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METHYLENE BLUE INTERACTIONS WITH REDUCED-CHARGE SMECTITES

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Abstract—The objective of this work was to prepare series of reduced-charge materials from different parent Li-saturated dioctahedral smectites, to investigate the effects of temperature, chemical composition and charge location in smectites on the charge reduction and to characterize reduced-charge smectites (RCSs) using methylene blue (MB) adsorption. The layer charge decrease, induced by Li fixation, is correlated with the trends in the spectra of MB-RCS dispersions in the visible region (VIS) spectra. Distribution of the negative surface charge of the clay minerals controls the distance between the adsorbed MB cations and thus affects the formation of MB dimers and higher agglomerates. Because each form of MB (monomer, dimer, higher agglomerate, J-aggregates) absorbs light at a different wavelength, the VIS spectra of MB depend sensitively on the charge density at the clay surface. Both cation exchange capacity (CEC) values and spectra of MB-clay dispersions clearly detect extensive reduction of the layer-charge density in reduced-charge montmorillonites (RCMs) upon Li-thermal treatment. The extent of charge reduction depends on the temperature of the thermal treatment, as well as on the octahedral charge of the montmorillonite. Reduction of the layer charge proceeds to a much lesser extent for smectites with mainly tetrahedral charge and high Fe content (Fe-rich beidellite and ferruginous smectite). Both CEC data and MB spectra detect only a slight decrease of the layer charge density, which relates to the low octahedral charge of these minerals. Following heating at higher temperatures (120–160°C), slightly higher Li fixation is indicated by CEC values; however, no charge reduction is confirmed by MB spectra. Release of protons accompanying Li^+ fixation in Fe-rich smectites heated at 180 or 200°C was detected in the spectra of MB-clay dispersions and confirmed by potentiometric titrations.

Key Words—Cation Exchange Capacity, Dye Cation Agglomerates, J-Aggregates, Layer Charge Reduction, Methylene Blue, Montmorillonite, Smectite.

INTRODUCTION

Layer charge reduction

The decrease of the CEC in Li-saturated montmorillonite following heating at 200–300°C has been known for decades (Hofmann and Klemen, 1950; Greene-Kelly, 1953, 1955; Glaeser and Mering, 1967) and is induced by the irreversible migration of Li^+ cations into the layers. The final position(s) of fixed Li(I) has been disputed in numerous works. Because of the body of evidence which shows that layer charge reduction does not proceed in beidellites and trioctahedral smectites, migration of Li^+ cations into the vacant octahedra was proposed (Hofmann and Klemen, 1950; Greene-Kelly, 1953; Farmer and Russell, 1967; Sposito *et al.*, 1983; Srasra *et al.*, 1994). However, the fixation of Li^+ in the bottoms of pseudohexagonal cavities within the tetrahedral sheets was suggested based on IR and NMR spectra (Tettenhorst, 1962; Luca *et al.*, 1989; Trillo *et al.*, 1994). Some authors suggest that Li(I) could occupy both of these sites (Russell and Farmer, 1964; Calvet and Prost, 1971; Madejová *et al.*, 1996, 1999).

Decrease in the layer charge significantly alters the properties of the treated minerals. Collapsed, pyrophyllite-like layers are formed upon nearly complete charge reduction (85–90%) in Li-saturated dioctahedral smectites with an initial layer charge located in the octahedral sheets (Brindley and Ertem, 1971; Ertem, 1972; Lim and Jackson, 1986; Bujdák *et al.*, 1991, 1992; Komadel *et al.*, 1996). This transformation has been used to distinguish montmorillonite from beidellite (Greene-Kelly, 1953; Schultz, 1969; Lim and Jackson, 1986). In heated beidellites, Li^+ ions are not fixed in the pseudohexagonal cavities in the tetrahedral sheets, as they can migrate back into the interlayer space upon re-hydration (Kawano and Tomita, 1989). Increase in charge reduction with the magnitude of the octahedral charge was observed (Calvet and Prost, 1971; Jaynes and Bigham, 1987; Williams *et al.*, 1991). Exchangeable Li^+ cations remaining in dioctahedral smectites that had been heated at 200–300°C can therefore be those compensating for the tetrahedral charge and/or the charge at the sites of broken bonds at clay particle edges. The extent of Li fixation, the charge reduction, and possibly the final site of fixed Li(I) also depend on the heating temperature (Calvet and Prost, 1971; Kawano and Tomita, 1989; Madejová *et al.*, 1996).

In addition to layer charge reduction, surface acidification upon Li fixation has been reported. The increased acidity was attributed to the reaction of Li^+ with the structural hydroxyl groups in the octahedral sheets (Russell and Farmer, 1964; Jaynes and Bigham, 1987; Williams *et al.*, 1991). Slightly greater Li retention *vs.* CEC reduction in nontronites was observed by

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Jaynes and Bigham (1987) whose results suggest that Li^+ ions replace protons preferentially from the hydroxyl groups bound to Fe(III). Lithium fixation did not cause charge reduction but rather surface acidification.

