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Spectral Properties, Formation of Dye Molecular Aggregates, and Reactions in Rhodamine 6G/Layered Silicate Dispersions

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A series of layered silicates with a systematically modified charge was prepared from montmorillonite, using the standard method of Li^+ cation fixation. The effect of the charge of the prepared materials on the optical properties of the adsorbed cationic dye, Rhodamine 6G, was tested. The layer charge of the silicate substrate controlled the formation of the dye's molecular assemblies, such as H-dimers and H- and J-aggregates. The dye species (monomers, aggregates) were characterized by distinctly different optical properties. Ultraviolet/visible and fluorescence spectroscopies were used for the characterization of the studied systems. Time difference spectroscopy was applied for the investigation of the reactions, which proceeded in dispersions after mixing the dye solution with silicate. The reactions included the formation of higher order aggregates at the surfaces of the high charge densities or dye deaggregation reactions at the surfaces of medium or low charge densities. Some trends and features of the R6G aggregation and the changes with time in relation to the layer charge are different from those that have been observed for other dyes in older studies. This may be due to the complicated structure and the specific shape of the R6G cation.

1. Introduction

Nanocomposite materials, which contain organic dyes incorporated in a solid matrix, are used in various applications, such as optical sensors, devices for photoinduced switching, solid lasers and in memory media. Rhodamines are traditionally used in dye lasers. The interactions of rhodamine dyes with various inorganic solid compounds have been studied and published in numerous papers. One could mention the studies of the optical properties of the materials formed by dye adsorption on the surfaces of glass,¹ quartz,² intercalation in the pores of silicas^{3,4} and silica gels,⁵ zeolites,⁶ layered compounds,⁷ and molecular sieves.^{8,9} Similar to other organic dyes with molecules having a flat structure or containing planar chromophore groups, rhodamine dyes form molecular assemblies (aggregates), which are characterized with various types of intermolecular associations and optical properties. Although the formation of such molecular assemblies proceeds in aqueous solutions of higher concentrations,¹⁰ it may be dramatically enhanced by the adsorption on solid surfaces.¹¹ The type of an intermolecular association (sandwich, head-to-tail) and the size of the supramolecular species significantly influence the optical properties of the dye molecules. Two main types of molecular aggregates are distinguished, which is based on the type of intermolecular association, their structure, and optical properties: The H-aggregates with a sandwich-type intermolecular association absorb light of significantly higher energies with respect to the isolated dye molecules. The J-aggregates, which are formed more rarely than the H-aggregates, absorb light of lower energies

and exhibit luminescent properties. They are assemblies with a head-to-tail association.¹²

The optical properties of rhodamine dyes in colloids of layered silicates, such as clays and micas, have been extensively studied.^{13,14} The formation of dye molecular aggregates has been proven.¹⁴ In some cases, the presence of the J-aggregates in clay colloids has also been claimed.^{15,16} Rhodamine 6G (R6G), used in this study, is a cationic dye, which has been very frequently studied. In dilute aqueous solutions, the R6G cations in a nonaggregated form absorb light at 526 nm.¹⁷ R6G forms dimers and higher order H-aggregates in concentrated aqueous solutions. The dimer, trimer, and tetramer absorb at significantly shorter wavelengths, i.e., at 498, 485, and 475 nm, respectively. However, the trimer and tetramer also exhibit a relatively strong absorbance at the longer wavelengths of 545 and 525 nm, respectively.^{17–19} Ideal H-aggregates with parallel transition moments should absorb only at higher energies, since the transition to the lower energy level is forbidden. The adsorption to both the higher and lower energy levels is related to the geometry of the formed molecular assemblies, which bears both features of the H- and J-aggregate types of association.²⁰ Numerous investigations on the optical properties of the R6G aggregates in clay dispersions produced similar results.²¹ For example, comparable extinction coefficients were determined for the bands at 478 and 528 nm assigned to the R6G dimer adsorbed on the surface of clay.²² This phenomenon was interpreted in terms of the geometry of the dimer with a nonperfect sandwich-type stacking. The nonideal sandwich association of the molecules is a typical property of rhodamine dyes as a consequence of the steric effects due to the presence of the substituted phenyl ring group, oriented perpendicular to a xantene ring.²⁰ There have been several attempts to determine some structural aspects of rhodamine dye molecular assemblies adsorbed on clays from spectroscopy data.^{23,24} Several papers

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studying the properties of the dye/silicate films have been published.²⁵

