

VISIBLE SPECTROSCOPY OF CATIONIC DYES IN DISPERSIONS WITH REDUCED-CHARGE MONTMORILLONITES

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Abstract—The aggregation behavior of one azine and three triphenylmethane cationic dyes in dispersions of reduced-charge montmorillonites (RCMs) was investigated. The extent and types of dye aggregation were monitored using visible spectroscopy. Similar relationships between dye aggregation and layer charge were observed, independent of the structure of the dye cations. High charge-density surfaces induced the formation of H-aggregates, with a face-to-face association between the dye cations that then absorb light at relatively lower wavelengths. Moderate reductions in layer charge were reflected in the lowering of the H-aggregation in favor of monomers, dimers and less densely-packed J-aggregates, absorbing light at higher wavelengths. Dye spectra in the presence of the lowest-charge RCMs resembled those of dilute dye solutions, indicating the absence of dye aggregation of any type in this case. The relationship between dye spectral changes and layer-charge densities of smectites is a general phenomenon which can potentially be used to estimate the layer charge of smectites. However, applying this method to triphenylmethane dyes, which have structurally more complicated cations, may reduce the sensitivity of the probe.

Key Words—Cationic Dyes, Dye Aggregates, Layer-Charge Density, Montmorillonite.

INTRODUCTION

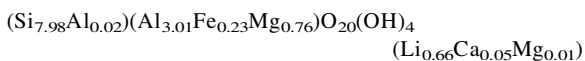
On clay mineral surfaces, dye cations are strongly adsorbed and can successfully compete with alkylammonium cations (Breen and Loughlin, 1994). Similar to long-chain alkylammonium cations, Van der Waals forces between adsorbed dye cations contribute to electrostatic adsorption forces (Margulies *et al.*, 1988). The association between dye cations on the clay surface can be monitored easily by visible (VIS) spectroscopy (Bergman and O’Konski, 1963; Cenens and Schoonheydt, 1988; Bujdák and Komadel, 1997; Bujdák *et al.*, 1998, 2001), providing information concerning the types of formed molecular assemblies. The collective optical response of dye cations in their aggregates is due to exciton delocalization and electrostatic dipole/dipole interactions between dye cations (Möbius, 1995). H-aggregates with face-to-face interactions between dye cations, are common in concentrated aqueous solutions of many dyes (Korppi-Tommola and Yip, 1981; Lueck *et al.*, 1992). They are characterized by a large spectral shift of the $\pi-\pi^*$ electron transition to lower wavelengths compared with the absorption due to isolated dye cations. On the other hand, J-aggregates, with head-to-tail interactions between the dye cations, absorb light at relatively higher wavelengths (Herz, 1977). Aggregation between dye cations significantly increases in the presence of clays. Several works have investigated clay-induced

dye aggregation, examining the effects of clay structure and swelling properties, the nature of the exchangeable cations, dye concentrations, pH and the presence of competing cations (Bergman and O’Konski, 1963; Cenens and Schoonheydt, 1988; Schoonheydt and Heughebaert, 1992; Breen and Loughlin, 1994; Bujdák and Komadel, 1997; Bujdák *et al.*, 1998, 2001). Recent works have investigated in detail the aggregation of methylene blue (MB) in smectite dispersion. The extent and types of dye cation aggregates are controlled by the density of negatively-charged sites at the clay surface. Clay minerals with high charge-density surfaces, *i.e.* with short distances between neighboring charged sites, promote dye cation association. On the contrary, smectites with low charge densities on their surfaces significantly suppress dye aggregation (Bujdák and Komadel, 1997; Bujdák *et al.*, 1998, 2001). The very high sensitivity of dye cation aggregation to layer-charge density may be potentially used for probing the charge distribution of clay minerals, as well as other inorganic layered materials. However, the above-described trends have been observed with MB only. There have been reports concerning the relationship between layer charge in silicates and aggregation of neither structurally similar (azine) dyes nor other, structurally different types of dyes. The present work shows for the first time that the relationship between dye cation aggregation and layer-charge density of clays is a general phenomenon that can potentially be applied to determine smectite charge density. The fundamental structural effects in the tested azine and triphenylmethane dyes are analyzed.

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MATERIALS

A series of reduced-charge montmorillonites (RCMs) was prepared by thermal treatment of Li⁺-saturated montmorillonite (Jeľšovy Potok, Slovakia) at 100–200C (Bujdak and Komadel, 1997). The structural formula of the Li⁺-saturated montmorillonite (Mo1) was determined from chemical analysis:



The cation exchange capacities (CEC) of the samples Mo1–Mo8, reflecting their layer-charge densities, were, in decreasing order, 1.07, 0.98, 0.96, 0.88, 0.71, 0.52, 0.24 and 0.11 mmol/g, respectively. Samples Mo1–Mo4 expanded fully in water and their dispersions were stable. Samples Mo5–Mo8 contained non-swelling interlayer spaces and the proportion of non-swelling phase increased with charge reduction. Dispersions of these samples were unstable, especially those of Mo7 and Mo8. Further details concerning the preparation and the properties of these RCMs are available elsewhere (Bujdak and Komadel, 1997; Bujdak *et al.*, 2000).

Four cationic, water-soluble dyes were chosen for this study: one azine dye, acridine orange (AO), which is structurally similar to the MB used in a previous work (Bujdak and Komadel, 1997), and three triphenylmethane dyes, crystal violet (CV), malachite green (MG) and brilliant green (BG). The structures of the cations for these dyes are shown in Figure 1. Data on the spectral properties of different forms of these dyes in various reaction systems are summarized in Table 1.