Interaction of methylene blue with clays

Methylene blue is a cationic dye, which absorbs visible light near 675 nm in dilute aqueous solutions (Lewis and Bigeleisen, 1943; Braswell, 1968). When mixed with clay dispersions it is rapidly and strongly adsorbed by the clay surfaces (Margulies *et al.*, 1988). The dye adsorption is always accompanied by color changes which are attributed to the formation of dye aggregates and acidification (protonation) at the clay surface. The MB cation dimers and higher agglomerates absorb near 600 and 570 nm, respectively, and protonated MBH^{2+} cations absorb near 775 nm (Cenens and Schoonheydt, 1988; Schoonheydt and Heughebaert, 1992; Breen and Loughlin, 1994; Breen and Rock, 1994; Gessner *et al.*, 1994). The latter spectral absorption has also been assigned to J-aggregates (Bergman and O'Konski, 1963). Head-to-tail interaction of the dye cations in J-aggregates leads to a dipole attraction, which decreases the excitation energy and shifts the dye absorption band to higher wavelengths. The most frequently investigated pseudoisocyanine absorbs the light at ~530 and 570 nm, monomers and J-aggregates, respectively. The formation of the J-band aggregates has been studied recently in the reaction systems of other cyanine dyes (Miyamoto *et al.*, 2000). J-aggregates are formed at solid-liquid interface, but not in the concentrated dye solutions (del Monte and Levy, 1999). The speciation of MB cations formed at the clay surface and, consequently, the color changes upon adsorption, depend on the charge of the clay mineral surface.

Orientation of MB cations nearly perpendicular to the clay mineral basal surface, as was proved recently for micas (Hähner *et al.*, 1996), enables the existence of large, multi-cation dye agglomerates that keep basal spacing d_{001} of MB-clay complexes $\leq$1.75 nm (Bodenheimer and Heller, 1968; Hang and Brindley, 1970). The orientation of MB cations parallel to the surface, frequently reported in the literature (*e.g.* Hang and Brindley, 1970; Brindley and Thompson, 1970; Kahr and Madsen, 1995; Yariv and Lurie, 1971; Gessner *et al.*, 1994; Cenens and Schoonheydt, 1988; Schoonheydt and Heughebaert, 1992), would not enable such agglomeration. The size of a MB cation is about the same as the average area per negative layer charge of one electron in smectites (Bujdák and Komadel, 1997; Bujdák *et al.*, 1998). The distribution of the negative layer charge controls the distances between the adsorbed neighboring MB cations at the smectite surface. Consequently, layer-charge distribution affects the amounts of MB dimers and higher agglomerates. Dependence of the MB agglomeration on the layer charge was recently investigated using the series of RCMs, as well as smectites of variable structure, composition and layer charge (Bujdák and Komadel, 1997; Bujdák *et al.*, 1998). At low MB loadings, smectites with higher layer charge density induced dye cation agglomeration to a greater extent. Due to the relationship between the extent of MB agglomeration and layer-charge density, measuring the MB-clay interaction can be a sensitive method for characterizing the layer-charge distribution of smectites. Preparation of series of RCSs from parent smectites by varying only the temperature minimizes possible differences in admixtures, tetrahedral Al for Si and octahedral Mg and Fe for Al substitutions, *etc.* (Komadel *et al.*, 1996). Thus, differences in MB sorption observed within individual series can then be ascribed directly to the differences in the layer charge.

EXPERIMENTAL

Materials

The <2 μm fractions of five bentonites were used in this study. The dominant minerals of the separated fractions include three montmorillonites: SAz-1, Apache County, Arizona (SAz); SCa-2, San Diego County, California (SCa); and Horní Dunajovice, Czech Republic (HD); an Fe-rich beidellite from Stebno, Czech Republic (ST), and a ferruginous smectite, SWa-1, Grand County, Washington (SWa). The bentonites were fractionated to <2 μm, Ca^{2+} saturated, washed free of excess ions, dried at 60°C and ground to pass a 0.2 mm sieve. The Ca^{2+}-saturated smectites were washed repeatedly with LiCl solution (c = 1 mol dm^{-3}) and the resulting Li^+-saturated smectites, separated by centrifugation, were washed in dialysis tubes until the test for Cl^- ions with $AgNO_3$ solution was negative. The washed samples were then dried at room temperature and ground to pass a 0.2 mm sieve. Each Li^+-saturated smectite was divided into nine equal portions. One portion of each sample was used as the parent smectite. The others were heated in silica vessels at temperatures between 110 and 200°C for 24 h to prepare RCSs.

Methods

The CECs of the RCSs were determined after replacement of Li^+ cations with NH_4^+ via repeated saturation with ammonium acetate solution (1 mol dm^{-3}, pH = 7). The amount of Li^+ cations in the supernatants was measured by atomic emission spectroscopy, using an AAS 30 Carl-Zeiss spectrophotometer. The acidity of smectites was determined by potentiometric titration according to the procedure of Jaynes and Bigham (1987).

Aqueous dispersions of Li^+-saturated smectites and RCSs (0.05 g/ml) were prepared by ultrasonic disag-

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Table 1. Coefficients in structural formulae of smectites per $O_{20}(OH)_4$.