The formation of the H-aggregates leads to the reduction of the luminescent properties of the dye.³ The fluorescence quenching is due to energy transfer from the excited state of the monomers to the aggregated species. This transfer can be via either an electron exchange or Coulombic interactions. Coulombic interactions (dipole–dipole type) are long range and are effective for the systems with a large overlap between the fluorescence spectrum of the donor and absorption spectrum of the acceptor.¹⁰ There have been several studies dealing with the preparation of materials with efficient luminescent properties and containing organic dyes in their isolated, nonaggregated form. In solutions, aggregation is suppressed by the presence of either neutral surfactants or that with an opposite charge. There is no significant effect by the surfactant of the same charge.²³ On the other hand, coadsorption of R6G with a long-chain cationic surfactant on the surface of a layered silicate dramatically increases the fluorescence of the dye.²⁶ R6G/layered silicate films without the presence of a surfactant did not exhibit luminescent properties.²⁷ Enhanced fluorescence of R6G was observed in organic–inorganic hybrid matrixes,²⁸ in inclusion complexes between rhodamine 6G and cyclodextrins,²⁹ or in the cavities of MCM-41 silica,³⁰ where R6G cations were adsorbed in a monomeric form. The presence of nonpolar solvents either reduces the formation of H-aggregates³¹ or induces the formation of fluorescent J-aggregates.^{32,33} Besides dye aggregation, there could also be other effects on the luminescence of the dye in the adsorbed state. For dye/solid-type materials, one of them could be light scattering or absorption by the solid substrate.¹⁵ Another effect relates to the deformation to a nonplanar conformation upon adsorption, which may significantly reduce the fluorescence yield.^{3,34}

The aggregation of dye cations on a clay surface may significantly vary depending on the clay specimen used.³⁵ The formation of R6G aggregates in clay dispersions has been mostly interpreted in terms of clay colloid properties.²¹ The effect of the layer charge density on the aggregation of dyes of various types has been observed (namely for cationic thiazine,^{35–37} cyanine,^{38,39} and triphenylmethane dyes⁴⁰). On the other hand, the effect of the layer charge on the aggregation of rhodamine dyes has never been studied or observed, although numerous papers related to this topic have been published. Therefore, the objective of this work was to experimentally investigate the formation of R6G molecular aggregates in the series of dispersions of reduced-charge montmorillonites (RCMs). The RCMs represent a series of similarly layered silicate materials with a systematically changed layer charge but of the same structure, composition, and particle size characteristics. Spectral changes with time as a consequence of the structural evolution of the dye assemblies and the fluorescent properties of the dye/silicate dispersions were also studied.

2. Experimental Section

The RCMs were prepared from one parent Li-montmorillonite Nanocor (N), which had been prepared from a commercially available Na-saturated form.³⁸ The Li-saturated montmorillonite was prepared by an ion-exchange reaction, performed as a repeated saturation with LiCl solution. Heat treatment of N was performed at 100, 110, 120, and 130 °C for 24 h. The materials prepared by heating are called N100, N110, N120, and N130, in which the numbers denote the heating temperature used for the preparation of the RCMs. The layer charge was characterized by cation exchange capacities (CECs). Exchangeable cations

were released from the samples upon saturation with neutral pH ammonium acetate and barium chloride solutions.⁴¹ The amounts of exchangeable cations were determined by using atomic absorption spectroscopy. The CECs were determined as the average number of exchangeable cations per 1 g of dehydrated sample and decreased for the N–N130 series: 1.35 (N), 1.24 (N100), 1.18 (N110), 1.14 (N120), and 1.05 mmol/g (N130). More details about the properties of the samples have been published elsewhere.⁴¹

The UV–vis spectra of the R6G/clay dispersions were measured. The concentration and loading of the dye cations in the dispersion were always 2.5×10^{-6} mol dm⁻³ and 0.05 mmol g⁻¹ of clay, respectively. The visible spectra were measured with a V-550 UV–vis spectrophotometer (Jasco Co., Ltd.). The spectra were measured 1 min after mixing the dye solution with the clay dispersion. The dispersions were then shaken for 24 h. Equilibrium was achieved and another series of spectra for the aged dispersions was taken. The spectra of the clay dispersions without the dye were subtracted from the dye/clay spectra to obtain the spectra for the adsorbed R6G species. The positions of the bands were always determined by second derivative spectroscopy.⁴²

The evolution of the dye species with the aging time was checked by difference spectra. Time difference spectra were calculated by subtracting the absorbance values measured at different reaction times for all the wavelengths according to the following equation:

$$A(\lambda_i) = A(\lambda_i, t=1 \text{ min}) - A(\lambda_i, t_j)$$

The spectrum of the fresh dispersion was recorded 1 min after mixing the dye solution with the clay dispersion. The spectra of the aged dispersions were measured after 5, 10, 15, 20, and 25 min.

The emission spectra were measured on a JASCO FP-750 spectrofluorometer. Only the aged reaction systems were tested after chemical equilibrium was achieved and no changes had occurred with time.