METHODS

Dilute water dispersions of the RCMs (0.05%) were prepared using ultrasonic treatment (5 min). Clay dispersions (2 mL) were mixed with 13 mL of distilled water and 5 mL of dye solution at concentrations of 10^{−5} mol dm^{−3}. Final dye loading was always 0.05 mmol/g, corresponding to between 0.05 and 0.45% CEC for samples Mo1–Mo8. The spectra were recorded 1 min after addition of the dye using a Carl-Zeiss UV-VIS spectrophotometer. Background due to scattering by clay particles was subtracted, in order to obtain the absorption spectra of pure dyes. Additional spectra were measured 24 h after mixing the dye solutions with the clay dispersions.

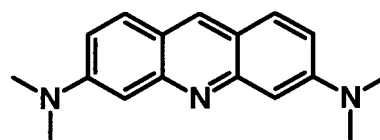
We proved that the dye cations were instantaneously and quantitatively adsorbed on clays, *i.e.* the clay surface was undersaturated with dye cations. The dispersions containing dyes with the lowest-charge clays (Mo7, Mo8) were filtered (0.2 m) and the spectra of supernatants were measured. The same procedure was carried out for a few representative dispersions containing dyes and clays Mo1–Mo6. There was no dye detectable in any supernatants, which proved complete

adsorption of dyes on the clay surface. This is in agreement with older observations that cationic dyes are completely adsorbed at loadings below the CEC of clay (Margulies *et al.*, 1998; Bujdak and Komadel, 1997).

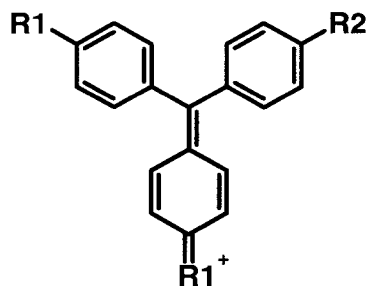
RESULTS AND DISCUSSION

VIS spectra of dye-clay dispersions

Mixing clay dispersions with the AO, CV and MG dye solutions led in some cases to visible changes in color. No apparent color change was observed for dispersions containing BG. The VIS spectra measurements confirmed these visual observations. The main absorption band of the AO solution shifted from 496 to 454 nm in the presence of Mo1 (Figure 2). Similarly, in the presence of this clay, the bands of the CV (588 nm) and MG (614 nm) solutions shifted to 545 and 581 nm, respectively (Figures 3,4). The shifts did not exceed 50 nm, which is considerably less than that observed with MB (Bergman and O’Konski, 1963; Schoonheydt and Heughebaert, 1992; Cenens and Schoonheydt, 1988; Bujdak and Komadel, 1997; Bujdak *et al.*, 1998, 2001). New bands in the spectra of the dye/clay dispersions are due to the formation of dye cation dimers and/or higher aggregates of an H-type. The occurrence of H-aggregation on the surface of high-charge montmorillonites is in agreement with conclusions made in our previous works (Bujdak and Komadel, 1997; Bujdak *et al.*, 1998, 2001). Similar changes for AO have been attributed to either dye dimerization or aggregation in various reaction systems (Braswell and Lary, 1981; Marakami *et al.*, 1986; Hachisako *et al.*, 1994; Coine *et al.*, 1998;



acridine orange



triphenylmethane dyes

Figure 1. Scheme showing the structural formulae for the cations of the acridine orange and the triphenylmethane dyes. Crystal violet: R1=R2=N(CH₃)₂; malachite green: R1=N(CH₃)₂, R2=H; brilliant green: R1=N(C₂H₅)₂, R2=H

Table 1. Spectral characteristics of the forms of the studied dyes.

Dye	Dye form	λ_{MAX} (nm)	Ref.
Acridine orange	monomer (solution)	490	1
	monomer (clay)	490–500	1
	H-dimer (solution)	464	2
	H-dimer (clay)	440–450, 476	1
	H-aggregate (clay)	<450	1
Crystal violet	monomer (solution)	590	3
	monomer (clay)	~600	3
	H-dimer (solution, clay)	550	3
	H-aggregate (solution, clay)	520	3
	H-aggregate (zirconium phosphate)	510	4
Malachite green	J-aggregate (polyphosphate)	620–665	5
	monomer (solution)	615	6
	H-dimer (oil/water interface)	580	6
Brilliant green	monomer (solution)	630	7
	H-dimer (solution)	600	7

References: 1: Garfinkel-Shweky and Yariv (1997a,b, 1999); 2: Antonov *et al.* (1999); 3: Chernia *et al.* (1994); 4: Hoppe *et al.* (1997); 5: Takatsuki (1980); 6: Yao *et al.* (1996); and 7: Karukstis and Gullledge (1998).

Antonov *et al.*, 1999). A shift in the CV band to lower wavelengths has been assigned to dye aggregation in concentrated water solutions (Lueck *et al.* 1992), in solutions of negatively-charged polyelectrolytes (Takatsuki, 1980; Pal and Ghosh, 1994), in Langmuir-Blodgett films (Miyata *et al.*, 1991), in silver colloids (Nickel *et al.*, 1997), as well as on the surfaces of ZnO crystals (Clark and Drickamer, 1984) and on glass (Kobayashi *et al.*, 1988). Although CV aggregates, intercalated in layered zirconium phosphates, absorb light at ~510 nm (Hoppe *et al.*, 1997), only a faintly detectable shoulder below 500 nm was detected in the

spectrum of the CV with Mo1 (Figure 3). An MG H-dimer was observed at the water/oil interface absorbing light at 580 nm (Yao *et al.*, 1996).

