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Interaction of Methylene Blue with Reduced Charge Montmorillonite

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Interaction of methylene blue (MB) with reduced charge Li–montmorillonites (RCM) in the aqueous suspensions was investigated using visible absorption spectroscopy. Dye cation agglomeration and protonation at the clay surface depended very sensitively on layer charge density. With increasing layer charge reduction, the content of agglomerates of MB cations decreased in favor of monomers and the protonated form of MB. Lower negative charge density on the clay basal surface induces a greater distance between neighboring MB cations sorbed at the clay surfaces, which suppresses dye agglomeration. Since each form of MB absorbs visible light at a different wavelength, different layer charge densities induce different colors of the resulting clay–dye suspension. Therefore, visible spectra of MB–smectite suspensions may be a simple but extremely sensitive method for the detection of layer charge density of smectites.

Introduction

Methylene blue (MB) is a heteroaromatic, cationic dye (Figure 1) readily soluble in water. Visible spectra of dilute solutions contain a band associated with monomeric MB at 665 nm with a shoulder attributed to the 0–1 vibronic transition of monomers at 605 nm. In aqueous solutions of concentrations greater than 2.5×10^{-6} mol dm⁻³, MB cations partially associate as cationic dimers in a face-to-face arrangement to minimize their hydrophobic interactions with water. The dimers absorb near 605 nm.¹

The surfaces of clay minerals exhibit a strong affinity for MB cations.² The cations are adsorbed via ion exchange, frequently accompanied by agglomeration, where micelles consisting of three or more cations at the clay surface orient via π – π interaction on both sides of the molecular plane with two neighboring cations. A partial protonation of MB cations may also take place at clay surfaces in a manner similar to that in very acidic solutions.^{1,3–7} Visible spectra of MB–clay suspensions contain several bands assigned to the absorption of monomers, dimers, agglomerates (near 575 nm), and protonated MBH²⁺ cations (at about 765 nm).³

MB agglomeration and protonation were found to be sensitive to many factors, such as the dye load rate, surface properties of the clay, exchangeable cations, pH, and the age of MB–clay suspension.^{3–4,6} The greatest extent of agglomeration occurs at high dye loadings, while monomers and protonated cations predominate at low loadings. The type of exchangeable cations affects the swelling properties of smectite and hence the accessibility of basal surfaces for large MB cations. MB is a sensitive fingerprint molecule for the detection of surface properties of clays in suspensions.³ However, some discrepancies still remain in previously reported interpretations of the site of dye agglomeration.^{3–4,6}

Methylene Blue Agglomeration on Clay Surface. The sites of MB agglomeration (edges, basal planes) have not been definitely identified yet. According to Gessner et al.,⁶ only monomers and protonated MB are present in the interlayer spaces of smectites. Agglomeration has been claimed to proceed at the external surfaces of clay layers.^{3,6} Dimerization may proceed also at basal surfaces.³ Consideration of the following

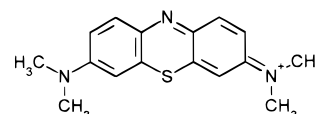


Figure 1. Molecular structure of methylene blue cation.

discussion will, however, indicate that MB dimerization and higher agglomeration may occur also at the basal surfaces.

(1) More than 75% of the dye may agglomerate at greater (MB amount/CEC; CEC = cation exchange capacity) loadings. Large amounts of agglomerates were found also in fresh suspensions.^{3–5} In dilute suspensions of Na–smectites, individual clay layers are present and both the edges and the basal surface sites are accessible for MB.³ An absence of agglomerates of MB cations at the basal surfaces would mean that adsorbed MB cations are predominantly located at the clay particle edges, which is not probable.

(2) The main argument for considering an absence of MB agglomerates at the basal planes is X-ray diffraction data of the basal spacings of MB–clay intercalates.^{8–10} Assuming an orientation of the MB molecular plane parallel to the basal surface of the clay, it is possible for two layers of MB cations to fill the interlayer space, yielding a basal spacing $d_{001} \cong 1.77$ or 1.72 nm observed for the MB–smectite complexes.^{8,9} However, considering a nearly perpendicular orientation of the MB molecular plane with basal surfaces and the height of the MB cation (0.74 nm),¹¹ the existence of larger MB agglomerates on clay basal surface is possible. The orientation of MB cations nearly normal to the basal plane of clay surfaces would explain why a d_{001} spacing of 1.72 nm was observed for MB–montmorillonite compounds at high (100% CEC) loadings.⁹ At high load rates of MB, agglomerates are expected to be predominant, while monomers and dimers are practically absent in MB–clay complexes. Recently, a detailed study used two independent methods, i.e., X-ray photoelectron spectroscopy and near-edge X-ray absorption fine structure spectroscopy, to determine the orientation of MB at the surface of mica.¹¹ Both methods concluded that MB cations are tilted at an angle of 65–70° with respect to the clay basal surface rather than arranged parallel with the layer plane, as assumed earlier.^{3,6} Indeed, a nearly perpendicular orientation of MB cations in the interlayer would enable a better alignment of adjacent aromatic rings of neighboring cations via hydrophobic interactions than orientation parallel to the clay surface. This would allow