3. Results and Discussion

3.1. Effect of the Layer Charge. The effect of the layer charge of the layered silicates has already been demonstrated for the interactions with methylene blue.^{35–37} The amount of H-aggregates of methylene blue increased with layer charge of silicates. The amount of H-aggregates decreased with aging, mainly for dispersions with layered silicates of moderate or low charge. Figure 1 shows the R6G spectra in clay dispersions of RCMs arranged in order of increasing layer charge. There was no free dye in the solution as confirmed by the spectra measurements of supernatants obtained by filtration of the R6G/RCM dispersions. The silicate was in excess with respect to the amount of dye. The dye amount added to the dispersions (0.05 mmol/g silicate) was much lower than the CECs of the RCMs (1.05–1.35 mmol/g). The spectra measured 1 min after mixing the dye solution with clay dispersions are shown in Figure 1a. These spectra are characterized by a dominant band, which is centered at about 535–540 nm, and broad shoulders at shorter wavelengths. The main, high-energy band was assigned to the R6G monomers adsorbed on the clay surface.²¹ Adsorbed monomers of the dye absorb light at slightly longer wavelengths with respect to the absorption in aqueous solutions (526 nm).¹¹ The band position does not significantly change with the layer charge of a clay substrate. It moves only slightly from 539 (N) to 536 nm (N100–N130), which was also

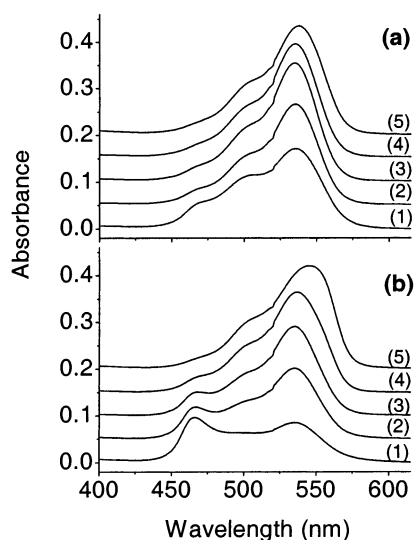


Figure 1. Rhodamine 6G spectra in the presence of reduced charge montmorillonites (1) N, (2) N100, (3) N110, (4) N120, and (5) N130, measured (a) 1 min and (b) 24 h after mixing the dye solution with the silicate dispersion.

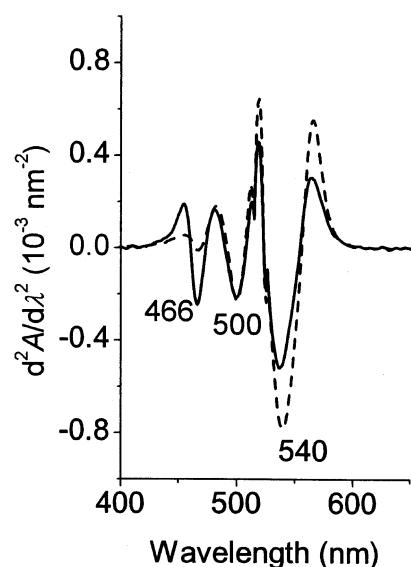


Figure 2. Second derivative spectra of rhodamine 6G in fresh dispersions of N (solid) and N130 (dashed).

confirmed by the second-derivative spectroscopy method (Figure 2). The absorption at relatively longer wavelengths (545 nm) has been assigned to the absorption of isolated R6G cations trapped in the interlayer spaces, whereas the dye cations on the external surface absorb light at relatively shorter wavelengths (535 nm).^{21e} However, there is no sufficient evidence to conclude whether such a small difference of a few nanometers in the main band position is due to the different distribution of R6G cations on the external or internal surfaces of the layered silicate, or if there are other causes. Within the series of spectra, there are some slight changes with the layer charge observed in a range of shorter wavelengths (<525 nm). With the increasing layer charge of the silicate, the amounts of the species absorbing light at shorter wavelengths partially increased at the expense of that for the monomers. This is clearly observed only for the R6G/N dispersion, with slightly reduced absorption at longer wavelengths and two relatively well-resolved shoulders in the high-energy range of the spectrum. Derivative spectroscopy⁴² was employed to distinguish the positions of these bands.

The bands with maximal absorptions at 500 and 466 nm were assigned to dimers and higher order aggregates, respectively, which is in agreement with the older interpretations proposed for the dye aggregation in water¹⁷ and clay dispersions.²¹ Moreover, derivative spectroscopy also provided some quantitative information. Fewer aggregates were detected in the R6G/N130 dispersion, whereas the amount of H-dimers was roughly the same for both the N and N130 reaction systems (Figure 2).