However, an alternative interpretation of the optical properties of dye/clay reaction systems has also been proposed, assuming charge transfer between the dye cations and the clay surface (Cohen and Yariv, 1984). This reaction requires the parallel orientation of dye cations on a clay basal surface. However, an almost perpendicular orientation was observed for MB on a mica surface (Hähner *et al.*, 1996) and at other solid-liquid interfaces (Higgins *et al.*, 1991; Campbell *et al.*,

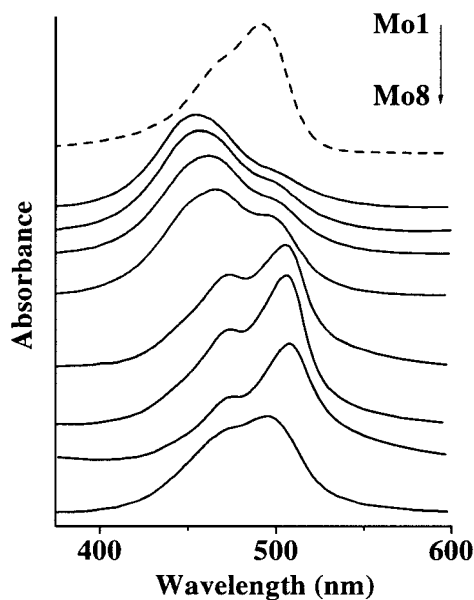


Figure 2. Acridine orange spectra measured 1 min after mixing the dye solution with dispersions of reduced-charge montmorillonites. The dashed line represents the spectrum of the dye solution.

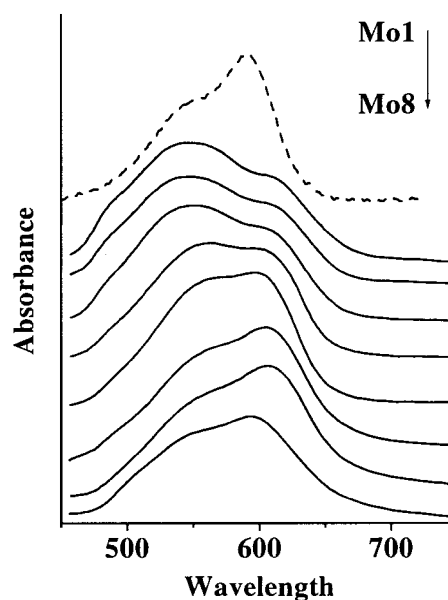


Figure 3. Crystal violet spectra measured 1 min after mixing the dye solution with dispersions of reduced-charge montmorillonites. The dashed line represents the spectrum of the dye solution.

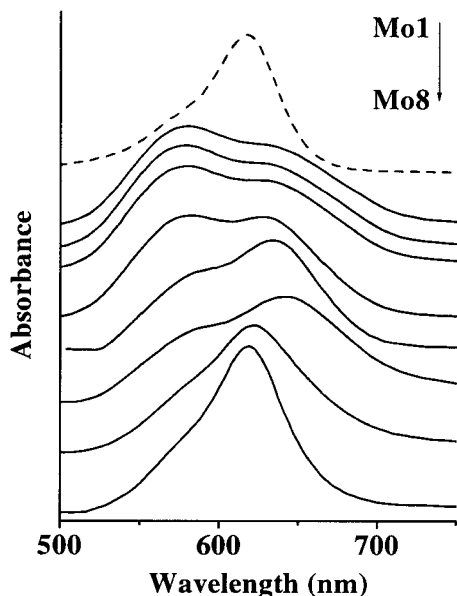


Figure 4. Malachite green spectra measured 1 min after mixing the dye solution with dispersions of reduced-charge montmorillonites. The dashed line represents the spectrum of the dye solution.

1990; Kobayashi *et al.*, 1988). In a similar way, a parallel orientation of triphenylmethane dyes, such as CV and MG, would be contrary to their non-flat, propeller-like structures (Fischer *et al.*, 1998, and references therein). Moreover, similar to azine dyes, a triangular plane of the cation center of these triphenylmethane dyes is tilted at a large angle to the clay surface (Fischer *et al.*, 1998; Yamaoka and Sasai, 2000). The possibility or extent of the contribution of charge-transfer reactions to the optical behavior of dyes therefore clearly requires further investigation. We will base our interpretation of the spectra exclusively on dye aggregation. As introduced above, we assume the orientation of the dye cations in aggregates is nearly perpendicular or at a large angle to the clay surface. The parallel orientation and stacking of the cations on top of each other could not lead to stable arrangements in aggregates because the cations would not be able to interact electrostatically with the negatively-charged basal surface. However, if the orientation of the cations is subperpendicular to the basal surface of the clay, the existence of large, two-dimensional dye aggregates on the clay surface is possible (Bujdák and Komadel, 1997). Such arrangements and orientations are very common for dyes adsorbed at flat surfaces or in Langmuir-Blodgett films (Clark *et al.*, 1984; Kobayashi *et al.*, 1988; Campbell *et al.*, 1990; Miyata *et al.*, 1991; Higgins *et al.*, 1991).

Effect of the layer charge

Similar to the spectra of MB/clay dispersions (Bujdák and Komadel, 1997; Bujdák *et al.*, 1998, 2001), the

