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Interaction of montmorillonite with phenothiazine dyes and pyronin in aqueous dispersions: A visible spectroscopy study

Research Article

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Abstract: Layer charge is one of the key parameters used for the characterisation of expandable clay minerals, smectites. It determines most significant properties of the material which are important from the industrial application point of view. This work is related to a novel method introduced to characterize the layer charge of smectites, based on using cationic organic dyes as molecular sensors. One xanthene and four phenothiazine cationic dyes were tested using reduced charge montmorillonites (RCMs) and compared with methylene blue, which has been used most frequently. The characterization of the charge was based on the formation of molecular assemblies (*H*- and *J*-aggregates) composed by dye cations, which were easily detectable using absorption spectroscopy in the UV/VIS spectrum. More detailed characterization of the spectra required calculations of second-derivative curves. For all of the reaction systems tested in this work, the molecular aggregation increased with the layer charge of RCMs. Slight to moderate differences in the formation of dye assemblies related to the differences in the molecular structures of the individual dye cations. For example, the molecular asymmetry of azure A brought about the formation of coexistent species of similar structures. The structure of the heteroaromatic skeleton affected the extent of the aggregation and spectral changes with time. The presence of reactive, non-substituted amino groups in thionine cations probably partially decomposed in the clay mineral colloids based on high-charge RCMs. Any of the tested dyes could be used as molecular sensors for empirical characterization of the layer charge of clays taking into account the differences mentioned above.

Keywords: *Layered silicates • Dye molecules • Molecular aggregates • Adsorption • UV/VIS spectroscopy*

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1. Introduction

Clay minerals are natural layered silicates composed of submicroscopic particles [1]. One of the most important groups of clay minerals is represented by expandable minerals, smectites. Due to isomorphic substitutions within the structure, smectite layers bear a negative charge. Some interesting physical and chemical properties, such as the tendency to form colloids and their inherent ion-exchange properties, relate to the layered structure and the presence of the net negative charge present in these minerals [2]. These properties have a great influence on many chemical and physical parameters of these materials and are important for some processes taking place in nature or utilized by industry.

When smectites are suspended in aqueous solutions, the expansion of the clay mineral structure occurs [3]. The swelling process relates to the expansion of interlayer spaces and is important for adsorption (intercalation) of various organic species. Numerous works have reported significant influence of clay minerals on optical properties of organic dyes [4,5]. Cationic chromophores are frequently adsorbed *via* an ion exchange reaction in the form of molecular assemblies [5]. This process is followed by significant changes of the electronic properties, which is observable using absorption spectroscopy in the visible region. The formation of dye molecular aggregates is due to hydrophobic interactions between dye molecules in water. Significant changes of electronic properties upon the formation of dye assemblies are due to coupling between transition

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moments of the chromophores [6]. Two main types of the molecular aggregates have been described in literature. The first type, called *H*-aggregates, is typical of a sandwich-type molecular association [7]. Electrostatic repulsion between interacting transition dipoles occurs in this case, which results in an increase of the excitation energy compared to a non-aggregated monomeric form. Consequently, the *H*-aggregates absorb visible light of higher energies than non-aggregated forms of these chromophores. The second type of the molecular aggregates, called *J*-aggregates, is characterised by a head-to-tail molecular association. It results in a decrease of the excitation energy compared to the monomeric form. *J*-aggregates, which are formed less frequently, can be identified by absorption bands at significantly lower energies [8].

Several works have studied the factors affecting spectral properties of cationic dyes adsorbed on clay mineral surfaces. Molecular aggregation and electronic properties of chromophores are strongly influenced by various parameters, including dye concentration and structure, pH and ionic strength, temperature and presence of organic cosolvents, *etc*. [4,5,9]. In the systems with clay minerals, the dye aggregation is also sensitive to the surface properties of clay mineral templates and depends on the type of exchangeable cations [9,10]. It has been proven that the main parameter which controls dye molecular aggregation on clay mineral surfaces is the layer charge [11]. Lower charge densities induce longer distances between adsorbed dye cations. Consequently, the monomeric form of isolated dye cations is preferentially adsorbed in such cases. If the layer charge density of clay minerals is sufficiently high, the distances between neighbouring adsorbed dye cations are smaller and *H*-aggregates are preferentially formed. Less densely packed *J*-aggregates resulting from a head-to-tail coupling [12] occur less frequently under specific conditions on the surfaces of clay minerals of medium to low charge densities [13].

