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Spectral and Structural Characteristics of Oxazine 4/Hexadecyltrimethylammonium Montmorillonite Films

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Competitive adsorption from oxazine 4/hexadecylammonium solutions on montmorillonite films was used for the preparation of hybrid materials with modified optical properties. The films were characterized using linearly polarized visible spectroscopy, X-ray diffraction, and fluorescence spectroscopy. The composition of the reactant solution influenced the amount of the dye adsorbed on the clay mineral template and secondarily affected the presence of variable dye species (isolated dye cations and dye molecular aggregates). Polarized spectroscopy revealed an almost perpendicular orientation of large-sized H-aggregates with a sandwich-type intermolecular association. A more-parallel orientation occurred for other dye species such as isolated dye cations, H-dimers, and J-aggregates. Coadsorption of the surfactant did not change the orientation of the chromophores significantly. The variation of the chromophore/surfactant amounts in the interlayer spaces of the montmorillonite did not lead to significant changes in the interlayer distance. On the other hand, the presence of the surfactant led to a higher emission efficiency. The large-sized H-aggregates did not exhibit luminescent properties, in contrast to the luminescent J-aggregates.

Introduction

Adsorption of cationic dyes on the surfaces of clay minerals is accompanied by the formation of molecular aggregates.[1] Molecular aggregates are supramolecular assemblies, which are built from two or more molecules (ions) held together by van der Waals forces.[2] The dye molecular aggregates are characterized by a specific structure and exhibit unique optical properties.[3] Two main types of the dye molecular aggregates include H- and J-aggregates, with sandwich- and head-to-tail-intermolecular associations, respectively. The H- and J-aggregates are just two marginal cases of all possible structural species of variable structures. The structure of the aggregates depends on the dye's molecular structure and secondarily on the reaction conditions of their formation.[4]

Xanthene dyes are one of the most studied fluorophores, which are known for their numerous applications, such as in laser dyes,[5] probes in biology, and biochemistry.[6] One of the modern trends in nanotechnology is the fabrication of thin-layer materials with defined optical or photochemical functionality and properties.[7] One kind of such materials is a composite film, which is composed of an inert and optically inactive inorganic substrate and an embedded organic dye.[8] To obtain suitable optical properties of the material, an optimal choice of both the dye and inorganic substrate is very important.[9] Formation of the molecular assemblies in the composite film usually alters the properties of chromophores; for example, the formation of the H-aggregates leads to the quenching of fluorescence, and therefore, the formation of the films of fluorescent dye/clay minerals often leads to a loss of fluorescence.[10] Another important aspect is the orientation of the chromophores. The orientation is likely nonrandom, because of anisotropy of the inorganic substrate.[11] A preferential orientation can be very important for the material application.[12] Improvement of the final optical properties sometimes requires more-complex materials, such as those premodified with organic surfactants. There have been some recent reports on the significant improvement of fluorescence properties by modification of the montmorillonite template with alkylammonium cations. The fluorescence of such materials exceeded that of a nonmodified dye/montmorillonite.[13,14] There is no definite evidence of what is the main effect of the present surfactant. The most probable answer is based on the hypotheses of a "solvating effect" of the surfactant molecules, which breaks or prevents

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the formation of dye molecular aggregates.[15] Moreover, the dilute state of the dye in the matrix of organically modified montmorillonite may prevent self-quenching and, therefore, is favorable for high-emission yields.[13]

The objective of this work was studying the structure and spectral properties of the films prepared from a xanthene dye, oxazine 4 (Ox4), together with a cationic surfactant, hexadecyltrimethylammonium (HDTMA) bromide and Kunipia-F montmorillonite. The variation of the dye/clay mineral ratio has been achieved by the competitive adsorption of the components. The spectra and structural characteristics are compared with the fluorescent properties of the formed materials.