spectra of AO, CV and MG are sensitively affected by the layer-charge density of the RCMs. The trends in the spectra with clay layer charge are basically the same as those reported for MB/clay interaction (Bujdák and Komadel, 1997). The RCM with the highest layer-charge (Mo1) contains the largest amount of dye cation H-aggregates, characterized as broad bands absorbing at lower wavelengths (Figures 2–4). The size and amount of H-aggregates decrease in favor of dimers and monomers with decreasing layer charge. Consequently, the absorption bands assigned to H-aggregates become weaker and shift to slightly higher wavelengths. In addition, these changes are accompanied by an increase in absorbance at high wavelengths. Bands at higher wavelengths become dominant with a moderate decrease in layer charge, as shown, for example, in the spectra of AO, CV and MG with Mo5 (Figures 2–4). Their positions are shifted to slightly higher wavelengths than that due to monomers. This shift is only ~10 nm in the case of the azine dye, AO, but is significantly higher for CV and MG, being 20 and 30 nm, respectively. Shifts to higher wavelengths of < 10 nm are always observed for dye monomers adsorbed at the clay surface. This change is explained by the effect of a more polar environment of negatively-charged clay particles (Coine *et al.*, 1998). The bands, at significantly higher wavelengths than those of monomers, are frequently observed in the spectra of MB/clay dispersions. They have been assumed to be related to bivalent cations formed by protonation of the dye at the clay surface (Schoonheydt and Heughebaert, 1992; Cenens and Schoonheydt, 1988). However, we did not observe any significant acidification with charge reduction and pH values were always neutral. On the other hand, dye species absorbing at higher wavelengths might also be J-type dimers or larger aggregates. Two kinds of CV dimers and tetramers, with absorbance bands at wavelengths shorter and longer than those of free monomers, have been identified in the spectra of this dye (Takatsuki, 1980; Miyata *et al.*, 1991). The replacement of H-aggregates by J-aggregates would be in accordance with the spectral trends expected, when layer charge decreases. It can be explained with the following assumptions: (1) the orientation of the dye cations in the aggregate is perpendicular or subperpendicular to the clay basal surface, which allows the formation of two-dimensional aggregates; (2) the distribution of dye cations reflects that of negative-charge sites, *i.e.* each negative charge is saturated with one cation.

On the basis of previous work, the existence of H-dimers (or larger H-aggregates) would require very short distances between neighboring negatively-charged sites. The clay surface would need to be almost fully covered with the dye in order to form homogeneous two-dimensional coverage of only H-aggregates (Figure 5a). J-aggregation is due to only partial, head-to-tail association between the dye cations (Antonov *et al.*, 1999; del

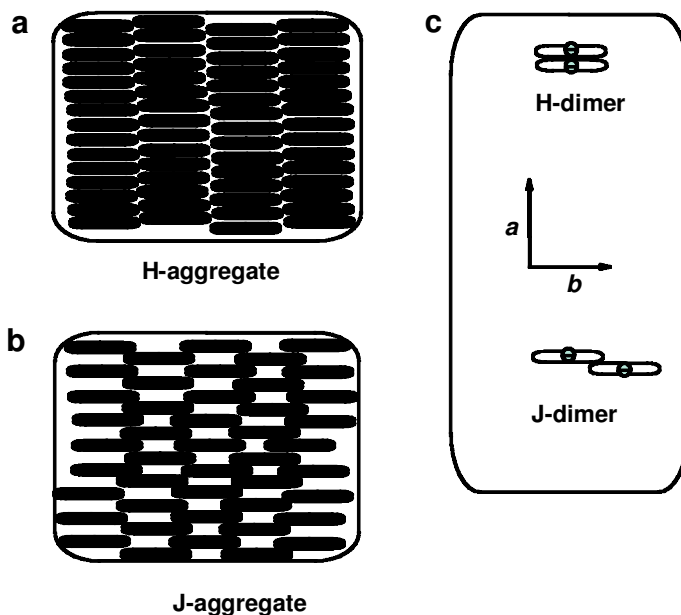


Figure 5. Scheme with structural models of the (a) dye H-, (b) J-aggregates and (c) dimers formed at the basal surface of the clay. Large rounded rectangles represent the clay basal surface with a , b directions shown. Small black (a, b) or empty (c) rounded rectangles are the edges of the dye cations. The dye cations are tilted or oriented nearly perpendicular to the clay basal surface. Gray circles (c) denote the centers of the negative-charge sites.

Monte and Levi, 1999). The formation of large two-dimensional J-aggregates does not require full coverage of the clay surface (Figure 5b). The distance between two neighboring negative-charge sites is larger for the formation of stable J-dimer than that required for the formation of H-dimer (Figure 5c). With decreasing layer-charge density the distances between neighboring dye cations increase. Consequently, the sandwich-type association with H-aggregates association breaks down in favor of J-aggregates with a 'head-to-tail' type association of transition dipoles and less dense packing of the dye cations (Antonov *et al.*, 1999). Ordered J-aggregates usually exhibit sharp bands in the spectra (Kobayashi, 1996). The sharp bands, absorbing at higher wavelengths than that of MB monomer, have been observed in spectra of clay dispersions (Breen and Loughlin, 1994). An absence of any sharp bands of studied dyes indicates the formation of less-ordered J-aggregates, which might also be related to the more complicated structures of the cations of triphenylmethane dyes.

Further decrease in layer-charge density (from Mo5 to Mo8) shifts the main absorption band back to lower values, approaching the position for the band of dye monomers. The dye dispersions containing the sample with the lowest charge, Mo8, absorbed light at similar wavelengths to their respective dilute solutions, namely at 496, 595 and 619 nm for AO, CV and MG, respectively (Figures 2–4). In this case, the layer-charge density is too small for the formation of dimers or higher aggregates of any kind. Dye species detected in

dispersions with the lowest-charge clays were assigned to monomers, which were adsorbed at the clay surface. Filtering the dispersions proved the absence of any free dye. One should note that average relative dye loading is highest for RCMs with lowest charge (45% CEC) and that the surface area is much less due to the presence of non-swelling interlayer spaces. Clay aggregates with a non-swelling phase might adsorb dye molecules at their external surfaces. High relative loading and higher average concentration of the dye on the surface of Mo8 might be the factors supporting dye aggregation. However, the absence of dye aggregates in the dispersions containing lowest-charge RCMs supports our theory that dye aggregation is mainly controlled by the distances between negatively-charged sites.