3.2. Changes with Time. R6G adsorption on a clay surface is very fast.⁴³ The dye adsorption on solid surfaces is a complex process, which also includes formation and decomposition of the dye aggregates. The study of the aggregation of methylene blue cations in clay dispersions revealed that the formation of H-aggregates already proceeds during the migration of the dye cations onto the silicate surface at the electric double layer of the clay colloid particles and before the adsorption is completed.^{37b} The H-aggregates of methylene blue formed in the very beginning of the reaction are thermodynamically unstable. Therefore, their amount usually decreases with time. The reversal process, which follows the dye aggregation, includes reactions for the decomposition of the H-aggregates to lower order aggregates such as J-aggregates, H-dimers, and monomers.^{35,36} The changes with time in the spectra of R6G in clay dispersions were also expected. The spectra recorded 24 h after mixing the dye solution with clay dispersions are shown in Figure 1b. Interestingly, the trend in Figure 1b is opposite to that having been observed for MB. There was an increase in the dye aggregation with time, mainly for the samples with the highest charge densities (N–N110). The band assigned to the dye aggregates (463 nm) was dominant in the spectrum for the R6G/N dispersion recorded after 24 h. The amount of dye aggregates significantly decreased with the charge reduction. The amount of aggregates was not as much as the methylene blue in the dispersions composed of the same RCMs and prepared under the same conditions (see Figure 1 and ref 37b). This difference is probably due to the structural differences between the cations of methylene blue and R6G. An efficient molecular aggregation occurs for the flat molecular structures, which enables the coupling of transition moments between associated chromophores subsequently leading to the spectral changes.⁴⁴ The presence of substituted phenyl groups, oriented in a perpendicular fashion to the xanthene-ring chromophores, may act as a kinetic, as well as a thermodynamic barrier for the dye aggregation. Therefore, the R6G aggregation is a slower process than that of the methylene blue cations. Another aspect is that the more complicated shape of the R6G cations controls the formation of the aggregates of a specified structure.¹⁶

3.3. Time-Difference Spectra. A comparison of panels a and b of Figure 1 provides information on the changes between the spectra measured 1 min and 24 h after mixing the clay dispersions with the dye solution. However, rapid and significant changes occurred at the beginning of the reactions, which were visually observed as changes in the dispersions' color. To see in more detail the evolution of the dye spectra during the beginning of the reaction, the time-difference spectra were measured for each R6G/RCM reaction system (Figures 3 and 4). The time-difference spectra show the changes taking place in the first 25 min and were calculated by subtracting the spectra of the aged dispersions from that of a fresh one. Bands of a positive absorption in the time difference spectra represent species, which decomposed with time to the reaction products. The species, whose presence was reflected by the bands of negative absorbance values, were products formed by the reactions. The time-difference spectra detected the reaction

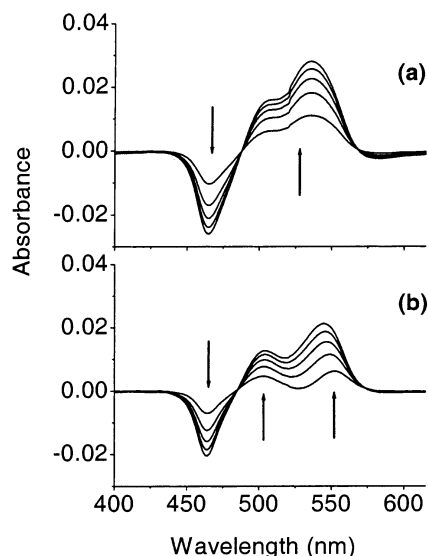


Figure 3. Time-difference spectra of rhodamine 6G in dispersions of (a) N and (b) N110. Time-difference spectra were calculated by subtracting the spectra of aged dispersions from that of a fresh one. The spectra of the aged dispersions were measured 5, 10, 15, 20, and 25 min after mixing the dye solution with the silicate dispersion. The spectrum of a fresh dispersion was measured 1 min after mixing the dye solution with the silicate dispersion. The arrows show an evolution of the time-difference spectra with time (5–25 min).

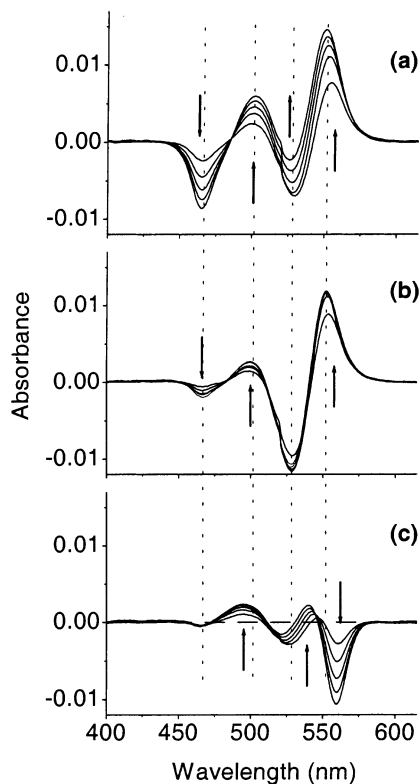


Figure 4. Time-difference spectra of rhodamine 6G in dispersions of (a) N110, (b) N120, and (c) N130. Time-difference spectra were calculated by subtracting the spectra of aged dispersions from that of a fresh one. The spectra of the aged dispersions were measured 5, 10, 15, 20, and 25 min after mixing the dye solution with the silicate dispersion. The spectrum of a fresh dispersion was measured 1 min after mixing the dye solution with the silicate dispersion. The arrows show an evolution of the time-difference spectra with time (5–25 min). Dashed grid lines are at 466, 502, 529, and 552 nm.