Smectite	Exchangeable cations M^+	Tetrahedral atoms		Octahedral atoms		
		Si	Al	Al	Fe	Mg
SAz	1.11	8.00	0.00	2.67	0.15	1.20
SCa	1.06	7.93	0.07	2.68	0.16	1.25
HD	0.73	7.89	0.11	2.70	0.52	0.85
ST	0.95	7.22	0.78	1.96	1.60	0.58
SWa	0.88	7.32	0.68	0.92	2.83	0.27

gregation treatment for 15 min. Water and MB solution (10^{-5} mol dm^{-3}) were added under stirring in order to obtain MB-clay dispersions of the final MB and clay concentrations of 2.5×10^{-6} mol dm^{-3} and 5×10^{-2} g dm^{-3}, respectively. The visible absorption spectra of MB-clay dispersions were measured with a UV-VIS spectrophotometer (Carl Zeiss Specord M 40) 2 min and 60 min after mixing of the MB solution with the clay dispersion. Then the MB-clay dispersions were shaken for 18 h and another set of spectra was recorded afterwards. After 18 h of agitation, the equilibrium of the dye cation distribution was achieved, *i.e.* the spectra of MB-clay dispersions no longer changed with ageing. It was not possible to record spectra for several of the low charge RCSs because of substantial flocculation of the clay mineral particles. The spectra of the pure clay dispersions (without MB) were subtracted from their dye-clay counterparts to obtain spectra of the adsorbed dye only in order to minimize the effects of light scattering on the clay particles.

RESULTS AND DISCUSSION

The structural formulae of the parent smectites (Table 1) were calculated from the chemical analyses according to Čičel and Komadel (1994). Because of the presence of impurities in the <2 μm fraction, individual oxides obtained from the analyses were considered as independent components for calculation of structural formulae and full tetrahedral occupancy was assumed. Consequently, all effects of admixtures present in the samples appear combined in the sum of octahedral coefficients (octahedral occupancy). In this way, the structural formula for sample ST was corrected for the presence of known admixtures, *i.e.* free silica, kaolinite, goethite and anatase (Čičel *et al.*, 1992) and that of sample HD for 17% of total Fe bound in goethite. Table 1 shows that octahedral occupancy is very close to 4.00 for samples SAz and SWa (4.02 for both) but it is clearly greater for samples SCa, HD and ST (4.07–4.14). This suggests partial occupancy of 'vacant' octahedra in these dioctahedral smectites and/or the presence of unidentified Al- or Mg-rich admixtures (Čičel and Komadel, 1994), possibly hydrated oxides. The exchangeable cation content in the structural formula is clearly less than the sum of tetrahedral Al and octahedral Mg coefficients (Table 1). Both SAz and SCa are montmorillonites with a small (if any) tetrahedral substitution and a large Mg content, covering ~30% of the octahedral positions. The HD montmorillonite has a lower Mg content, a lower octahedral charge, and a slightly higher fraction of the total layer charge due to tetrahedral substitution than either SAz or SCa. The Mg content in Fe-rich beidellite ST is approximately half of that found in the SAz and SCa samples. Most of the layer charge in ST is tetrahedral due to the substitution of Al for Si. Estimates for the distribution of layer charge in the ST are sensitive to the accuracy of corrections for admixtures and the assumptions used in the structural formulae calculation. Nevertheless, ST is clearly an Fe-rich beidellite, where Fe occupies ~40% of the central atom sites in the octahedral sheets. Ferruginous smectite SWa contains the largest amount of Fe, covering >70% of the octahedral positions.

Layer charge reduction

Figure 1 shows the relationships between the CEC of RCSs and the temperature of their preparation. Heating all smectites induces irreversible migration of Li^+ cations into the layers causing a decrease in the CEC. The extent of Li^+ fixation is related to both the temperature and the layer charge location. The amount of exchangeable Li^+ decreases and the amount of fixed Li(I) increases with increasing heating temperature. Parent smectites with a higher proportion of octahedral charge were transformed into RCS with lower CECs, on heating at a given temperature. The similar compositions of the SAz and SCa montmorillonites are reflected in very similar CEC values of the RCSs prepared from these minerals by heating at the same temperatures. A similar dependence of Li^+ fixation on heating temperature results from the CEC data of the HD montmorillonite series (Figure 1). A lower Mg content gives rise to a smaller amount of fixed Li(I) (~78 % of CEC of HD in HD_{200}, where the subscripted 200 denotes the temperature of preparation of the RCS). Much lower Li^+ retention is observed in all heated ST and SWa samples which have a substantially higher proportion of tetrahedral charge. The lower amounts of fixed Li(I) in these heated smectites support the hypothesis that Li^+ fixation relates to the octahedral charge. Linear correlation between the amount of fixed Li(I) and the proportion of octahedral charge of different RCSs prepared at 250°C was reported earlier (Jaynes and Bigham, 1987). The extent of CEC reduction is correlated linearly ($r = -0.958$ to -0.998) with the $Mg/(Mg + Al_{tetr})$ coefficient ration (Figure 2) for a broad range of temperatures of RCS preparation. The ratio CEC_t/CEC_0 should be equal to 1.0 for an ideal beidellite, *i.e.* a smectite without any octahedral charge. However, extrapolations of regres-