Experimental Section

The host material was a purified sample of montmorillonite Kunipia-F (Na^+-ion exchange form) from Kunimine Industries. Montmorillonite was used as received, without any other modification, special treatment, or purification. The high purity of this material was confirmed by X-ray diffraction (XRD) and infrared spectroscopy (not shown). Its cation exchange capacity was 124 meq/100 g of dried sample, which is an average of the values determined by the two methods, on the basis of an ion exchange with ammonium acetate or barium chloride.[16] A few drops of the mineral dispersions (5×10^{-3} w/w) were deposited on quartz slides (Nihon Sekiei Glass), which are composed of a special quartz material transparent to UV light of wavelengths > 190 nm. A multiple-step deposition was performed by a spin-coating method at 500 (5 s) and 2000 rpm (20 s), to obtain thin films with a preferential orientation of the montmorillonite-layered particles parallel to the quartz slide surface. Aqueous solutions containing Ox4 and HDTMA bromide were prepared by mixing the components to achieve molar fractions of 100, 95, 90, 85, 80, 75, 50, and 0% amounts of the dye cations. The sum concentration of the dye and surfactant cations was 1 mmol/L. An ion exchange was conducted in about 50 mL dye/surfactant solutions by immersing the plates for 3 h at 52 °C. After the ion exchange, the concentration of the dye in the supernatant was not changed significantly because of the excess of organic cations with respect to the amount of montmorillonite in the films. The films with adsorbed dye were washed in deionized water in order to remove the excess dye and surfactant. The montmorillonite films with adsorbed dye and surfactant were dried at 50 °C for 2 h. No irreversible adsorption of the dye and the surfactant on the quartz surface (without clay minerals) was observed.

XRD measurements of the films were conducted at a scanning speed of $2°\ \mathrm{min}^{-1}$ using an RINT 1200 (Rigaku) diffractometer with Ni-filtered Cu Kα radiation ($\lambda = 0.15418$ nm). UV−vis absorption spectra of the complexes were recorded at 250−900 nm by a V-550DS (JASCO) using a JASCO polarizer (RSH-452) at a 400 nm min^{-1} scanning speed. X-polarized light (light having an electric vector polarized horizontally) and Y-polarized light (light having an electric vector vertically polarized) were introduced into a specimen, and the absorption intensities were recorded. The angle of the film normal with respect to the light direction (α) was changed from $-40°$ to $+40°$ for both of the experiments performed using X- and Y-polarized incident light. The film spectra were corrected by the subtraction of the host material absorption and scattering in order to obtain the absorption intensity due to the dye molecules. The orientation angle Θ was calculated using eqs 1 and 2 introduced elsewhere:[17]

$$R = \frac{A_y}{A_x} = \frac{2 \sin^2 \alpha - (3 \sin^2 \alpha - 1) \sin^2 \gamma}{\sin^2 \gamma} \tag{1}$$

The dichroic ratio (R) is defined as the ratio of the absorbance

$$\Theta = 90° - \gamma \tag{2}$$

values, which were recorded using Y-polarized light (A_y) and X-polarized light (A_x). As mentioned above, the angle α represents the angle between the light beam and a normal surface and is altered by rotation of the slides with respect to the y axis. The angle γ represents the angle between the vector of the transition moment and the normal vector of the surface plane and can be calculated from eq 1 using a regression analysis of the data measured for various angles α. Θ is the complementary angle of the angle γ and is the angle between the surface plane and the transition moment of the dye, along its longest molecular axis. More details about the method and the determination of the dye orientation have been published elsewhere.[17,18]

The orientation of the dye could not be determined for the films obtained in the reactions with solutions with dye molar fractions of < 75%. The fluorescence spectra of the films were measured on a Shimazu RF5300PC spectrofluorometer.

Results and Discussion

UV−Vis Spectroscopy. Figure 1 shows the absorption spectra of montmorillonite films with adsorbed Ox4 and HDTMA cations measured using X- (a) and Y-polarized (b) light. The measurements were carried out with the films tilted around the x axis at angle $\alpha = 40°$. The spectra not only provide information on the species formed but the comparison of X- and Y-polarized spectra is also useful for the estimation of the dye's molecular orientation.[17] The spectra are arranged in order of decreasing content of the dye in the starting solutions. Apparently, the spectra significantly depend on the initial dye concentration. Ox4 competes with the surfactant in the adsorption reactions and is adsorbed in significant amounts in the films. This is in accordance with another study which described in detail competitive adsorption in the montmorillonite dispersions between the mixed cationic dye and alkylammonium surfactants.[19] The spectra of the Ox4/HDTMA films indicate a higher affinity of the montmorillonite surface for HDTMA (Figure 1). This is apparent if one compares the light absorption in dependence on the dye amounts in the starting solutions. For example, the film prepared from the solution with 100% dye (line 1) contains more than double the Ox4 amount compared to the film prepared from the solution containing only half the amount of the dye (Figure 1a, line 7). This is just a rough estimation, because the determination of exact dye amounts would require the identification of all the dye species and the determination of their molar absorption coefficients. Ox4 forms various species such as monomers, dimers, and molecular aggregates of variable types and sizes; the species