Due to the sensitivity of methylene blue (MB) aggregation to layer charge density of clay minerals, MB has been studied in numerous works where it has served as a sensitive probe for fast qualitative characterisation of layer charge distribution of smectites [5,11,13,14]. Besides MB, there are several structurally similar cationic dyes, which exhibit metachromatic behaviour, which has not been described for dye/clay mineral system yet. In this study, we compared optical properties of four phenothiazine dyes, including MB and one xanthene dye in the systems based on reduced-charge montmorillonite (RCM) dispersions. Metachromatic properties of these dyes could be used to characterize the surface charge of clay minerals and potentially also other charged solid materials and their colloidal systems. The main objective of this study was to characterize molecular aggregation of the dyes for their potential application as molecular probes for material characterization.

2. Experimental Procedures

2.1 Materials

The commercially available Na^+-saturated montmorillonite Nanocor PGV (Nanocor Inc., USA) was used in this study. The chemical composition of the original sample was determined at the Geoanalytical Laboratory of the Geological Survey of Slovak Republic. The coefficients were calculated from chemical analyses of the sample according to the method published elsewhere [15]. The calculated structural formula of the parent sodiated material is as follows:

$$Na_{1.31}\,[(Si_{7.47}\,Al_{0.53})\,(Al_{2.68}\,Fe_{0.42}\,Mg_{0.95})O_{20}\,(OH)_4].$$

Li^+-saturated montmorillonite was prepared from parent Na^+-saturated montmorillonite (Nanocor PGV from Nanocor Inc., USA) by an ion exchange reaction with LiCl solution (c =1 mol dm^{-3}). The series of reduced-charge samples was prepared by thermal treatment of Li^+-Nanocor at 100, 110, 120, 130, or 140°C for 24 hours. The samples of non-heated sample and those obtained by thermal treatment at 100-140°C are called N, N100, N110, N120, N130, N140, where the numbers for N100-N140 denote the heating temperature used for the thermal treatment. Detailed general information about the preparation and characterization of the series of RCMs prepared by thermal treatment has been described elsewhere [16].

Five cationic dyes, namely azure A (AzA), azure B (AzB), thionine (Th), methylene blue (MB) and pyronin G (Pyr) were used in this work. AzA, AzB, MB and Th were purchased from Sigma-Aldrich, Pyr from Merck. All the dyes are of standard P.A. purity. The molecular structures of these dye cations are shown in Fig. 1.

2.2 Methods

Cation exchange capacity (*CEC*) of the samples was determined *via* repeated saturation with 0.1 mol dm^{-3} solution of barium chloride and subsequent detemination of released cations by atomic absorption spectroscopy. The *CEC*s were re-calculated per weight of a completely dehydrated clay mineral sample. The samples before determination of *CEC* values were heated at 100°C overnight to remove water. The amount of water present was