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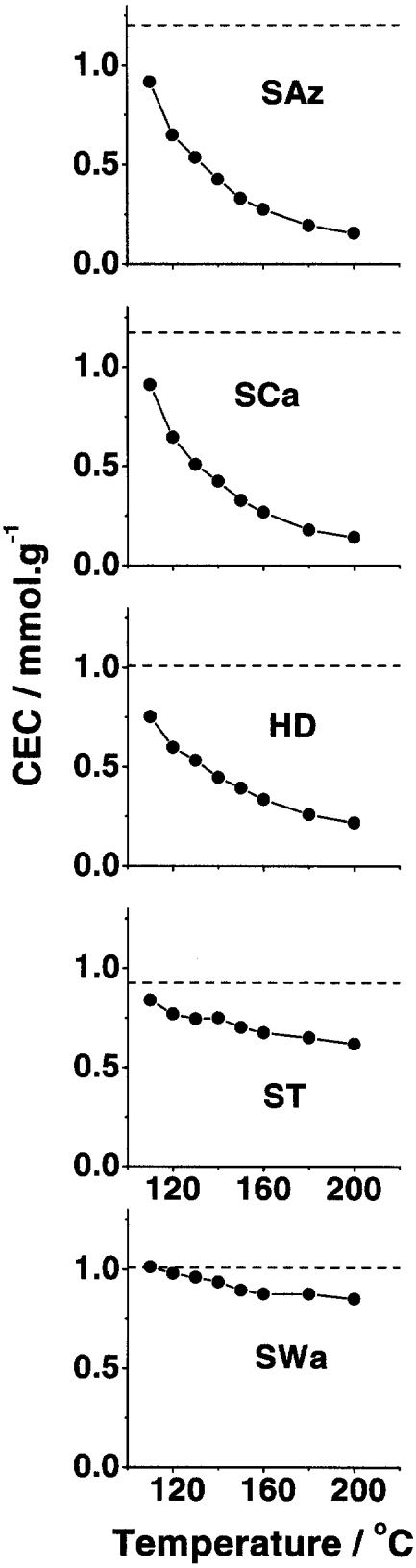


Figure 1. Cation exchange capacities of reduced-charge smectites prepared at various temperatures. Dashed lines show the CEC values for the unheated Li^+-saturated samples.

Table 2. Band positions of different forms of methylene blue in clay dispersions.

Species	λ (nm)
$(MB^+)_n$	570–590
$(MB^+)_2$	≈600
MB^+	650–675
MBH^{2+} or J-aggregates	≈770

sion lines overestimate this value. The effects of octahedral and tetrahedral charge combine and a greater charge density on basal oxygen atoms due to tetrahedral substitution could partially hinder migration of Li^+ into vacant octahedra in the vicinity of tetrahedral substitutions (Tettenhorst, 1962; Luca *et al.*, 1989; Trillo *et al.*, 1994). If this occurs, the RCS will have less Li^+ fixation and larger CEC_t values than expected from the Mg content.

Interaction with methylene blue

Figures 3 and 4 show MB absorption spectra in the presence of clay dispersions. The relative amounts of MB monomers, dimers, higher agglomerates, and the protonated form (and/or J-aggregates) of dye cations can be estimated from the absorption intensities of appropriate spectral bands (Table 2). The high layer-charge density of both unheated SAz and SCa montmorillonites is reflected in enhanced absorption at 570 nm due to MB cations present, mostly in the form of larger agglomerates. The absorption band near 570 nm is dominant in their spectra and does not change much with dispersion ageing (Figure 3). The resistance of the dye cation agglomerates against a re-distribution with time (ageing) indicates the presence of rather densely packed 2-dimensional dye cation agglomerates at the surface of these smectites. The properties of such agglomerates can be compared to the adsorbed long-chain alkylammonium cations. The high affinity of the clay surface to long-chain alkylammonium cations was ascribed to strong van der Waals forces between alkyl chains. These forces increase with the size of the alkyl chains (Grim *et al.*, 1942; Vasant and Uytterhoeven, 1972). In a similar approach, a face-to-face interaction between the dye cations increases the adsorption energy of the dye adsorbed at the clay surface. Consequently, the strong van der Waals forces between adsorbed dye cations may prevent re-arrangement and desorption of the dye cations and their migration and re-distribution on the uncovered surface of the clay mineral particles.