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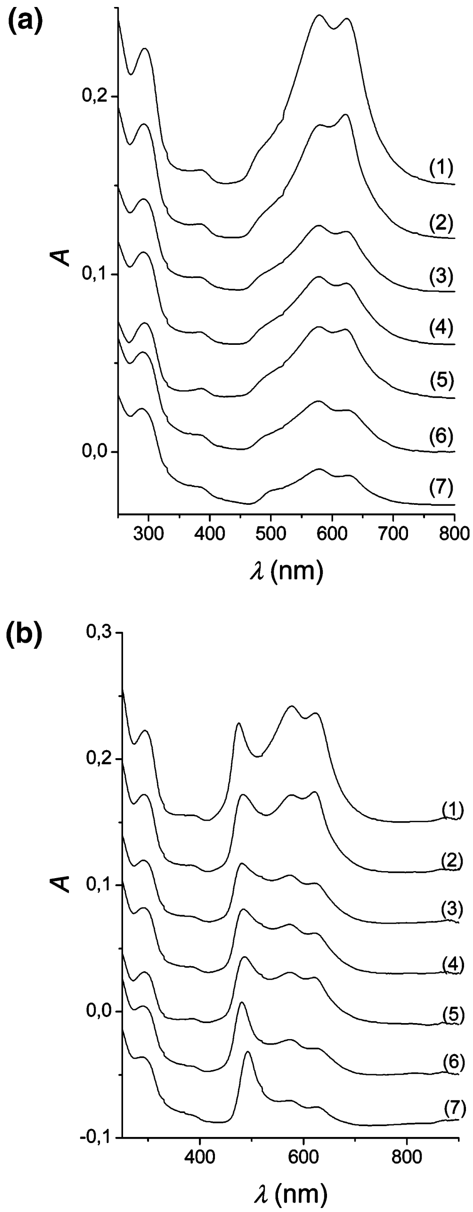

Figure 1. Absorption spectra of montmorillonite films with adsorbed oxazine 4 and hexadecyltrimethylammonium cations measured using *X*- (a) and *Y*-polarized light (b). The films were prepared from binary oxazine 4/hexadecyltrimethylammonium solutions with dye molar fractions of 100 (1), 95 (2), 90 (3), 85 (4), 80 (5), 75 (6), and 50% (7). The measurements were carried out with the films tilted around the *x* axis at angle $\alpha = 40°$.

are adsorbed at various sites and environments of different properties.[20]

There is a difference between the competitive adsorption of Ox4 with HDTMA cations as observed here and that of methylene blue (MB) with the same surfactant in dispersions reported elsewhere.[19] A large fraction of MB cations were solubilized in the HDTMA surfactant micelles on the clay mineral surface in the dispersions.[19] This apparently does not seem to occur for Ox4. On the other hand, the distribution of the Ox4 species in the films changes with the presence of the surfactant (Figure 1). For example, the film, which does not contain any HDTMA cations, is characterized by the spectrum having two dominant bands, which are assigned to dye monomers and H-dimers (Figure 1a, line 1). The shoulder at a lower wavelength indicates the presence of large-sized H-aggregates. This band does not seem to be influenced by the total amount of adsorbed dye; that is, the relative amount of the H-aggregates versus the amounts of the monomers and H-dimers increases with decreasing dye adsorption. This is a rather surprising observation, because one could assume that the presence of the surfactant would contribute to the decomposition of large-sized H-aggregates as had been observed for the MB/HDTMA dispersions.[19] This difference can be explained in terms of different reaction systems as well: The study on the MB/HDTMA competitive adsorption[19] was performed for the systems in aqueous dispersions. Excess water promotes dye aggregation in the dispersion,[21] whereby the presence of the surfactant creates a hydrophobic phase on the surface of the montmorillonite.[22] The presence of water molecules in both the dye and surfactant cation-exchanged montmorillonite films is significantly reduced, as has been observed for similar systems.[23,24] The surfactant and Ox4 cations are adsorbed or intercalated into the films in the form of micelles and molecular aggregates, respectively. In the process of competitive adsorption, individual and isolated cations of either the dye or the surfactant cannot compete with large molecular assemblies such as molecular aggregates and micelles, because the adsorption of the latter forms is enhanced by attractive van der Waals forces.[25] Indeed, this was also true for the adsorption of MB with HDTMA, although the surfactant was preferentially adsorbed on the montmorillonite surface; once the dye was adsorbed, it was not re-exchanged by the addition of the surfactant.[19]