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TABLE 1: Preparation Temperatures and Selected Properties of Reduced Charge Montmorillonites

RCM	<i>T</i> (°C)	CEC ^a (meq/g)	<i>d</i> ₀₀₁ ^b (nm)	pH ^c	pH ^{MB} ^c
Mo1		1.07 ± 0.01	1.22	6.2	6.3
Mo2	100	0.98 ± 0.01	1.22	6.1	6.0
Mo3	105	0.96 ± 0.01	1.22	6.1	6.1
Mo4	110	0.88 ± 0.02	1.22	6.3	6.2
Mo5	120	0.71 ± 0.02	1.13	6.2	6.0
Mo6	130	0.52 ± 0.02	1.09	6.0	6.1
Mo7	160	0.24 ± 0.01	0.98	6.0	6.1
Mo8	210	0.11 ± 0.01	0.95	6.0	6.0

^a CEC = cation exchange capacities. ^b *d*₀₀₁ = basal spacings of oriented samples. ^c pH and pH^{MB} = pH of suspensions without and with MB, respectively

formation of large agglomerates at the basal surfaces, and simultaneously, each MB cation would be electrostatically bound at the negatively charged siloxane surface. Moreover, such orientation is more suitable for electrostatic attraction between the positively charged parts of the MB cation (localized on dimethylamino groups and the sulfur atom) and the negatively charged sites of the phyllosilicate layers.¹¹ A nearly perpendicular orientation has been found to be common also for other aromatic compounds at clay surfaces.^{12–19}

MB–clay interaction has been claimed to be extremely sensitive for probing the surface properties of smectites in water suspensions.³ However, no data on the effect of smectite composition, layer charge location and density, and clay particle size on the MB–clay interaction have been published. Therefore, the objective of this work was to study the effect of layer charge on MB–montmorillonite interactions in suspension using a set of montmorillonites with differentially reduced layer charge prepared from the same parent, Li-saturated montmorillonite (RCM). In this way the influence of other possible factors associated with the clay, such as the chemical composition, and/or the presence of impurities (other exchangeable cations, admixtures) was eliminated. All MB-reduced charge montmorillonite (MB–RCM) suspensions were treated in the same manner to ensure that all observed differences in their visible spectra were due to differential layer charge reduction alone.

Experimental Section

Materials. The Li–montmorillonite (Jelšovský Potok, Slovakia) was prepared in the same way as reported elsewhere.^{20,21} Reduced-charge montmorillonites were prepared by heating Li–montmorillonite at different temperatures (Table 1) for 24 h. Li–CEC samples were measured by atomic absorption spectroscopy (AAS 30, Carl Zeiss Jena) after repeated ion exchange with ammonium acetate solution (pH = 7). The *d*₀₀₁ spacings of oriented clay samples dried under ambient conditions were obtained by X-ray diffraction (PW 1050, Philips).

Suspensions (0.02%) of RCM in distilled water were prepared after ultrasonic disaggregation treatment for 15 min. Water and MB solution (10^{−5} mol dm^{−3}) were added with stirring to obtain MB–RCM suspensions with final MB and clay concentrations of 2.5 × 10^{−6} mol dm^{−3} and 5 × 10^{−2} g clay dm^{−3}, respectively. Two parallel MB–clay suspensions were prepared for each RCM in new polyethylene vessels.