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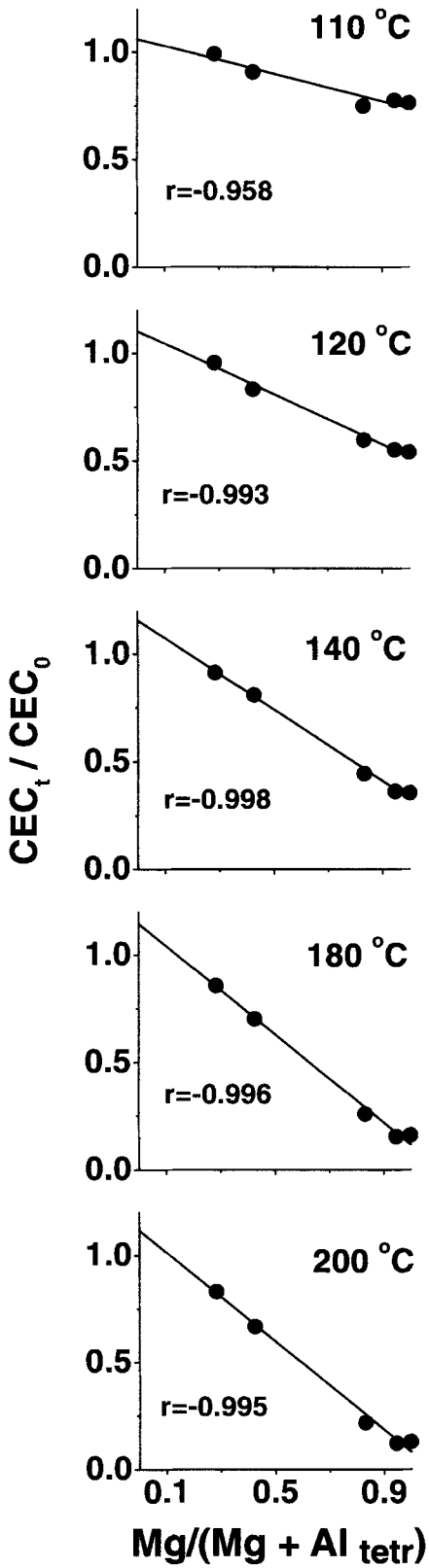


Figure 2. Relationships between the relative CEC and Mg/(Mg + Al_{tetr}) coefficient ratio for various preparation temperatures. Relative Mg occupancy is the Mg coefficient divided by the sum of the coefficients of all octahedral atoms in the structural formula. It increases in the order: SWa, ST, HD, SCa, SAz. CEC_0 and CEC_t are cation exchange capacities of unheated and reduced-charge smectites, respectively.

The layer charge decrease in heated SAz and SCa smectites results in significant changes of the spectra (Figure 3). The intensity of the band assigned to the dye agglomerates (near 570 nm) decreases. Both the shift of the band to a higher wavelength and the broadening of the band near 570–600 nm indicate a decrease in the content of higher agglomerates and an increase in MB dimers, absorbing near 600 nm. On the other hand, the relative intensities of the absorption bands assigned to the dye cation monomers (675 nm) and that attributed to the protonated MBH^{2+} cations or alternatively J-aggregates (775 nm) increase with decreasing layer charge. The lower charge density in heated SAz and SCa samples results initially in a less stable structure of agglomerates of smaller size and/or with less densely packed arrangement of the dye cations. Consequently, van der Waals forces between the dye cations decrease, which results in more re-distribution of dye cations upon ageing. Changes in the absorption band near 570–600 nm in the spectra of SAz_{110} and SCa_{110} dispersions aged for up to 18 h prove re-distribution of MB agglomerates (575 nm) in favor of monomers (670 nm) and the dye species absorbing near 775 nm, respectively (Figure 3). The existence of MBH^{2+} cations was attributed to the reaction of MB^+ with H_3O^+ cations at the clay surface (Cenens and Schoonheydt, 1988). The MB^+ monomers exposed to the environment of H_3O^+ ions are acidified more easily than MB^+ forming large agglomerates, which are not readily accessible for acidification reactions. Indeed, the intensity of the band, absorbing near 775 nm, increases with the amount of MB monomers. However, the possibility of formation of dye J-aggregates, absorbing light near 775 nm (Bergman and O'Konski, 1963) cannot be ruled out. Absorption spectra of J-aggregates are characterized by strong, narrow bands that are shifted to longer wavelengths with respect to absorption bands for the monomers. J-aggregates are a coherent head-to-tail coupling of dye cations, where the ions are inclined with the longitudinal axis at angles <55°, relative to the surface (Yao *et al.*, 1999), as was observed for MB orientation on the mica surface (Hähner *et al.*, 1996). A less densely packed structure of J-aggregates, resulting from head-to-tail coupling (Yao *et al.*, 1999), should prevail on lower charge density surfaces. This is in agreement with the trends observed in Figure 3. Hence, besides the formation of MBH^{2+}, the re-distribution of agglomerates in favor of