Low absorption of *X*-polarized light by the H-aggregates, as observed in Figure 1a, can be assigned not only to the low amount of these species but also to their molecular orientation. Recently, there were some reports on an almost perpendicular orientation of the chromophores of Ox4 dye[17,20,26] and also those of other xanthene dyes[18,27,28] on the surfaces of clay minerals and related synthetic materials. Indeed, the band assigned to the H-aggregates of Ox4 is clearly observable in the spectra recorded using *Y*-polarized light (Figure 1b). The spectra in Figure 1b confirm the assumption that the amount of the H-aggregates does not change with the addition of the surfactant. On the other hand, the bands assigned to dye dimers and monomers, which absorb light at about 580 and 630 nm, decrease significantly with a decreasing initial dye concentration. This can be explained in terms of the strong adsorption of competing large-sized H-aggregates. On the other hand, the competitiveness efficiency of the surfactant molecular assemblies

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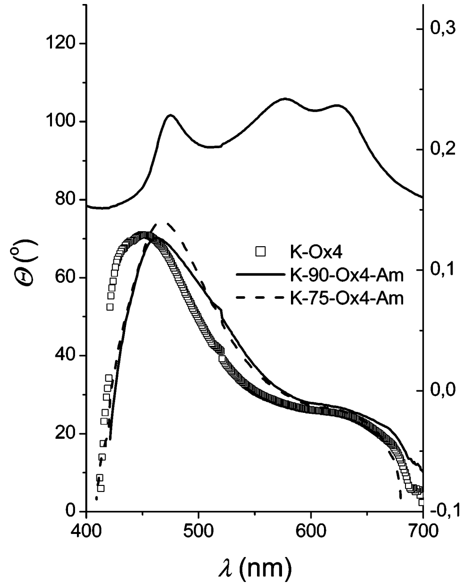

Figure 2. Dye molecular orientation angles for oxazine 4/hexadecyltrimethylammonium montmorillonite films. The films were prepared by adsorption from binary oxazine 4/hexadecyltrimethylammonium solutions with dye molar fractions of 100 (scatter), 90 (solid line), and 75% (dashed line). The angles are compared with the spectrum taken from Figure 1a (line 1).

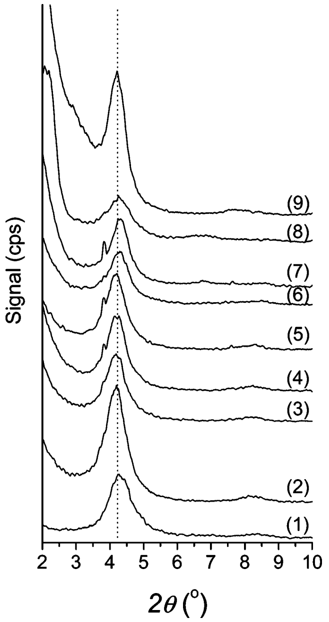

Figure 3. X-ray diffraction patterns of oxazine 4/hexadecylammonium montmorillonite films. The films were prepared from the binary oxazine 4/hexadecyltrimethylammonium solutions with dye molar fractions of 100 (1), 95 (2), 90 (3), 85 (4), 80 (5), 75 (6), 50 (7), 25 (8), and 0% (9).