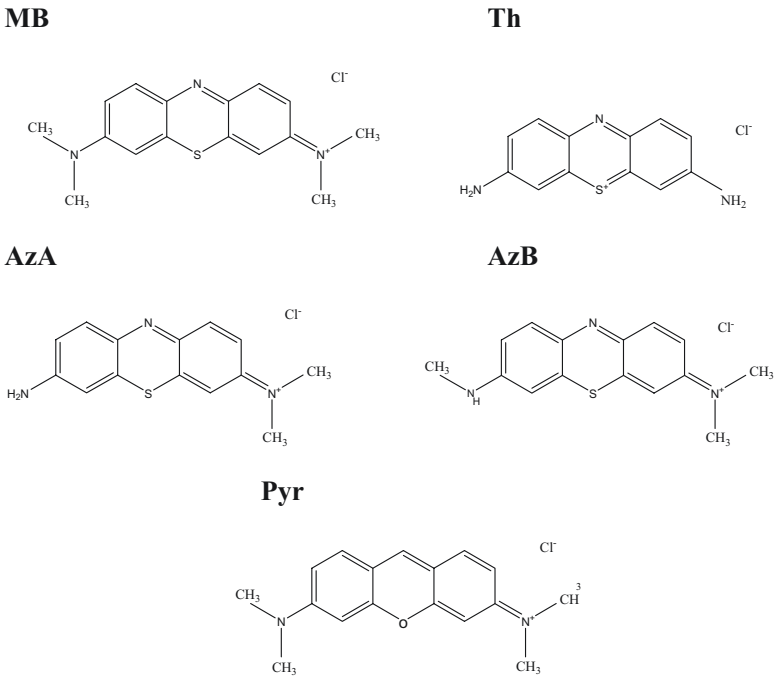

Figure 1. Molecular structure of MB, Th, AzA, AzB, Pyr.

determined as a weight difference before and after heating. UV/Vis absorption spectra of the dye/smectite colloidal systems were measured with a UV/Vis spectrophotometer (Cary 100, Varian). Aqueous colloidal dispersions of smectites (0.02%) were prepared using ultrasonic disaggregation treatment for 20 minutes. Water and organic dyes solutions were mixed to obtain dye/smectite colloidal dispersions with final dye and smectite concentrations of 5×10^{-5} mol dm^{-3} and 5×10^{-2} g dm^{-3}, respectively. The spectra were recorded 1 minute after mixing the dye solutions with smectite dispersions. The dispersions were then shaken and the UV/Vis absorption spectra measurements were repeated after 24 h. After this time, the spectra were not changed with aging. The background absorptions due to light scattering from clay mineral particles in the dispersions were subtracted from all the spectra. For comparison, the spectra of aqueous solutions 5×10^{-5} mol dm^{-3} dye were measured as well.

The second derivative spectra (2DS) were calculated using a second-polynomial, five-point smoothing algorithm. The 2DS, defined as the function $d^2A(\lambda)/d\lambda^2$ [17], were calculated for a complete series of the absorption spectra measured between 1 minute and 24 hours. Complete series of the absorption spectra and 2DS are provided as supplementary data available in internet. This paper presents selected results in order to demonstrate the main trends of the molecular aggregation of the dyes in RCM colloidal dispersions.

3. Results and discussion

3.1 Determination of the cation exchange capacity

Cation exchange capacities (*CEC*) values of RCMs are listed in Table 1. The number of exchangeable cations reflects the number of negative charge sites. Therefore, the *CEC* value is a useful and easily measurable parameter for the characterisation of the layer charge of clay minerals. The highest *CEC* value was confirmed for untreated samples prepared by drying at 60ºC. With increasing temperature of preparation, the *CEC* values gradually decreased. This can be explained by migration of Li^+ cations from interlayer spaces in to the layers during the thermal treatment. This process leads to a reduction of layer charge [16]. The *CEC* values of samples heated at 100, 110 and 120°C represent 93, 87 and 84% of the *CEC* value of a parent sample. They represent typical smectites with fully expandable structure and belong to a 'middle-charge' regime of smectites. The higher reduction of the *CEC* was determined for N130 and N140, which led to the lowering of their *CEC*s to 79 and 69%, respectively. These samples are comparable to low charge smectites, with a phase of swelling/non-swelling interlayer spaces. Besides dominant Li^+ ions, only a small fraction of other exchangeable cations (Na^+, Ca^{2+}, Mg^{2+}) was identified to be below 10% of the *CEC* values.