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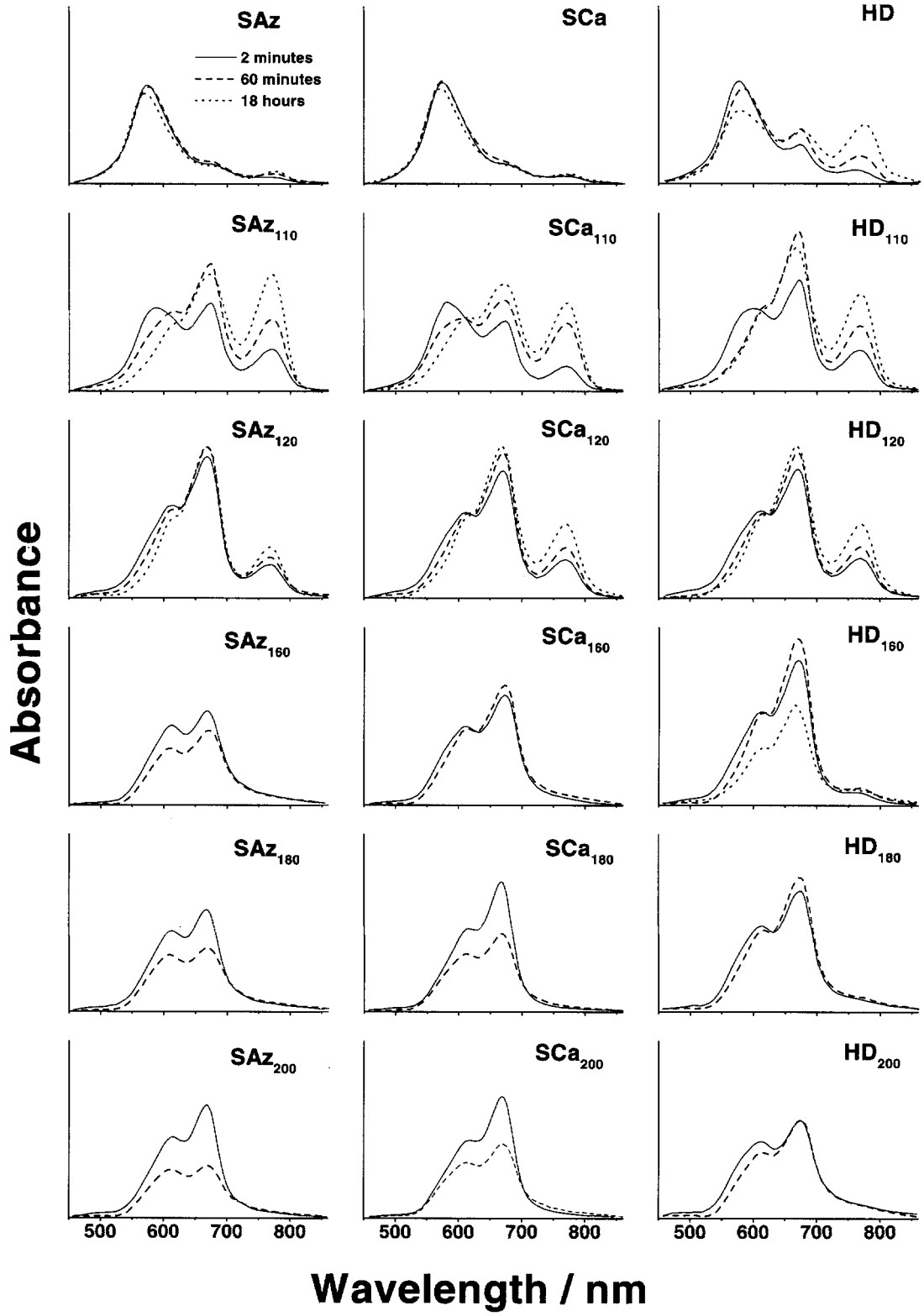


Figure 3. Selected absorption spectra of methylene blue in reduced-charge SAz, SCa and HD dispersions measured 2 min, 60 min and 18 h after preparation.

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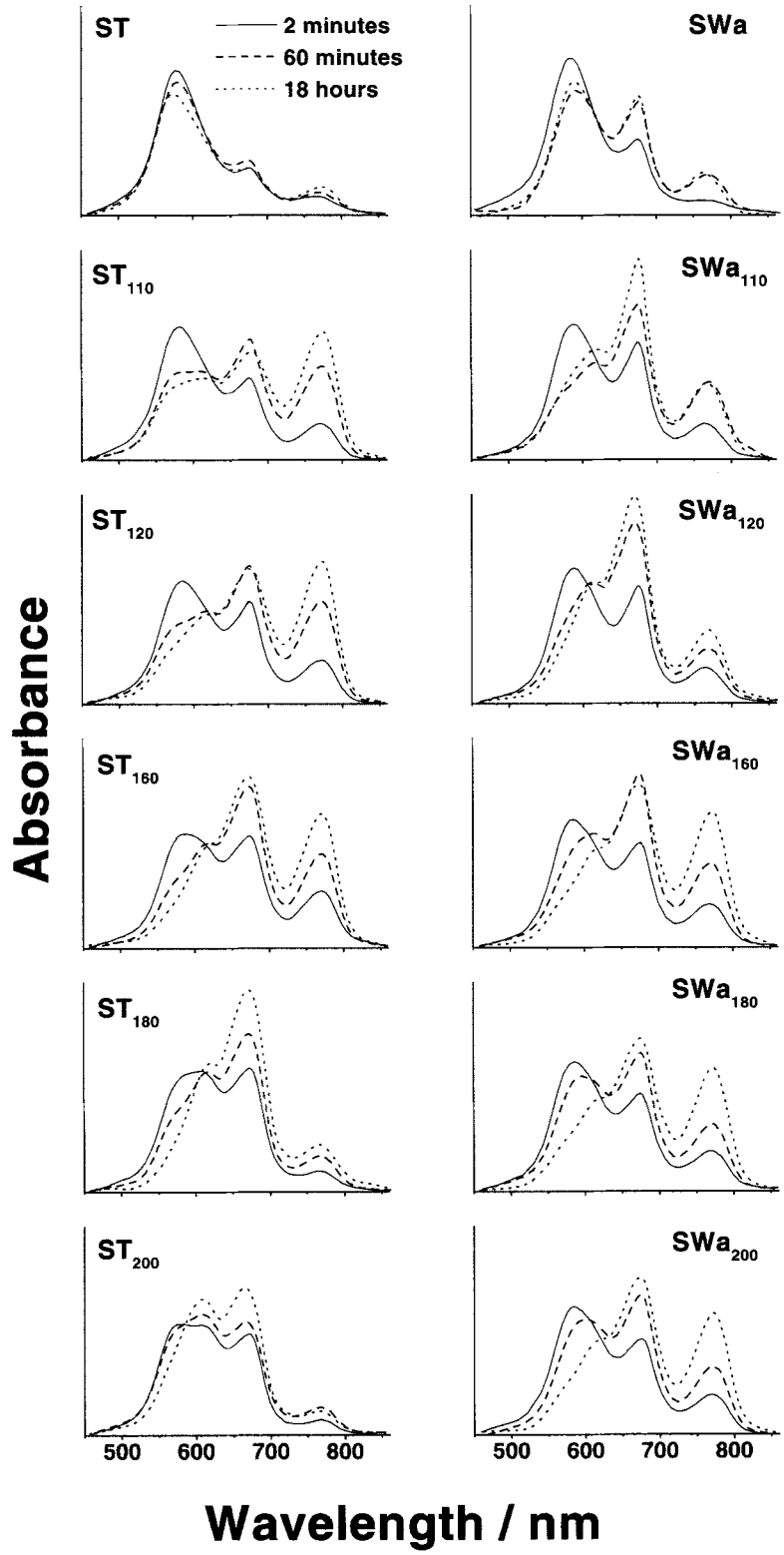