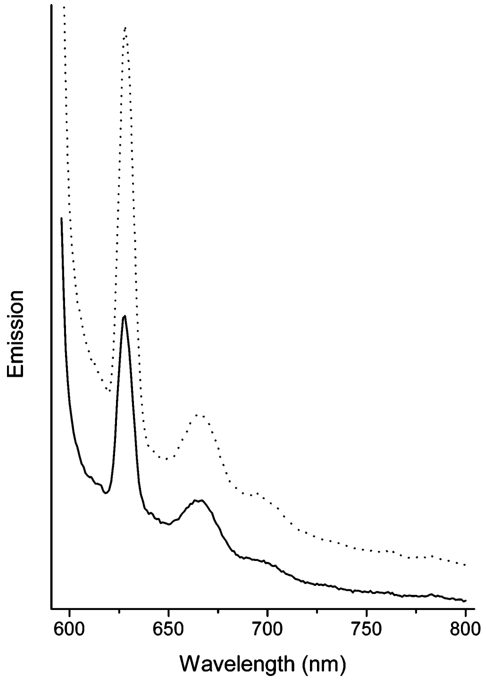

Figure 4. Emission spectra of the films obtained after excitation at 586 nm. The films were prepared from binary oxazine 4/hexadecyltrimethylammonium solutions with dye molar fractions of 100 (solid) and 25% (dotted).

with respect to the adsorption of dye monomers and dimers is much higher.

Molecular Orientation. The angles between the longest axis of the dye and the montmorillonite surface were calculated for each measured wavelength. For the accuracy of the method, the absorbances should not be too low. The measured absorption for the films also includes the components related to the light scattering and the reflection from the montmorillonite film and quartz slide. The light scattering and reflection may interfere mainly when the light absorption is very low. Therefore, the spectra of montmorillonite film deposited on a quartz slide but without adsorbed dye were measured as well. These spectra were subtracted from those of the dye/montmorillonite films in order to obtain the light absorption intrinsic to the dye chromophores. The absorption values related to the intrinsic dye absorption were used for the calculation of the dichroic ratio R (eq 1).

The calculated values of the angle Θ are shown in Figure 2. A representative spectrum helps to identify the position of the species, which otherwise are not distinguishable from the continuous angle change with the spectral wavelength. The functions of the angle Θ versus the wavelength are in general very similar, regardless of the composition of the intercalated phase. The orientation angles Θ increase with decreasing wavelengths of absorbed light. This indicates the existence of a species which is characterized by a light absorption of higher energies and which is oriented in a more perpendicular fashion. Very similar trends have been observed for similar specimens of oxazine and rhodamine dyes.[26−28] Monomers absorbing at around 625 nm are oriented at low angles, being around 25°. This is in agreement with the results of another study, where the angle of the Ox4 monomers was in the range of 22−25°.[26] With increasing wavelength, the angles decrease (Figure 2). The continuous decrease can be due to the overlap of the bands related with monomers and H-dimers with those of the H- aggregates. Although the H-aggregates absorb at lower wavelengths, their absorption bands likely overlap those of the other dye forms. For example, the real angle of isolated (nonaggregated) dye cations absorbing at 620 nm can be slightly lower than that of the value determined and identified in the Figure 2. The determined value can be overestimated because of the contribution of traces of H-dimers but is mainly because of that of the H-aggregates, which are the species characterized by higher inclination angles and whose absorption bands likely, at least partially, overlap those of the monomers.