adducts and products whose spectra were at least partially different, so it is very suitable for distinguishing various dye

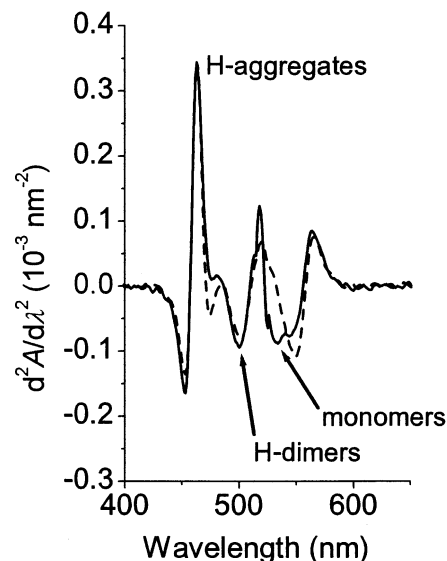


Figure 5. Second-derivative spectra calculated from time-difference spectra of rhodamine 6G in dispersions of N (solid) and N100 (dashed). Time-difference spectra were calculated by subtracting the spectra of aged dispersions measured 25 min after mixing the dye solution with the silicate dispersion from the spectrum of fresh ones measured after 1 min.

forms, such as monomers, aggregates, etc. Their disadvantage is a low sensitivity for potential products having no absorbance in the visible or UV spectral ranges. However, this should not be the case for the formation or decomposition of the dye aggregates, where only the changes in the band positions within the visible range of the spectrum are expected, although the absorptivities of some species may significantly vary as well. The presence of dye species with two or more bands cannot be neglected. Figure 3a shows the time-difference spectra for the R6G/N reaction system. The dye species, which decomposed with time, were represented by two positive-absorbance bands at longer wavelengths. The band at longer wavelengths has been attributed to dye monomers. It is composed of at least two bands as resolved by the derivative spectroscopy. One species of monomers absorbed light at about 534, the other nearby at 545 nm (Figure 5). The former one may represent the dye cations adsorbed at the external surface, the latter cations adsorbed at the polar environment, possibly in the interlayer spaces of the silicate colloid particles.²¹ The shoulder at partially shorter wavelengths (about 500 nm) represents another adduct that decomposed with time. It was assigned to the H-dimers, which is in agreement with the assignment in previous studies.¹⁶ The reaction product, which is characterized by the band of negative-absorbance values and absorbing at short wavelengths (463 nm), was assigned to the larger H-aggregates. The complex character and the broad shape of the bands (Figure 3a) indicate the presence of potentially more dye molecular assemblies of similar spectral properties, but partially different in structure and/or size. Formation of dye species exhibiting light absorption characterized by two or more bands also cannot be neglected. The possibility of the formation of different and various species of rhodamine dyes on silicate surface has been reported recently.⁴⁵

Similar trends in the spectral changes were observed for the R6G/N100 dispersion (Figure 3b). Adducts, which included monomers and H-dimers, were represented by the bands at longer wavelengths and converted to H-aggregates, which absorb light at shorter wavelengths. In contrast to the R6G/N dispersion, relatively more H-dimers and fewer monomers are converted

to the H-aggregates. The amount of H-aggregates was relatively lower. The monomers included subspecies, which absorbed light at longer wavelengths (550–555 nm). The different position of the band assigned to the monomers is clearly observed by second-derivative spectroscopy (Figures 5). In summary, the reactions in the R6G/N and R6G/N100 dispersions can be interpreted as the formation of high-order H-aggregates from monomers and H-dimers. The reactions are practically the same for both the N and N100 dispersions, which is in contrast to the significantly different reactions detected for the samples with lower charge densities, as shown below.