These results are in full agreement with the conclusion from another study (Bujdák *et al.*, 2002) which revealed that the effect of the dye/clay loading is much less than that of the layer-charge density. For example, relatively large amounts of dye aggregation took place on high-charge clays, even in cases of extreme under-saturation of the clay surface with dye (Bujdák *et al.*, 2002). This contradiction can be explained by the kinetics of the dye adsorption. Dye adsorption proceeds almost instantaneously and is completed before the mixing of a dye solution with clay dispersion is finished. Such fast adsorption of the dye leads to the heterogeneous distribution of the cations on the clay surface. The sites or zones, where the dye is adsorbed, are probably almost fully occupied with the dye, although an average dye loading is very low (Bujdák *et al.*, 1998).

The first step of the aggregation process takes place in the vicinity of clay particles (Bujdák *et al.*, 2002) due to an enhanced polarity of water molecules induced by present inorganic ions in electric double layer. The presence of water as a polar solvent is essential for the aggregation of dye cations (Yu *et al.*, 2000). Increasing the polarity of the environment increases the degree of the aggregation. Enhanced aggregation was observed in aqueous solutions of inorganic salts and was found to be related to the polarizing effects of ions (Bose, 1987). The aggregation on clays in the first step increases with the concentration of the ions thus reflecting the magnitude of the negative charge. The second step of the reaction represents a re-arrangement of the dye cations in extant aggregates. The re-arrangement is directed by the charge distribution so that each cation balances one negatively-charged site, thus mapping an intrinsic distribution of the negative charge on the clay surface (Bujdák *et al.*, 2002).

Effect of the structure of dye cations

In addition to layer-charge density of the clay host, the effect of molecular structure of cationic dyes on the aggregation of cations was also investigated. There was no significant difference in the basic trends in spectral changes with layer charge when using the azine dye, AO, or the triphenylmethane dyes, CV and MG. This is surprising, considering the different structures of azine and triphenylmethane dyes. Only the spectra of BG, measured 1 min after mixing the solution with the clay dispersion, seemed to be almost independent of the layer charge of the RCM (Figure 6). The position of the main band changed with clay layer charge in a similar fashion to that observed for previous dyes, but the shifts were much smaller. For example, Mo1/BG absorbed light at 635 nm, which might be assigned to adsorbed BG monomers (Karukstis and Gulledge, 1998). A shoulder at lower wavelengths indicates the presence of only a few H-aggregates of the dye cations. With decreasing layer charge the shoulder disappears and the main band shifts to higher (642 nm for Mo5/BG) and then back to lower wavelengths (625 nm for Mo8/BG). Although the positions for the main bands in the AO, CV or MG spectra were in some cases >50 nm apart, the maximum absorbance position of the only major band, present in the RCM/BG spectra, moves within a narrow range of 17 nm. Changes to the optical properties require a short distance between associated dye cations, which enables electrostatic interaction of the chromophores. We assume that the presence of a bulky diethylamine group bound to a triphenylmethane cation brings about a distortion caused by steric hindrance and possibly 'self-solvation' of aromatic rings. In spite of the relatively higher hydrophobicity of the BG dye, the presence of the bulky groups either markedly suppresses initial dye aggregation or breaks or minimizes the electrostatic interaction between chromophores in aggre-

gates. These assumptions are consistent with the trends observed with various dyes adsorbed on anionic membranes (Hachisako *et al.*, 1994).

Spectra of aged dispersions

The spectra of AO, CV, MG and BG were also measured after 24 h. The samples with the lowest charge (Mo6–Mo8) flocculated due to their lower dispersion stability, similar to the trend observed with MB (Bujdák and Komadel, 1997). Therefore, it was not possible to record spectra for aged dispersions with Mo7 and Mo8. The changes in the spectra of AO, CV and MG with reaction time were much lower (Figures 7–9) than those in reaction systems with MB (Bujdák and Komadel, 1997). The intensities of the bands at lowest wavelengths increased after 24 h in the spectra of triphenylmethane dyes CV and MG. The CV species absorbing near 500 nm were only poorly resolved as a weak shoulder in the spectra recorded after 1 min (Figure 3). On the other hand, this band becomes more clearly resolved in spectra of Mo1/CV and Mo2/CV after 24 h (Figure 8). However, the optical properties of the BG/clay dispersions changed markedly with time. The spectra of the BG recorded 24 h after mixing the dye solution with the clay dispersions are shown in Figure 10. With time, the band assigned to H-aggregates (595 nm) increased in intensity and a new, sharp band appeared near 505 nm. It should be noted that the wavelength of this band is lower by ~150 nm than that of the band assigned to the dye monomers. The light absorption of the H-aggregates and species, related to the new, low-wavelength band, decreases with charge reduction, and is absent from the

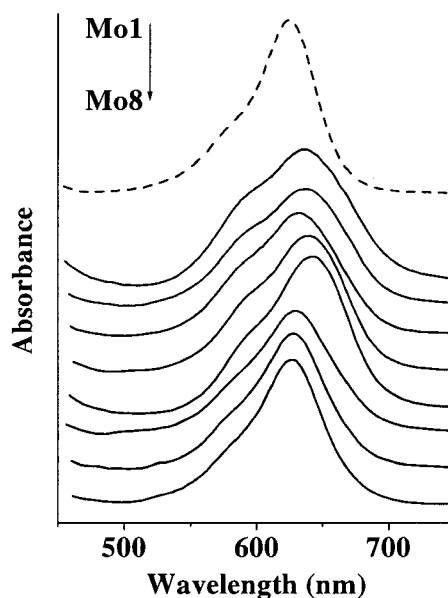


Figure 6. Brilliant green spectra measured 1 min after mixing the dye solution with dispersions of reduced-charge montmorillonites. The dashed line represents the spectrum of the dye solution.