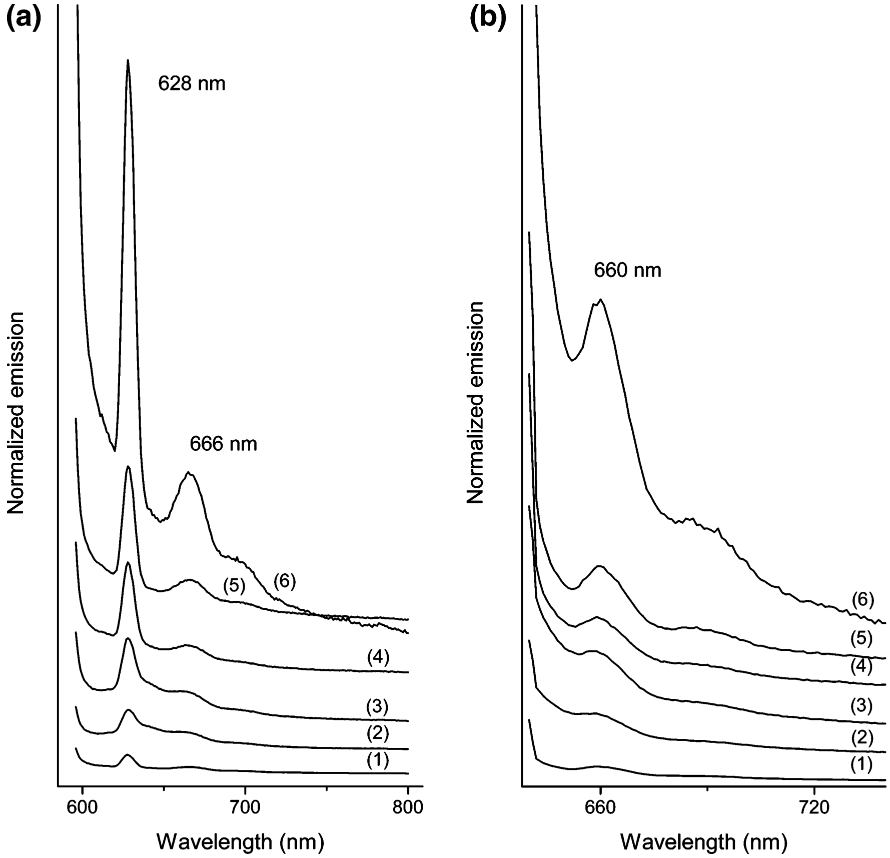

Figure 5. Normalized emission spectra recorded after excitation at (a) 586 and (b) 630 nm. The films were prepared from the binary oxazine 4/hexadecyltrimethylammonium solutions with dye molar fractions of 100 (1), 95 (2), 90 (3), 75 (4), 50 (5), and 25% dye (6).

Therefore, one cannot accurately identify the molecular orientation of all of the species separately but can see the resulting orientation angles determined for all of the species, which are in common with the energy of absorbed light.

As mentioned above, the presence of an organic surfactant did not much affect the number of the H-aggregates present in the film. In a similar way, the orientation angle, which is high mainly for the H-aggregates, was not reduced but actually increased for the films with the surfactant. The angle of molecular orientation for an Ox4/montmorillonite film, which did not contain the surfactant, and that for a dichroic band of maximal intensity at 475 nm was 64°. It reached even higher values (70°) at partially lower wavelengths (460 nm). The presence of the cationic surfactant led to a slight increase in the angle. The angle increase was more pronounced for higher wavelengths up to about 600 nm (Figure 2). This interesting phenomenon can be interpreted as follows: HDTMA cations are relatively large, covering a large area on the montmorillonite surface. The large surface area covered by the surfactant could also contribute to the lack of space available for the adsorption of dye cations. The restricted space between the alkyl chains could cause reorientation of the dye cations in order to occupy less space on the montmorillonite surface. Both of the effects could lead to the trends observed in the spectra and molecular orientation determined for Ox4/HDTMA/montmorillonite films (Figure 2).

X-ray diffraction patterns of the montmorillonite films containing Ox4 and HDTMA are shown in Figure 3. It is interesting that the film, which contains the Ox4 dye alone, exhibits similar basal spacing (2.1 nm) to that observed for Ox4 adsorbed on N110, a reduced charge montmorillonite (Nanocor), which has been published elsewhere.[26] Moreover, the spectra, dichroism, and orientation angles determined for the H-aggregates for both of the systems are very similar.[26] The similarity can be assigned to a similar charge distribution in the Kunipia montmorillonite and the N110 sample.

Basal spacings do not reflect the changes in the presence of HDTMA much (Figure 3). The position of the basal reflections remained unchanged, but the intensity of X-ray light diffracted at lower angles slightly increased. This is apparent mainly for the film which contains only HDTMA (without Ox4 dye) or for that with the lowest dye amount (molar fraction of 25%). Probably some disordered interstratified phases of larger interlayer spacing were present. Enhanced diffraction at the low angles indicates that the inclusion of the surfactant did lead to a significant increase in the average interlayer distance.