Table 1. The cation exchange capacities determined using the barium chloride method, and standard deviations.

	NAN 60	NAN 100	NAN 110	NAN 120	NAN 130	NAN 140
CEC [mmol g^{-1}]	1.35	1.24	1.18	1.14	1.05	0.95
δ	0.05	0.03	0.02	0.04	0.03	0.03

3.2 Absorption spectroscopy

Series of absorption spectra in the visible region were measured to characterize molecular aggregation of the dyes. Since, in some cases, the absorption spectra were not sufficient to provide all the details on the differences between molecular aggregations of tested organic dyes, the second-derivative spectra were calculated additionally.

3.2.1 Absorption spectra of dye solutions

The absorption spectra of aqueous solutions of the dyes together with 2DS are parts of Figs. 2-5. The 2DS were used to determine exact positions of the absorption bands. Basic characteristic of the species in the dye solutions and colloidal dispersions with RCMs are shown in Table 2. The maximum of the absorbance band for MB aqueous solution is at 662 nm with a shoulder at 610 nm (Fig. 2a). The shoulder is attributed to a vibronic component of a main transition 0→1 (14). AzA and AzB aqueous solutions exhibit maximal absorbancies at 630 and 645 nm, respectively (Fig. 3a). The spectral shifts with respect to MB are due to differences in substitutions at amino groups of the cations (Fig. 1). A vibronic component was found for both the dye solutions at about 580 nm. Th, without any substituents on the amino groups of its cation, exhibits maximal absorption at further lower wavelengths (600 nm) with a shoulder at 550 nm (Fig. 4). The absorption at 545 nm and a vibronic transition shoulder at ~ 500 nm were observed for Pyr (Fig. 5a). Significantly higher energies of Pyr electronic transitions are due to the properties of xanthene chromophoric unit.