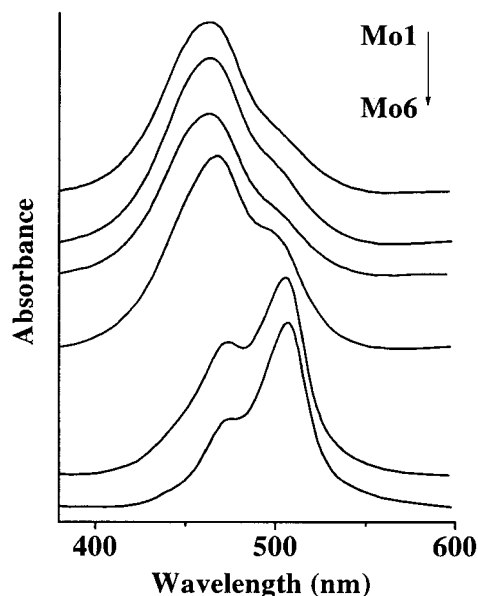


Figure 7. Acridine orange spectra measured 24 h after mixing the dye solution with dispersions of reduced-charge montmorillonites.

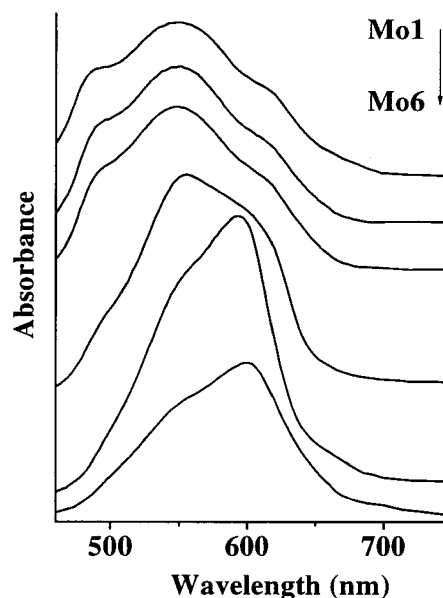


Figure 8. Crystal violet spectra measured 24 h after mixing the dye solution with dispersions of reduced-charge montmorillonites.

spectrum of the aged BG/Mo5 dispersion. The appearance of such a band has not been reported for this dye. We assume that the spectral changes of the BG with time relate to a re-arrangement and re-organization of the dye cation assemblies at the clay surface. In order to appreciate this process completely, one has to consider the following: (1) the dye cation of BG is larger than the other dye cations studied here. (2) Triphenylmethane dye cations have a low degree of freedom to adjust to their shape, in order to fill the space at the clay surface. The only possibilities are a rotation of the phenyl groups and the greater flexibility of the ethyl groups in the case of BG cations. (3) Positively-charged N atoms in the BG cation are blocked by two relatively large ethyl groups, which may interfere with the electrostatic interaction between the dye cation and clay surface.

In summary, the re-arrangement of densely-packed BG cations at the surface of high-charge clays is likely to be accompanied by slight structural changes in the chromophore. Such changes probably result from the larger size of the cation and the relatively high charge densities of some RCMs, *i.e.* there is less surface available per cation. Possible structural changes in triphenylmethane dyes at the clay surface have been assumed elsewhere (Chernia *et al.*, 1994), and the appearance of additional bands has been attributed to a tilting of the phenylamine ring. However, no additional bands appeared in the spectra of other triphenylmethane dyes (CV, MG) with time. This indicates that only slight changes in dye cation structure and/or size, such as replacing methyl groups with ethyl groups, may lead to significantly different behavior of the dyes at the surface of clays.

Other bands, of relatively low intensities, occurred in the low-wavelength range of the spectra of the MG and BG solutions, both at ~ 430 nm. These were also present in the spectra of clay dispersions with these dyes. The occurrence of these bands is because of the lower symmetry in the cations of MG and BG dyes (Figure 1), reflected in two electron transitions for different energies associated with R1-Ph-C-Ph-R1 and R1-Ph-C-

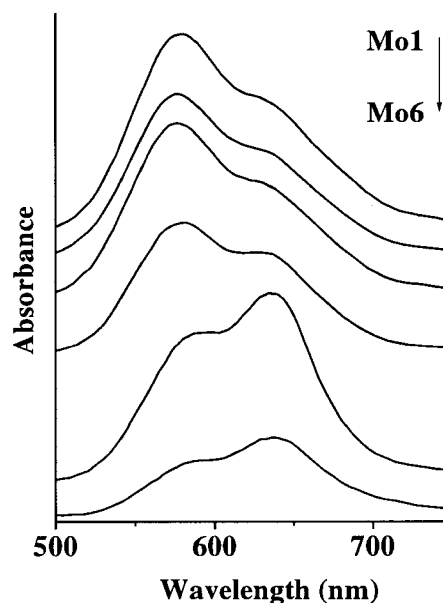


Figure 9. Malachite green spectra measured 24 h after mixing the dye solution with dispersions of reduced-charge montmorillonites.

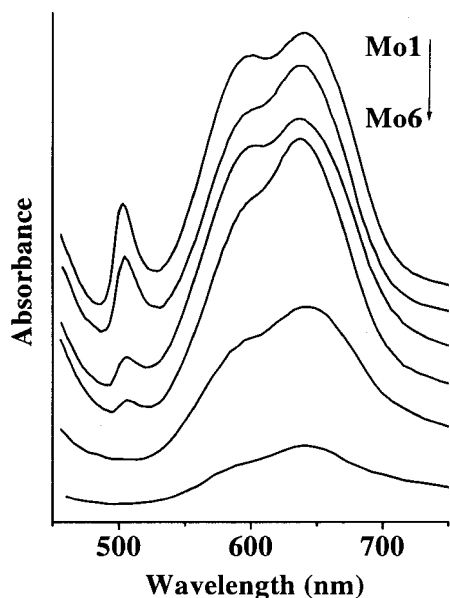


Figure 10. Brilliant green spectra measured 24 h after mixing the dye solution with dispersions of reduced-charge montmorillonites.