Methods. Visible spectra of MB–clay suspensions were obtained with a UV–vis spectrophotometer (Zeiss Specord M 40). The spectra were measured 2 and 60 min after mixing MB solution with the clay suspension. The suspensions were then shaken for 18 h, and another set of spectra were taken. The spectra of untreated RCMs (without MB) were subtracted from the MB–RCM spectra to obtain spectra specific for

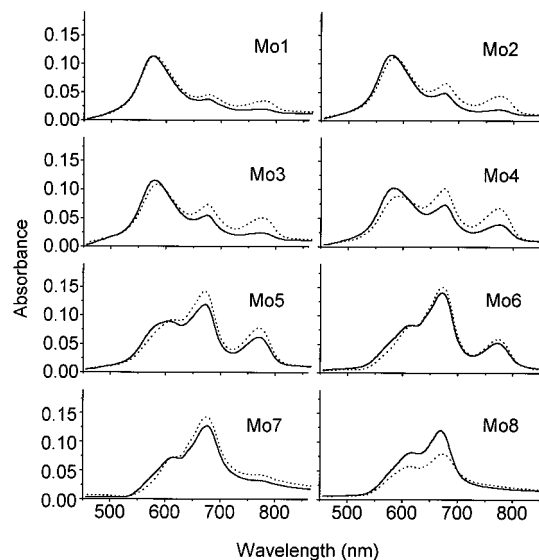


Figure 2. Absorption spectra of methylene blue in reduced charge montmorillonite suspensions measured after 2 and 60 min (dotted line).

adsorbed dye. No differences in the spectra of two parallel MB–RCM suspensions were observed.

Visible spectra of supernatants were measured to verify that all MB added was adsorbed by the clay. Supernatants were obtained by filtration of MB–RCM suspensions through a 0.2 μm pore size filter. Filtration was efficient for separating MB–RCM from the supernatant. No adsorption of MB from the solution by the cellulose material used in the filter was detected; i.e., visible spectra of MB solutions did not change after the passing of MB solution through the filter.

Results and Discussion

Table 1 lists preparation temperatures, CEC amounts, basal spacings (*d*₀₀₁) of RCM samples, and pH values of RCM suspensions. The CEC decreased with increasing temperature of RCM sample preparation. Samples Mo1–Mo4 fully expanded in water, as indicated by their basal spacings (1.22 nm), despite differences in measured layer charge resulting from Li fixation. RCMs of greater charge reduction (Mo5–Mo8) also contain collapsed and/or expanded layers, as indicated by the decreased *d*₀₀₁ values (Table 1). Komadel et al.²¹ found that 45 and 90% of layers, present in Ca–RCM samples prepared by the heating of Li–montmorillonite at 160 and 210 °C, respectively, were nonexpandable and pyrophyllite-like. Although suspensions of Mo1–Mo4 were stable, Mo5 suspensions partially settled after 6 h. Substantial portions of Mo6 and Mo7 sedimented within 1 h. Sample Mo8 exhibited strongly hydrophobic properties and was difficult to resuspend. The same trend of decreasing suspension stability was observed for the MB–RCM suspensions. All suspensions had pH values of 6.0–6.3 (Table 1). Thus, no acidification can be attributed to the possible changing surface acidity as a consequence of the lithium thermal treatment.²²

The color of MB–clay suspensions depended on the measured layer charge of RCM. The montmorillonite suspension with the highest charge with MB (MB–Mo1) resulted in a violet-blue suspension. The MB–RCM suspension color changed to blue and greenish-blue as the clay layer charge decreased. The spectra of MB–RCM suspensions measured 2 and 60 min after preparation are shown in Figure 2. The amount of MB agglomerates (bands at 570–600 nm)³ decreased with decreasing layer charge in favor of monomers (675 nm) and

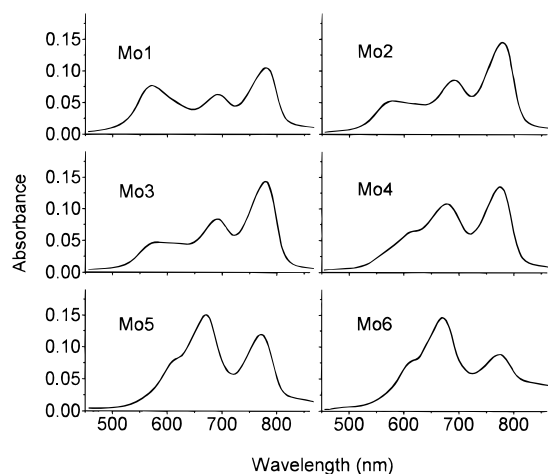


Figure 3. Absorption spectra of methylene blue in reduced charge montmorillonite suspensions measured after 18 h.

protonated MB (775 nm). A fresh suspension of MB–Mo1 contained MB predominantly in the form of larger agglomerates (strong band at 573 nm), while only small amounts of monomeric and protonated MB were present. On the other hand, fresh suspensions of MB–RCMs with intermediate levels of reduced layer charge (Mo2–Mo4) contained more monomeric and protonated MB cations (Figure 2). Their amounts increased with decreasing layer charge, although the charge reduction of Mo2–Mo4 was only 10–18% based on measured CEC values (Table 1). No difference between the spectra of Mo2 and Mo3 samples, which contained approximately equal amounts of CECs, was observed.