For the RCMs of the lower charge densities, the spectral changes were more complex and complicated (Figure 4). Similar to the reactions in the N and N100 dispersions, the amount of higher order H-aggregates also increased with time in R6G/N110 dispersion (Figure 4a). The H-aggregates formation was observed as a negative band at short wavelengths. Another product was detected as the band of a negative value centered at about 530 nm. However, this species was produced only in the first 5 min, and as the reaction progressed, its amount decreased with time as indicated by the changes in the band toward less negative values (see the arrow in Figure 4a). In previous studies, species absorbing at this wavelength have been assigned to the dye monomers.¹⁶ The band at 500 nm, which was assigned to the H-dimers, represents an adduct of the reaction. Another species, which absorbed light at about 550 nm, also decomposed with time. In some previous studies, R6G cations, which were formed in dispersions of layered silicates and absorbed light at higher wavelengths (around 550 nm), were assigned to monomers intercalated in the interlayer spaces of silicate tactoids.¹⁶ The amount of dye cations adsorbed in the interlayer spaces (550 nm) decreased with the reaction time in favor of the externally adsorbed monomers (530 nm). However, a rather opposite reaction is expected, first the adsorption of the dye cations at the more accessible external surface and then the penetration of the cations into the interlayer spaces.¹⁶ Therefore, the species that absorbed light at 550 nm were more probably the monomers, which had been adsorbed in a polar environment, also including the external, easily accessible surface, and not only the internal surface located between the clay layers. For example, such polar sites may include those next to inorganic ions, or at silicate particle edges, nearby structural defects, etc. One should not neglect the potential formation of J-aggregates. The J-aggregates are molecular assemblies characterized by a head-to-tail intermolecular association. They absorb light at higher wavelengths with respect to the isolated, nonassociated cations. They are preferentially formed in solutions and in other reaction systems of some cyanine dyes due to the specific molecular shapes and properties.⁴⁶ On the other hand, the formation of head-to-tail intermolecular assemblies can be formed at interfaces and under specific conditions for dyes, which commonly form only H-aggregates.⁴⁰ Another possibility of the interpretation would be based on the assignment of the bands at 500 and 550 nm to the same species, namely oblique J-dimers. Both of these bands changed with time in the same fashion and at a similar rate for both R6G/N110 and R6G/N120 (Figure 4a,b). On the other hand, although the band at 500 nm appeared also in other time-difference spectra, the band at 550 nm accompanying the higher wavelength component was either absent (Figure 3) or evolved differently with aging (Figure 4c).

As mentioned above, the amount of externally adsorbed monomers (530 nm) increased during the very beginning of the reaction. One possible pathway would be the formation of

externally adsorbed monomers from initially formed H-dimers (500 nm) and possibly J-aggregates (550 nm). The H-dimers were formed rapidly in the very beginning of the reaction at the electric double layer of the clay colloid particles.^{37b} We could not detect this reaction, because it was an almost instantaneous process.^{37b} Indeed, the H-dimers of R6G were formed in fresh dispersions and then deaggregated with time regardless the effect of the layer charge of the clay (Figures 3 and 4). The H-dimers, having been formed in the first step in the electric double layer zones of the colloids, were partially destabilized at the clay surface or at sites with a charge density, that was lower with respect to that specific for the H-dimer assemblies. The H-dimers deaggregated, liberating the monomeric dye cations, which were detected as externally adsorbed monomers (530 nm) rapidly formed during the first 5 min of the reaction. One should note that the formation of monomers was not detected for the R6G/N and R6G/N100 reaction systems (Figure 3). Apparently, the layer charge density affects not only quantitatively the distribution of the dye species on the silicate surface but also some qualitative aspects. It controls the reaction pathways of the dye cation re-distribution. It is a very interesting phenomenon, which has not been reported to date. Possibly the higher charge densities of N and N100 either stabilized the dye molecular assemblies, including a fraction of the H-dimers, or induced other reactions, such as the conversion of the H-dimers to the aggregates of a large size. Indeed, the H-aggregates were produced in the R6G/N and R6G/N100 reaction systems as the only products from the beginning of the reaction (Figure 3). Similar to higher charge silicates, the H-aggregates were produced as the only reaction product also in the R6G/N110 reaction system, but only after the first 5 min (Figure 4a).

Similar processes were observed in the R6G/N120 dispersion (Figure 4b). The reaction rate for the H-aggregates formation was significantly lower in this case. This is in agreement with the assumption that higher order H-aggregates are mainly formed at the surfaces of high negative-charge densities.³⁶ The lower extent of H-aggregate formation was due to a lower charge density at the surface of N120 and large average distances between neighboring negative charge sites. Interestingly, the number of decomposed H-dimers was also much lower than that for the case of the R6G/N110 reaction system (Figure 4a,b). The amount of decrease in the cations absorbing at 555 nm was of similar magnitude to that observed for the R6G/N110 reaction system (Figure 4a,b). Similar to the previous case, the amount of externally adsorbed monomers (530 nm) increased during the first 5 min of the reaction, but remained almost constant for the next 20 min. In general, the reactions taking place in the R6G/N120 dispersion finished or approached equilibrium much faster, and the changes observed in the last measurement were almost negligible (Figure 4b).