Ph-R2 (Ph = phenyl) chromophores. The transition in the latter case is assigned to the low-wavelength band mentioned above. The positions of these bands are summarized in Table 2. The bands of the MG changed with the layer charge of the clay host in a similar fashion to their high-wavelength counterparts. The MG band moved from 417 (Mo1) to 436 (Mo6) and shifted back to 429 nm (Mo8) in the spectra of fresh dispersions. The changes in the BG spectra with the layer charge of the RCMs were negligible.

CONCLUSIONS

(1) The layer-charge density of smectites can be monitored using VIS spectroscopy of dye/smectite dispersions. The effect of layer-charge density on the spectral properties of dyes is explained in terms of dye aggregation on the clay surface. Layer charge affects both the extent and type of dye cation aggregates. In general, H-aggregates decrease in size or change to

Table 2. λ_{MAX} of the bands in low-wavelength parts of the spectrum of malachite green (MG) and brilliant green (BG) in the presence of reduced-charge montmorillonites.

	MG	BG
Mo1	417	430
Mo2	420	430
Mo3	421	430
Mo4	424	432
Mo5	428	433
Mo6	436	430
Mo7	430	430
Mo8	429	429

H-dimers or J-aggregates and further to monomers with decreasing layer charge.

(2) The relationship between dye spectral changes and layer-charge density in layered silicates seems to be a general phenomenon. The general trends of the spectral changes for azine and triphenylmethane dyes are independent of the structure of the cations. Almost any dye with planar cations or with planar aromatic groups, forming aggregates with optical properties different from those of isolated dye cations, is suitable for probing the layer-charge densities of smectites.

(3) The first information on the layer-charge density can be obtained from the color of the mixtures of dye solution with clay dispersions. This simple method could be widely used in geology, geochemistry and industry for the characterization and qualitative comparisons of large sets of specimens of similar materials.

(4) Many cationic dyes and chromophores embedded in inorganic substrates are used in industry, e.g. in photography, in various materials for signal processing and memory storage media, as catalysts, as energy antennas and transducers in photochemical reactions, etc. All these applications depend crucially on the optical properties of dye. Therefore, the relationship between dye aggregation and the parameters of inorganic hosts might be very significant in the applied research and engineering of the materials mentioned above.

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REFERENCES

- Antonov, L., Gerkov, G., Petrov, V., Kubista, M. and Nygren, J. (1999) UV-Vis spectroscopic and chemometric study on the aggregation of ionic dyes in water. *Talanta*, **49**, 99–106.
- Bergman, K. and O'Konski, C.T. (1963) A spectroscopic study of methylene blue monomer, dimer and complexes with montmorillonite. *Journal of Physical Chemistry*, **67**, 2169–2177.
- Bose, H. (1987) Environmental effects on dye aggregation/ effect of electrolytes on metachromasy of thiazine dyes. *Indian Journal of Chemistry, Section A*, **26**, 652–655.
- Braswell, E.H. and Lary, J. (1981) Equilibrium-sedimentation studies of some self-associating cationic dyes. *Journal of Physical Chemistry*, **85**, 1573–1578.
- Breen, C. and Loughlin, H. (1994) The competitive adsorption of methylene blue onto Na-montmorillonite from binary solution with n-alkyltrimethylammonium surfactants. *Clay Minerals*, **29**, 775–783.
- Bujdák, J. and Komadel, P. (1997) Interaction of methylene blue with reduced charge montmorillonite. *Journal of Physical Chemistry, B*, **101**, 9065–9068.
- Bujdák, J., Janek, M., Madejová, J. and Komadel, P. (1998) Influence of the layer charge density of smectites on the interaction with methylene blue. *Journal of the Chemical Society, Faraday Transaction*, **94**, 3487–3492.