The wavelength of the absorbance maximum attributed to larger agglomerates of adsorbed MB increased with decreasing layer charge from 573 nm for Mo1 to 580 nm for Mo4 (Figure 2). The spectrum of fresh MB–Mo5 suspension contained a broad band in the 540–620 nm region composed of two main components—dimers (near 605 nm) and agglomerates (near 575 nm). Only minor portions of MB agglomerates, if any, were present in fresh suspensions of montmorillonites with the greatest levels of charge reduction (Mo6–Mo8). These spectra are dominated by an absorption band for monomers near 675 nm. All MB was adsorbed even on the RCMs with the lowest layer charge; i.e., no MB was detected in the supernatants.

The spectra of the suspensions containing montmorillonites of the highest charge (Mo1–Mo4) changed substantially with time (Figures 2 and 3). In comparison with fresh suspensions, more monomeric and protonated MB were present and decreases in larger aggregates were observed after 1 h of aging (Figure 2). This trend continued with aging until an equilibrium of MB components was achieved (Figure 3). The bands of monomeric and protonated MB are dominant in the spectra after 18 h equilibration of MB–RCM suspensions (Figure 3). The observations reported here are in accordance with the time dependence of MB–clay spectra observed by Gessner et al.⁶ Nevertheless, the influence of layer charge on spectra following 18 h aging was similar to that observed for the fresh and 1 h old suspensions. Although the band attributed to larger MB aggregates was most intense in spectra of fresh suspensions, the 18 h old suspensions contained predominantly protonated and monomeric forms of MB, indicating substantial loss of MB agglomerates with aging. The spectra of suspensions with Mo5 and Mo6 did not change significantly upon aging, although partial flocculation occurred for MB–Mo6 after 18 h. Both MB–Mo7 and MB–Mo8 suspensions were unstable and flocculated completely during the 18 h shaking. Therefore, their spectra could not be measured.

Effect of Time. Li–montmorillonite swells macroscopically in distilled water and can form very stable suspensions of fully expanded clay layers.²³ The distance between individual clay layers is large, and hence, the layer basal planes and edges are fully accessible to MB cations. If MB was homogeneously distributed at the clay surface with a loading of 0.05 mmol/g, no dye aggregation would proceed. Taking into account the size of the MB cation (1.69 nm × 0.74 nm × 0.38 nm),¹¹ MB would cover less than 5% of the total clay surface area (about 800 m²/g) at this loading. However, most MB cations present in the fresh suspension of MB–Mo1 were agglomerated (band at 573 nm; Figure 2). A possible explanation for this observation is that MB adsorption at the smectite surface was nearly instantaneous. This implies that adsorption of MB was completed upon initial contact between MB and the clay surface, possibly before homogeneous mixing of MB solution with the clay suspension occurred. Consequently, micelles of MB cations adsorbed at sites where first contact took place. This would result in some clay particles having high MB coverage and others with low MB coverage in fresh MB–RCM suspensions. The spectra of fresh suspensions prepared in this manner are similar to those of equilibrated suspensions with higher initial MB loadings.^{4,5} Suspension aging promotes a redistribution of MB cations onto surfaces previously without adsorbed dye as described above. This process was found to be very slow; spectral changes were observed on a time scale of days.⁴ The rate of MB redistribution can be significantly increased by agitation,⁷ when the probability of collision between clay particles is greater. MB redistribution was accompanied by a decrease in the amount of larger agglomerates (bands at 570–600 nm) and an increase in monomeric MB (band near 675 nm) as observed mainly for the more highly charged samples (Figure 3). Nevertheless, a portion of MB cations remained as cation agglomerates after 18 h of equilibration. Redistribution of MB may have proceeded to the same extent also in suspensions of RCMs with lower layer charge (Mo5 and Mo6) as well. However, the spectra of these suspensions did not change significantly with the time, since the fresh suspensions of Mo5 and Mo6 contained adsorbed MB mostly in the form of monomers (band at 675 nm).