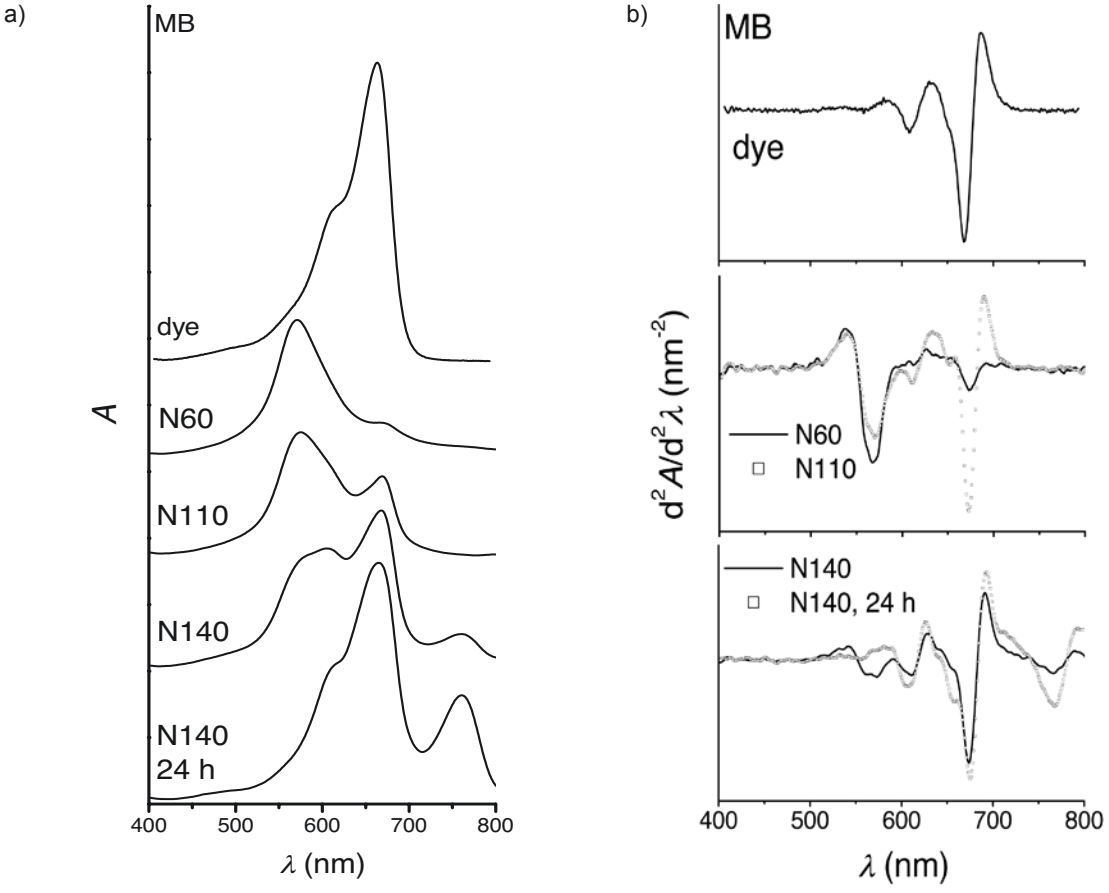

Figure 2. a) Absorption spectra of methylene blue/reduced-charge montmorillonite colloidal dispersions; b) Second-derivative spectra of methylene blue/reduced-charge montmorillonite colloidal dispersions