Fluorescence Spectroscopy. The emission spectra for the montmorillonite films with the dye obtained after the adsorption from solutions with molar fractions of 100% Ox4 and 25% Ox4 + 75% HDTMA are shown in Figure 4. The emission was measured for the wavelengths higher than that of the excitation (586 nm). Much smaller amounts of dye were adsorbed from the solutions with molar fractions of < 75% HDTMA, as shown by the light absorption spectra (Figure 1). This is reflected in much lower light absorption at almost the whole spectrum range, including the wavelength used for the excitation. Nevertheless, the film with the lowest concentration of Ox4 emitted the light in significantly higher yields (Figure 4). This phenomenon can be explained in terms of a self-quenching. Self-quenching is a process which can be characterized by the interaction of the excited molecules with the molecular entities of the same species in the ground state, that is, with nonexcited Ox4 cations. Self-quenching due to high local concentrations of the dye is a common phenomenon.[1] In another study, the films of montmorillonites saturated with the dye rhodamine 6G did not exhibit luminescent properties at all.[13] In the film containing 100% oxazine 4, the self-quenching was more efficient and reduced the emission yield more significantly. Indeed, the reduced emission in the film with the higher dye concentration is observed mainly for the emission at lower wavelengths (628 nm). A broad band at 660 nm and a shoulder nearby at 700 nm are not so much influenced by the composition of the films. The whole series of the films was measured; the characteristics of both the 660 nm bands and the 700 nm shoulders were found not to change much with the dye loading (not shown).

As discussed above, there is no simple method for a sufficiently accurate determination of the amounts of adsorbed dye and surfactant cations in the films. To compare the fluorescent properties of the prepared films, we calculated the normalized intensities of emitted light. The normalized emission was calculated by the division of the intensity of the emitted light by the values of absorbance at the excitation wavelength. This function relates to the fluorescence quantum yield and, therefore, is useful for the comparison and characterization of the luminescent properties of the prepared films. The normalized emission spectra recorded after the excitation at 586 nm are shown in Figure 5a. The spectra are arranged in order of the increasing amount of the dye. One can see much higher luminescent efficiency for the films containing less dye and more surfactant ions. On the other hand, the shapes of the spectra are not significantly changed. All of the spectra contain the band at 628 nm, the lower intensity band at 666 nm, and the shoulder at about 700 nm. The shoulders are not well-resolved in some spectra because of the scale of the plot, but their existence was proved in non-normalized emission spectra, for example, in the spectrum of the 100% Ox4 film in Figure 4. The highest difference between normalized spectra was observed for the films with the lowest dye concentrations. In a similar way, the normalized spectra were recorded and calculated also for the emission measured after the excitation at 630 nm (Figure 5b). In this case, only the band and the shoulder at higher wavelengths could be measured. Similar to the previous series of the spectra, the largest difference is observed for the specimens with the lowest dye concentrations. The positions of the bands and the shoulder seem to be the same as those observed for the spectra obtained after excitation at 586 nm.

Excitation spectra were measured in order to identify the chemical origin of the bands observed in the emission spectra (Figure 6). The spectra of all of the films were measured; only those for two representative samples are shown here.