Effect of Layer Charge Density. MB agglomeration occurs even in the clay suspensions at low initial solution concentration of dye because of the concentration of MB at clay surface sites. Such agglomeration is partially suppressed at very low MB loadings after aging because of MB redistribution over the surface of clay.^{3–5} However, dye cation agglomeration was also limited by the layer charge density (Figures 2 and 3). Considering the dimensions of MB cation¹¹ and a nearly perpendicular orientation with respect to the clay basal plane, the area of MB in proximity to the clay surface is about 1.69 nm × 0.38 nm = 0.64 nm². The actual area is slightly greater than this value, depending on MB orientation, but this value is much greater than the equivalent area for a charge deficit of one electron on mica surfaces (0.20–0.30 nm²/charge).²⁴ To fully compensate negatively charged sites on mica, MB cations would be tilted at greater angles with respect to the mica surface to occupy a smaller area, as shown by Hähner et al.¹¹ On the other hand, the average equivalent area of charge for smectite is 0.60–1.20 nm²/charge²⁴ and is greater than the area occupied by one MB cation. Therefore, MB cations can be arranged at the basals with minimal tilting. At low surface coverage MB cations do not cover the entire surface of most smectites. In fresh suspensions of Mo1 (Figure 2), most MB formed agglomerates (band at 573 nm). However, monomers and protonated cations were also present, probably at sites of low charge density (bands

near 675 and 775 nm, respectively). Decreased layer charge density after thermal treatment within the Mo1–Mo8 series (Table 1) results in a lower concentration of MB cations on the clay basal surface and, hence, greater distances between neighboring MB cations. Thus, the amount of cationic agglomerates decreased from Mo1 to Mo5, as is indicated by the decreased intensity of the band near 570 nm, in favor of monomers and protonated MB (Figure 2). Monomers, partially protonated, predominate at the surfaces of fresh suspensions of Mo5 and Mo6. In these clays the layer charge density was low enough to suppress MB cation agglomeration.

The layer charge distribution on montmorillonite layers is heterogeneous.^{24,25} The amounts of MB monomers and aggregates, as detected by visible spectroscopy, qualitatively reflect the layer charge distribution at the basal surfaces. MB suspensions of smectites of low charge density absorbed mainly at longer wavelengths (bands near 675 and 775 nm) and those of higher charge density absorbed at shorter wavelengths (near 575 nm; Figures 2 and 3). The broad band of MB agglomerates (at 570–600 nm), present in the spectra of the montmorillonite samples of higher layer charge (Mo1–Mo4), is probably composed of several components of similar wavelengths, depending on the size of overlapping areas and the angles between the interacting MB cation neighbors.³ The larger size of areas where MB cations overlap due to neutralization of the layer charge promotes greater agglomeration, and the wavelength of the maximal absorbance decreases.

Protonated MB absorbs light at about 775 nm. Protonation of monomers probably was due to the greater autoionization of water at the clay surface, which was induced by the layer charge.³ The pH values of RCM suspensions, both with and without MB (Table 1), confirm that changes in the amount of MBH²⁺ cations with layer charge reduction (Figures 2 and 3) were not a consequence of the surface acidification invoked by a Li thermal treatment.^{22,26} The amount of protonated dye cations in the fresh suspensions increases with the amount of monomeric MB (Figure 2). The ratio of absorbance intensities $A(\text{MBH}^{2+})/A(\text{MB}^+)$ of the bands at 775 and 675 nm, respectively, was approximately equal to 0.5 in the spectra of Mo1–Mo5 suspensions and decreased with charge reduction for Mo6. The decrease in the amount of protonated MB in MB–Mo6 suspension may be caused by the lower layer charge and hence lower extent of water autoionization. The main site of MB sorption in the suspension of Mo8 and partially also on Mo7 was particle edges because of the inaccessibility of a substantial portion of the basal surface for MB cations in both samples.²¹ The smaller amounts of protonated dye cations on Mo7 and Mo8 may be explained by an inefficiency of clay particle edge sites to acidify MB cations. High intensities of the bands near 775 nm, assigned to protonated MB, were observed in the spectra of Mo1–Mo6 suspensions after 18 h of equilibration (Figure 3). In these systems MB cations were redistributed over more clay particles and the acidification could proceed to a larger extent.

Conclusions

Visible spectra of suspensions changed upon aging because of redistribution of the MB surface coverage. Dye cation

agglomerates, initially formed at sites of high layer charge, were partially dispersed because of MB redistribution over the uncovered clay surface.

The visible spectra of MB–clay suspensions provide qualitative information on the layer charge density of the clays. The layer charge density of basal surfaces appears to control the extent of MB agglomeration. High layer charge density of the smectite surface results in a smaller distance between the neighboring adsorbed MB cations at the clay surfaces and promotes agglomeration. Low layer charge density results in larger distances between MB cations and inhibits MB agglomeration. Owing to the simplicity and high sensitivity of this method, MB adsorption could be used as a sensitive tool for detecting differences in the layer charge and its distribution in similar materials, e.g., after the thermal treatment of Li-saturated montmorillonites or upon reduction of structural Fe(III) in their structure.

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