- Bujdák, J., Hackett, E. and Giannelis, E.P. (2000) Effect of layer charge on the intercalation of poly(ethylene oxide) in layered silicates: Implications on nanocomposite polymer electrolytes. *Chemistry of Materials*, **12**, 2168–2174.
- Bujdák, J., Janek, M., Madejová, J. and Komadel, P. (2001) Methylene blue interactions with reduced-charge smectites. *Clays and Clay Minerals*, **49**, 244–254.
- Bujdák, J., Iyi, N. and Fujita, T. (2002) The aggregation of methylene blue in montmorillonite dispersions. *Clay Minerals*, **37**, 121–133.
- Campbell, D.J., Higgins, D.A. and Corn, R.M. (1990) Molecular second harmonic generation studies of methylene blue chemisorbed onto sulfur-modified polycrystalline platinum electrode. *Journal of Physical Chemistry*, **94**, 3681–3689.
- Cenens, J. and Schoonheydt, R.A. (1988) Visible spectroscopy of methylene blue on hectorite, Laponite B and Barasym in aqueous suspensions. *Clays and Clay Minerals*, **36**, 214–224.
- Chernia, Z., Gill, D. and Yariv, S. (1994) Electric dichroism. The effect of dialysis on the color of crystal violet adsorbed to montmorillonite. *Langmuir*, **10**, 3988–3993.
- Clark, F.T. and Drickamer, H.G. (1984) The effect of pressure on the adsorption of crystal violet on oriented ZnO crystals. *Journal of Physical Chemistry*, **84**, 1024–1029.
- Cohen, R. and Yariv, S. (1984) Metachromasy in clay minerals. *Journal of the Chemical Society, Faraday Transaction 1*, **80**, 1705–1715.
- Coine, A.P.P., Neumann, M.G. and Gessner, F. (1998) Time-dependent spectrophotometric study of the interaction of basic dyes with clays. *Journal of Colloid and Interface Science*, **198**, 106–112.
- del Monte, F. and Levy, D. (1999) Identification of oblique and coplanar inclined fluorescent J-dimers in rhodamine 110 doped sol-gel-glasses. *Journal of Physical Chemistry B*, **103**, 8080–8086.
- Fischer, D., Caseri, W.R. and Hähner, G. (1998) Orientation and electronic structure of ion exchanged dye molecules on mica. An X-ray absorption study. *Journal of Colloid and Interface Science*, **198**, 337–346.
- Garfinkel-Shweky, D. and Yariv, S. (1997a) Metachromasy in clay-dye systems: the adsorption of acridine orange by Naponite. *Clay Minerals*, **32**, 653–663.
- Garfinkel-Shweky, D. and Yariv, S. (1997b) The determination of surface basicity of the oxygen planes of expanding clay minerals by acridine orange. *Journal of Colloid and Interface Science*, **188**, 168–175.
- Garfinkel-Shwenky, D. and Yariv, S. (1999) Metachromasy in clay-dye systems: the adsorption of acridine orange by Nabeidellite. *Clay Minerals*, **34**, 459–467.
- Hachisako, H., Yamazaki, T., Ihara, H., Hirayama, Ch. and Yamada, K. (1994) Recognition of molecular planarity of cationic dyes by anionic, crystalline bilayer aggregates. Evidence using metachromic and solvatochromic properties. *Journal of the Chemical Society, Perkin Transactions 2*, **7**, 1681–1690.
- Hähner, G., Marti, A., Spencer, N.D. and Caseri, W.R. (1996) Orientation and electronic structure of methylene blue on mica: A near edge X-ray absorption structure spectroscopic study. *Journal of Chemical Physics*, **19**, 7749–7757.
- Herz, A.H. (1977) Aggregation of sensitizing dyes in solution and their adsorption onto silver halides. *Advances in Colloid and Interface Science*, **8**, 237–298.
- Higgins, D.A., Byerly, S.K., Abrams, M.B. and Corn, R.M. (1991) Second harmonic generation studies of methylene blue orientation at silica surfaces. *Journal of Physical Chemistry*, **95**, 6984–6990.
- Hoppe, R., Alberti, G., Constantino, U., Dionigi, C., Schulz-Ekloff, G. and Vivani, R. (1997) Intercalation of dyes in layered zirconium phosphates. 1. Preparation and spectroscopic characterization of α -zirconium phosphate crystal violet compounds. *Langmuir*, **13**, 7252–7257.
- Karukstis, K.K. and Gulledge, A.V. (1998) Analysis of the solvatochromic behavior of the substituted triphenylmethane dye brilliant green. *Analytical Chemistry*, **70**, 4212–4217.
- Kobayashi, M., Tokunaga, H., Okubo, J., Hoshi, T. and Tanizaki, Y. (1988) Measurements of the polarized ATR spectra for adsorbed dye layers by using a stack of thin glass plates. *Bulletin of the Chemical Society of Japan*, **61**, 4171–4176.
- Kobayashi, T. (1996) *J-aggregates*. World Scientific Publishing Co. Pte. Ltd., Singapore.
- Korppi-Tommola, J. and Yip, R.W. (1981) Solvent effect on the visible absorption spectrum of crystal violet. *Canadian Journal of Chemistry*, **59**, 191–194.
- Lueck, H.B., Rice, B.L. and McHale, J.L. (1992) Aggregation of triphenylmethane dyes in aqueous solution: dimerization and trimerization of crystal violet and ethyl violet. *Spectrochimica Acta, Part A*, **48**, 819–828.
- Marakami, K., Mizuguchi, K., Kubota, Y. and Fujisaki, Y. (1986) Equilibrium and kinetic studies of the dimerization of acridine orange and its 10-alkyl derivatives. *Bulletin of the Chemical Society of Japan*, **59**, 3393–3398.
- Margulies, L., Rozen, H. and Nir, S. (1988) Model for competitive adsorption of organic cation on clay. *Clays and Clay Minerals*, **36**, 270–276.
- Miyata, A., Unuma, Y. and Higishigaki, Y. (1991) H-aggregate of a long-chain crystal violet dye in Langmuir-Blodgett films. *Bulletin of the Chemical Society of Japan*, **64**, 2786–2791.
- Möbius, D. (1995) Scheibe aggregates. *Advanced Materials*, **7**, 437–444.
- Nickel, U., Halbig, P., Gliemann, H. and Schneider, S. (1997) Charge transfer like complexes of organic dyes adsorbed at colloidal silver studied by cyclic voltammetry, UV-vis and SERS spectroscopy. *Berichte der Bunsen-Gesellschaft-Physical Chemistry Chemical Physics*, **101**, 41–49.
- Pal, M.K. and Ghosh, J.K. (1994) Circular dichroic and spectrophotometric probes of the competitive binding between DNA and other anionic polymers. *Spectrochimica Acta, Part A*, **50**, 119–126.
- Schoonheydt, R.A. and Heughebaert, L. (1992) Clay adsorbed dyes: methylene blue on Laponite. *Clay Minerals*, **27**, 91–100.
- Takatsuki, M. (1980) Multiequilibrium system by the Principal Component Analysis method. *Bulletin of the Chemical Society of Japan*, **53**, 1922–1930.
- Yamaoka, K. and Sasai, R. (2000) Pulsed electric linear dichroism of triphenylmethane dyes adsorbed on montmorillonite K10 in aqueous media. *Journal of Colloid and Interface Science*, **225**, 82–93.
- Yao, H., Inoue, Y., Ikeda, H., Nakatani, K., Kim, H.B. and Kitamura, N. (1996) Micrometre size effect on dye association in single laser-trapped water. *Journal of Physical Chemistry*, **100**, 1494–1497.
- Yu, C.H., Newton, S.Q., Norman, M.A., Miller, D.M., Schafer, L. and Teppen, B.J. (2000) Molecular dynamics simulations of the adsorption of methylene blue at clay mineral surfaces. *Clays and Clay Minerals*, **48**, 665–681.

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