Figure 4. Selected absorption spectra of methylene blue in reduced-charge ST and SWa dispersions measured 2 min, 60 min and 18 h after preparation.

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monomers and less densely packed J-aggregates with decreasing layer charge must be taken into account.

The MB higher agglomerates are scarcely detectable in fresh dispersions containing SAz and SCa samples heated at 120°C (Figure 3). The MB monomers (band near 675 nm) are dominant on the surfaces of these clays. The formation of MB agglomerates is suppressed substantially when the preparation temperature exceeds 120°C (Figure 3), when arrangement of the dye cations reflects lower negative charge density. This does not favor the formation of the MB cation agglomerates. On the contrary, the 775 nm band, assigned to either MBH^{2+} or J-aggregates, decreases for samples heated above 130°C, *i.e.* with further lowering of the layer charge. The disappearance of this band with decreasing charge can be interpreted as a consequence of less water autoionization and/or suppressed formation of J-aggregates at the surface of low charge density. The trends of the dye agglomeration, as described above, are in agreement with some results and interpretations published earlier. (Bujdák and Komadel, 1997; Bujdák *et al.*, 1998). However, besides the influence of the layer charge, a significant alternative effect of the swelling properties of smectites on the dye agglomeration was proposed by Gessner *et al.* (1994) and by Cenens and Schoonheydt (1988). They stated that poorly-swelling clays form large particle associates with less external surface area accessible for initial adsorption of the dye cations. Consequently, the dye cations adsorbed on such clays should be more concentrated, which might favor the dye aggregation. However, this is not confirmed in the experiments presented here. The formation of larger clay particle associates was proven with a light scattering of dispersions for the SAz and SCa samples heated at ≥120°C. Clay particle association and reduced dispersion stability is due to the decrease in inter-particle electrostatic repulsion forces as the charge decreases. However, almost no dye cation agglomeration is observed in dispersions of the low-charge SAz and SCa samples (Figure 3), contrary to the theory of the clay mineral swelling effect on the dye aggregation, as mentioned above. As a consequence of the formation of large clay particles, flocculation of dispersions of the lowest charge samples in SCa and SAz series occurred. In some cases it was observed in the form of light blue flocs or coating on the inside of the bottle. The lowering of the absorbance of MB^+ bands in the spectra with time confirms this observation (Figure 3). Similar trends for CECs with the preparation temperature in SCa and SAz series (Figure 1) yield almost identical spectra for MB-clay dispersions (Figure 3). The results of both these methods confirm the ability of SAz and SCa montmorillonites to fix Li^+ cations upon heating.

The spectrum of MB in fresh dispersions of unheated montmorillonite HD (Figure 3) is slightly different from those of MB-SAz and MB-SCa dispersions. This difference is due to a lower charge density for the HD, confirmed by the lower CEC of HD (Figure 1). A lower layer charge induces longer distances between the adsorbed MB cations. Consequently, the HD surface contains fewer and/or smaller dye cation agglomerates (band near 575 nm) and more dimers (600 nm) and monomers (670 nm). The coverage of MB cations on the surface of HD montmorillonite is less dense and therefore more susceptible to re-distribution of adsorbed dye species, compared to SAz and SCa (Figure 3). The spectrum of the fresh MB-HD_{110} dispersion is only slightly different from the spectra of fresh dispersions containing SAz_{110} and SCa_{110}. Greater absorption intensity associated with monomers indicates a lower charge density of HD_{110} compared to SAz_{110} and SCa_{110}, in accordance with the CEC values (Figure 1). The dispersions containing MB and HD montmorillonite heated at 120°C yield very similar spectra to those of SAz and SCa heated at the same temperatures. The trends observed with further charge decrease are the same as observed with the SAz and SCa series. However, the MB spectra reveal differences between the charge reduction in high-charge SAz and SCa montmorillonites, and HD montmorillonite with lower CEC and a greater fraction of tetrahedral charge (Figure 3).