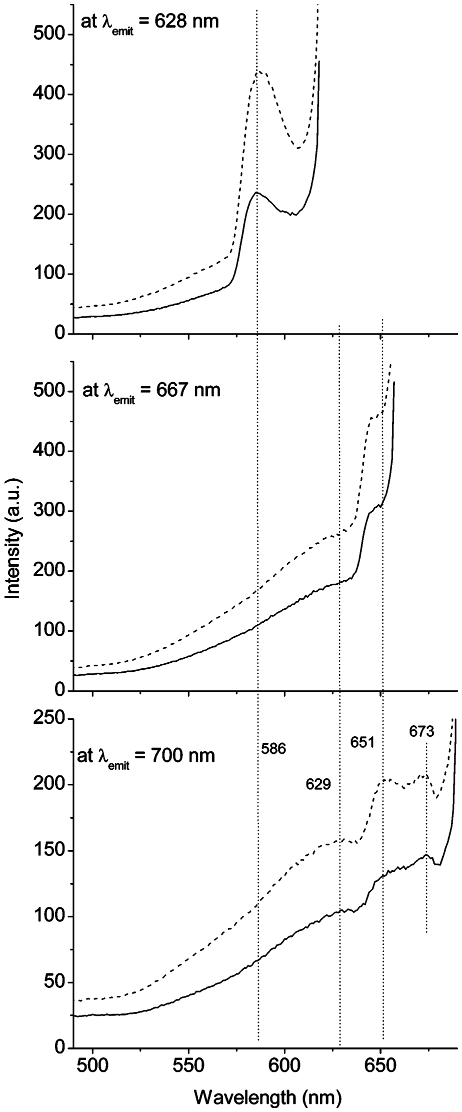

Figure 6. Excitation spectra of the films for emissions at 628, 667, and 700 nm. The films were prepared by adsorption from the binary oxazine 4/hexadecyltrimethylammonium solutions with dye molar fractions of 100% (solid) and 25% (dashed) on montmorillonite film.

Higher luminescence was always observed for the film containing the lowest amount of the dye, in a fashion similar to the trend described for the emission spectra. The composition of the film did not significantly affect the spectral shape. The excitation spectra suggest the presence of two main types of the luminescent species regardless of the film composition. There is a significant difference between the excitation spectra recorded after the excitation at 628 nm and those measured after the excitations at higher wavelengths (667 and 700 nm). The light emitted at 628 nm is mainly related to the species which are excited at 586 nm (Figure 6). These can be monomers, whose spectral band overlaps nonluminescent H-dimers. Indeed, Ox4 monomers significantly absorb at this wavelength because of a $0-1$ vibronic component of the electronic transition. The assignment of the light emission at 628 nm to the monomers is in accordance with a very small Stokes shift (around 10 nm) found for a dilute Ox4 solution, as well as dye/clay mineral dispersions (not shown). With an increasing amount of the dye, the amount of H-dimers increases. The H-dimers significantly quench the luminescence of the dye, which was observed as decreasing emission with increasing dye concentration (Figure 5a,b). On the other hand, no well-resolved bands are present in the other excitation spectra at around 586 nm (Figure 6). The emission of the light at 667 and 700 nm significantly increases with increasing wavelength of the excitation. The emission at 700 nm exhibits a shoulder at 630 nm in the excitation spectrum and two peaks in the excitation range of 650−675 nm. This is in contrast to the decreasing amount of the dye species, which absorb light in this range of wavelengths (Figure 1). The species which absorb light at 650 and 670 nm, respectively, can be identified as J-dimers or J-aggregates. The J-aggregates are luminescent molecular assemblies in contrast to nonluminescent aggregates of an H-type. One cannot neglect an energy transfer from monomers to J-dimers, up to J-aggregates, that is, to the species absorbing the light of the lowest energies. This would explain the continuous increase in the light emitted at 770 nm with increasing excitation wavelength. One should mention that no emission is associated with the species absorbing light at the lowest wavelengths (around 500 nm) and characterized by an almost perpendicular orientation at the surface of the montmorillonite. These species were assigned to the large-sized H-aggregates, which are generally nonluminescent.[4]

Conclusions

The cationic dye oxazine 4 competes with large surfactant cations, hexadecyltrimethylammonium, although the adsorption of the surfactant is preferential to that of the dye. Adsorption is likely controlled by the formation and stability of the micelles and molecular aggregates of the surfactant and the dye, respectively. Isolated cations probably cannot compete with the adsorption of the larger-sized molecular assemblies.

Variation in the dye/surfactant concentration in the reactant solution led to changes in the composition of the films. Whereas increasing proportions of the surfactant reduced the adsorbed amount of dye monomers and possibly smaller-sized aggregates, the adsorption of the large-sized H-aggregates remained unchanged.

The molecular orientation of the dye chromophores is related to the type of the species formed. An almost perpendicular orientation was observed for the large-sized molecular aggregates. A slightly tilted orientation was found for the dye monomers and dimers. The orientation angle is relatively lowest for the species which absorb light at the highest wavelengths. The presence of the surfactant cations does not influence the dye molecular orientation significantly.

Large-sized H-aggregates do not exhibit luminescent properties. Fluorescence spectroscopy indicates the phenomenon of quenching for the films with a high dye concentration and a higher emission efficiency for the films with low fluorophore amounts. An analysis of the emission and excitation spectra indicates the presence of the J-aggregates, which absorb and emit light at higher wavelengths.

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