species could be assigned to either the J-aggregates or monomers adsorbed in a new, more polar environment. The J-aggregates of R6G often coexist with the H-ones, but their formation depends much on the reaction conditions and counterions.³⁵

R3B is the most hydrophobic dye used in this study. The TDS indicate more significant changes in the reaction on the Sap surface (Figure 8). Perhaps the dye interacted less with the FH surface. It may be related to the high charge of FH and hydrophilic properties of its surface in contrast to the hydrophobic properties of the dye. In the FH dispersion, a relatively low amount of monomers (565 nm) was converted into the species absorbing light of a lower energy (593 nm), probably the J-aggregates and/or monomers in a more polar environment. The drift in the baseline indicates flocculation and sedimentation of the dye/FH dispersion. More extensive changes occurred for a R3B/Sap dispersion (Figure 8a). In contrast, the reaction adducts also included a small amount of H-dimers (522 nm), and the absorbance ratio for the monomers (561 nm) and J-aggregates (587 nm) were significantly different from that observed for the R3B/FH reaction system. This difference could be due to the conversion of the H-dimers with a relatively low molar absorption coefficient to the J-aggregates, typical for a

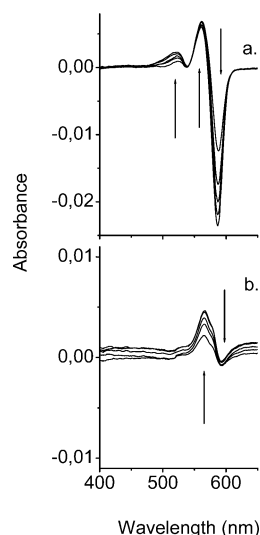


Figure 8. Time-difference spectra for the reaction systems in saponite (a) and fluorohectorite (b) dispersions with rhodamine 3B.

high molar absorptivity. It indicates that the species absorbing light of low energy and that formed on the surface of FH are not the same as those formed on the surface of Sap. Moreover, the decrease in monomers was mainly detected in the beginning of the reaction in the presence of Sap, whereas the amounts of the H-dimers and J-aggregates continually changed with time.

Conclusions

Molecular aggregation occurs together with dye adsorption. In general, dye molecular aggregation in silicate dispersions significantly depends on both the properties of the layered silicate and the dye itself.

The absence of any dye adsorption does not lead to significant changes in the dye spectra. This was observed for the dyes with carboxyl acid groups in their molecules (R19, RB, R560), which did not adsorb on the FH colloid particles.

For the R dyes with esterified carboxyl groups (e.g., R123, R6G), relatively large spectral changes due to the dye molecular aggregation are observed. These changes were more significant for the dispersions with FH. The dye aggregation significantly depends on the properties of the colloid particles, namely the layer charge density in this case. Similar phenomena were observed for rhodamine dyes adsorbed on other colloid materials.³⁶ The dye molecular aggregation in aqueous dispersions of layered silicates is usually much higher than that in dry solid films composed from same components.¹³

The slow process of reorganization of molecular aggregates accompanies a fast adsorption.³⁷ Dye species, including monomers and molecular aggregates, which were formed or decomposed with time, can be sensitively detected by the time-difference spectra measurements. Reaction pathways including the formation, decomposition, and rearrangement of the dye molecular assemblies very sensitively depend not only on the type of the dye, but also on the properties of the layered silicate colloid particles. The surface charge and parameters affecting the electric double layer of colloid particles probably control the initial dye molecular aggregation and following reactions.

Monitoring and understanding the basic laws of the influence of the silicate substrate on the reactions in nanosized molecular assemblies can be very important for a general understanding of the template-controlled reactions in complex supramolecular systems. This can provide a new insight into the basic as well as applied research. The results of this study may be important

for development of new materials based on dye/layered inorganic compound systems.³⁸

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