The VIS spectra of MB-clay dispersions confirm a lesser charge reduction in the ST and SWa smectites (Figure 4) relative to SAz, SCa and HD, in accord with the CEC values (Figure 1). Partial decrease of the layer charge in ST and SWa heated at 110°C is indicated by the intensity increase of the bands near 675 and 775 nm. However, these changes are much less extensive than those observed for montmorillonites heated at the same temperature (Figure 3). Heat fixation of Li^+ in ST_{120}–ST_{160} and SWa_{120}–SWa_{160} samples resulted in minimal changes in the spectra of these samples (Figure 4). The extent of the charge reduction in ST and SWa smectites was probably almost the same in the 120–160°C temperature range. However, an opposite trend is observed for the ST_{200} sample. Higher agglomerates at the surface of MB-ST_{200}, absorbing near 575 nm, exhibit greater resistance to re-distribution than MB-ST_{180}. Negligible change in the 575 nm absorption band is detected after 60 min for the MB-ST_{200} sample, whereas it decreases considerably for MB-ST_{180}. This observation may indicate formation of clay mineral surfaces with slightly higher charge density in ST_{200} than in ST_{180}.

A similar trend is observed for the SWa series. Namely, the spectra of MB with SWa_{180} and SWa_{200}, measured after 60 min ageing, indicate more agglomerates (band near 575 nm) than those of SWa_{120}–SWa_{160} samples. These reversal trends indicate a partial charge increase with increasing preparation temperature. Such an increase in layer charge is inconsistent with the CEC measurements, which detect the

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Table 3. Temperature of preparation and titratable acidity of selected samples.

Preparation temperature (°C)	Titratable acidity (mmol H_3O^+/g)	
	ST	SWa
120	0.006	0.003
130	0.009	0.024
140	0.019	0.029
150	0.019	0.038
160	0.015	0.027
180	0.027	0.038
200	0.079	0.078

lowering of the exchangeable Li^+ content over the whole temperature range. One possible explanation could be a partial release of protons from the OH groups coordinated to octahedral Fe and/or from surface hydroxyls. Hence, measured change in the layer charge upon heating can result from two opposite contributions: Li^+ fixation and H^+ release.

Acidification after heating of Li^+-saturated smectites has been detected only for Fe-rich minerals (Russell and Farmer, 1964) due to easier destabilization of hydroxyl groups coordinated to octahedral Fe (Russell, 1979). The types of hydroxyl groups and their relative amounts in the smectites analyzed reflect the composition of the octahedral sheets, as was calculated in the structural formulae. The amount of protons in heated Li^+-saturated SWa and ST samples was measured by titration with NaOH solution. The results obtained are summarized in Table 3 and are similar to those reported by Jaynes and Bigham (1987) for other smectites. Montmorillonites SAz_{200} and SCa_{200} are characterized by low acidity, 0.011 and 0.016 mmol H^+/g, respectively. A higher value (0.027 mmol H^+/g) determined for HD_{200} is probably due to the greater Fe content in the octahedral sheets of this clay mineral. The Fe-rich smectites ST and SWa are the most acidic minerals after heating at 200°C. The dependence of titratable acidity on the preparation temperature indicates that the greatest release of protons proceeds at the highest temperature. However, the total H^+ release probably exceeds the amount detected by the titration experiment because protons formed from this reaction would probably react with, and partly destroy, the smectite structure. Some structural atoms, such as Mg(II), Al(III) and Fe(III), may be released and thus lead to the formation of structural defects within the clay mineral network. Release of the protons explains why the different extent of Li^+ fixation in reduced charge ST and SWa samples, as detected in CEC values (Figure 1), is not reflected in the trends of the absorption spectra of MB in ST and SWa dispersions (Figure 4).

CONCLUSIONS

Reduction of the layer charge upon Li^+ fixation depends significantly on the charge location and the temperature of thermal treatment. The CECs are reduced substantially in montmorillonites heated at 180–200°C. Layer charge decreases only slightly in heated Li^+-saturated smectites of low octahedral charge. These results are confirmed by the interaction of reduced-charge smectites with methylene blue. Higher agglomerates of the dye cations are formed predominantly at the surface of high-charge smectites. Layer charge reduction leads to a decrease in the extent of dye cation agglomeration on smectite surface in favor of monomers, protonated dye cations and/or J-aggregates. The VIS spectra of methylene blue detect differences between the charge reduction of the studied smectites. Besides the heating temperature, the octahedral charge of smectite plays a crucial role in Li^+ fixation. Release of protons accompanying Li^+ fixation in Fe-rich smectites was detected in the spectra of methylene blue clay dispersions and confirmed by the mineral's acidity measurements.

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