Particularly different spectral changes with time were observed for R6G adsorbed on the silicate with the lowest charge density N130 (Figure 4c). Two adduct species initially formed on the silicate surface converted with time to the three reaction products. The first adduct was probably dye cation monomers and absorbed light at 540–546 nm. The second product included H-dimers or lower order H-aggregates characterized by a broad band at about 496 nm. Interestingly, the position of the band assigned to the monomeric adduct changed with time from longer to shorter wavelengths. A similar feature was observed for the reaction product assigned to the external monomers, which absorbed light at 526–521 nm. The spectral changes observed for the N–N120 samples could be expressed as the changes in the absorbance values of the present species

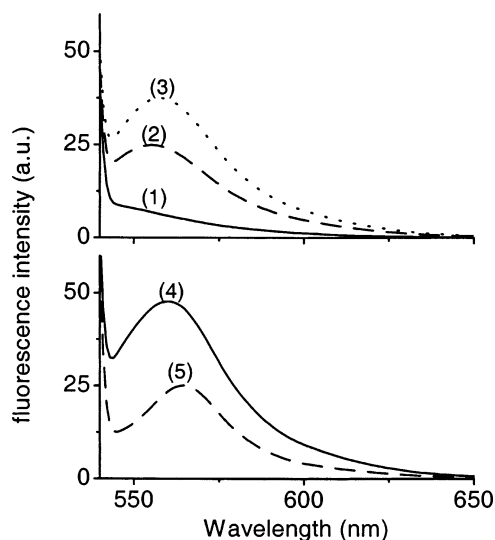


Figure 6. Emission spectra of R6G in aged dispersions of (1) N, (2) N100, (3) N110, (4) N120, and (5) N130 after excitation at 530 nm.

(quantitative changes, Figures 3 and 4a,b). On the other hand, the changes observed for the N130 dispersions also include the shifts in the spectral bands (qualitative changes) (Figure 4c). This indicates evolution of the reaction system due to partial flocculation of the clay particles induced by a relatively significant charge reduction,³⁶ which had taken place for the N130 sample. The partial flocculation of the N130 dispersion led to the formation of a substrate with different properties, which might have affected the spectral properties of the dye species. Interestingly, only the positions of the dye monomers were changed with time. Very small amounts of H-aggregates were formed with time as indicated by the hardly detectable negative band at about 465 nm. The amount of the H-aggregates did not practically change after a 5-min reaction. Interestingly, a strong negative band appeared at relatively long wavelengths (560 nm). This is a new feature of the R6G/N130 reaction system. The formation of the dye species, which absorbs at 560 nm, was not observed for the higher charge silicates N–N120. Similar species appeared in the spectra of the R6G cations embedded in silica gels, which were attributed to the J-aggregates of the dye cations.^{4b} The absorption at longer wavelengths was also directly observed in the spectrum of R6G/N130 measured 24 h after mixing the dye solution with the silicate as shown in Figure 1b and discussed above. One should note the shift to shorter wavelengths for the band assigned to the H-dimers and measured for the R6G/N130 reaction system (495 nm) with respect to those measured for the other dispersions (>500 nm).

3.4. Fluorescent Spectra. Emission of R6G in silicate dispersions was significantly reduced with respect to the solution spectra (not shown). It was likely due to dye aggregation, quenching, and light scattering effects, which were discussed in detail above. Figure 6 shows the fluorescence emission spectra of aged R6G/RCM dispersions recorded after excitation at 530 nm. At this wavelength, light absorption and subsequently the excitation of mainly the R6G monomers is expected. Therefore, the intensity of the emitted light should be related to the amount of the present dye monomers in the reaction system. Indeed, no peak is observed in the spectrum of the excited R6G/N dispersion (Figure 6) with the lowest amount of monomers and mostly contained H-aggregates as observed in the absorption spectrum (Figure 1b). The background emission indicates the presence of only traces of active fluorochroms, which emitted light after the irradiation at 530 nm (Figure 6). A small peak

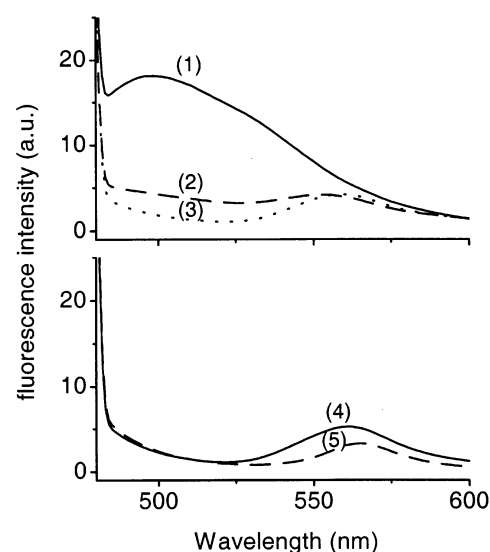


Figure 7. Emission spectra of R6G in aged dispersions of (1) N, (2) N100, (3) N110, (4) N120, and (5) N130 after excitation at 470 nm.

with a position at about 555 nm was resolved in the spectrum of the R6G/N100 dispersion. With the decreasing layer charge, the intensity of the emitted light increased to the spectrum of R6G/N120 sample. The band position changed only slightly to longer wavelengths with the charge reduction. However, the decrease in the absorbance value was observed with a further charge reduction for the spectrum of the R6G/N130 dispersion. This might be a consequence of the shift in the light absorption to longer wavelengths observed for this dispersion (Figure 1b). The reduction of emitted light was more probably due to light scattering induced by dispersed silicate particles, which was higher for N130 because of the flocculation of silicate particles.¹⁵ Significant charge reduction in the case of this sample induces the formation of nonswelling phases or zones, which brings about the formation of larger colloid particles in dispersions. Such an effect would most likely occur in the N130 dispersion with the lowest layer charge, which was confirmed by the measurements of the background scattering spectra in the UV and vis ranges (not shown). Larger particles scatter light more, which might have contributed to the lower fluorescence efficiency.

Quenching of the fluorescence due to the presence of layered silicates in the dye/clay dispersions has been attributed to the presence of iron or other transitional metal atoms. The transitional metals can be directly present in the structure of natural silicates or in the form of mineral admixtures, such as TiO₂, iron oxides, etc.⁴⁷ Their content did not change with the charge reduction for the samples used in this work, so the quenching due to the presence of transitional metals should be constant for all samples. An absence of the fluorescence properties was also expected for the H-aggregates, which was mainly due to the transfer of the excitation energy between monomers and the aggregates.¹⁰ The number of H-aggregates is controlled by the charge density on clay layers. The H-aggregates absorb light at about 470 nm. The fluorescence properties of the H-aggregates were inspected by measurements of the fluorescence spectra after the excitation at this wavelength. Figure 7 shows the fluorescence spectra recorded for aged R6G/RCM dispersions, which contained relatively more H-aggregates than the fresh ones. For the samples with a reduced charge, low emission at relatively long wavelengths (555–565 nm) was observed. We suppose that these bands are related to the fluorescence of monomers, excited at the spectral band edge. The monomers

were present in these reaction systems in sufficient amounts. Another broad band envelope appeared at short wavelengths. It was clearly distinguished only in the spectrum of the R6G/N dispersion. The maximum intensity of emitted light was observed at about 500 nm. The predominant presence of the H-aggregates in the reaction system of R6G/N indicates that this band relates to the emission by the dye in the H-aggregates. However, the H-aggregates mostly do not emit light because of the energy transfer between the H-aggregates and monomers. The absence or a very low amount of the monomers in the aged R6G/N dispersion might not have suppressed the luminescent properties of the H-aggregates. Fluorescent aggregates of rhodamine dye have been observed for the dye absorbed in porous silica gels.¹² These species were, however, rather oblique J-aggregates, which absorbed the light at both longer and shorter wavelengths. Moreover, the emission mostly occurs from an excited state, which is energetically the lowest (Kasha's rule).⁴⁸ This is because of the short lifetime of the electron at higher excitation states and its fast transition to the lowest excited state. In the case of H-aggregates, there is also lower energy excited state. Transition to the lower energy excited state from the basic state is forbidden, and therefore, R6G H-aggregates do not absorb light at lower energies. As mentioned above, according to Kasha's rule, only emission from the lowest excited state is possible. However, there are some exceptions to this rule. In some cases, H-aggregates can also exhibit specific luminescent properties, e.g., the H-aggregates of oligophenylene-vinyls.⁴⁹ In this case, the superradiant properties of the H-aggregates were attributed to the long-range orientational order and constructive interference between the molecular transition dipole moments.⁴⁹ The presence of the structure of large-size and ordered H-aggregates of R6G also occurs on the silicate surfaces, which has been observed by polarized spectroscopies and XRD.^{25–27} One of the most common exceptions to Kasha's rule⁴⁸ is the case of the reaction that follows the excitation of the molecule and originates from the upper excited state. R6G adsorbed on surfaces can undergo certain changes upon excitation.⁵⁰ Various conformers of R6G are formed on the clay surface³⁴ and other solid materials³ depending on the intrinsic properties of the substrate. The complete understanding of luminescent properties of the R6G/silicate materials, especially the fluorescence of the R6G H-aggregates, requires further investigation, which is planned for the future.

4. Conclusions

The adsorption of a cationic, xantene dye, rhodamine 6G, on the surface of negatively charged layered silicates is followed by the aggregation of the dye cations. The extent of molecular aggregation, as well as the type of molecular assemblies formed is determined by the layer charge properties of the silicate. The large-order H-aggregates are formed on surfaces with high charge densities. The dye/silicate dispersions are dynamic systems, where complex and complicated re-organization and re-distribution of the dye assemblies take place. These changes are different from those observed for the cationic dyes of other types and very sensitively depend on the layer charge of the silicate. Observed trends could lead to the development of a spectroscopic method, to probe the surface charge properties of the layered silicates. Fluorescence spectroscopy revealed the luminescent properties of adsorbed dye cations, which were adsorbed in the form of monomers. Surprisingly, also the H-aggregates exhibited weak luminescent properties mainly in the reaction system with the highest charge silicate, which

contained mainly ordered, large-size aggregates with a negligible fraction of the monomeric form. The explanation of this phenomenon requires further studies.

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