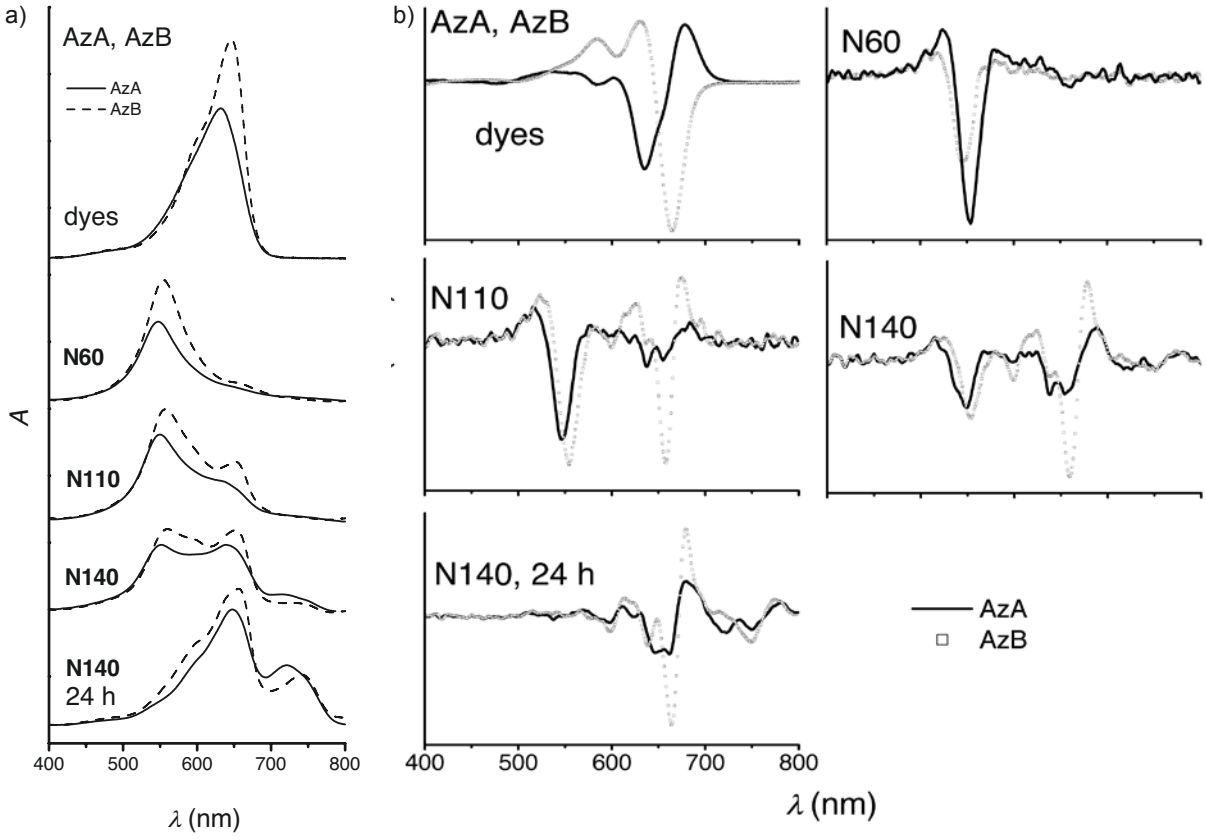

Figure 3. a) Absorption spectra of azure A and azure B in reduced-charge montmorillonite colloidal dispersions; b) Second-derivative spectra of azure A and azure B in reduced-charge montmorillonite colloidal dispersions

Table 2. Positions of absorption bands of dyes in solution and clay dispersions (nm)

DYE	MONOMER	H-DIMER	H-AGGREGATES	*J*-AGGREGATES
	solution / clay	clay	clay	clay
MB	664 / 673	610	570	760
AzA	630 / 639	590	548	720
AzB	649 / 651	599	554	740
Th	600 / 608	561	521	700
PYR	545 / 550	511	475	-

3.2.2 Absorption spectra of dyes in dispersions of reduced charge montmorillonites

Complete series of spectra based on the dyes and RCM colloidal dispersions measured 1 min and 24 h after preparation are shown in supplementary materials. Only representative spectra are shown in Figs. 2-5 in order to demonstrate similarities or differences between the properties of studied dyes to form molecular assemblies in clay mineral dispersions.

3.2.3 Methylene blue aggregation

The interactions of MB with smectites and several series of RCMs have been studied in several works [4,5,7,9-11]. MB molecular aggregation in RCM dispersions is introduced in this work in order to compare the metachromic properties of studied phenothiazine dyes and Pyr with that of the most frequently investigated MB. Selected absorption spectra of MB/RCM colloidal dispersions are shown in Fig. 2a. High-charge density sample N60 induced the formation of *H*-aggregates which absorb light at 570 nm. Lowering the layer charge (N110) partially destabilized the *H*-aggregates (Fig. 2a) in favour of the monomers. Monomeric forms of MB absorb light in smectite dispersion at 670 nm, which is at higher wavelengths than the absorption of the aqueous solution (Table 2). This difference is relatively small, and similar trends have been repeatedly observed for MB, as well as other cationic dyes, and attributed to

the influence of the polarity of clay mineral surface on dye electronic properties [11,18]. Significantly fewer cations forming the *H*-aggregates were detectable in the cases of low-charge RCMs (*e.g.* N140). In this case, isolated cations (monomers) were the main form of MB. The cations adsorbed on the surfaces of low charge RCMs were probably less concentrated, which was reflected in longer intermolecular distances as a consequence of the low charge density of the RCM. The lower concentration of the ions on the surface partially suppressed the formation of the molecular aggregates. *H*-dimers absorbing at about 600 nm were likely formed in all of the reaction systems, but their bands were overlapped and hardly distinguishable from vibronic components of monomers' main transitions. A significant amount of *H*-dimers was probably present in the colloidal dispersion of N140, being identified as a shoulder at about 600 nm. The band detected at 760 nm was attributed to *J*-aggregates with a head-to-tail molecular association. They were found only in the presence of the lowest charge samples (Fig. 2a).

After 24 h agitation of the dye/RCM colloidal dispersions, the spectra partially changed. In general, the amount of *H*-aggregates decreased, which could be explained in terms of partial decomposition and re-arrangement of these molecular assemblies. The amount of monomers and *J*-aggregates increased with time. The spectral changes increased with decreasing layer charge of the RCMs. A selected example of an aged MB/N140 dispersion is shown in Fig. 2a. The basic trends in the MB spectra for colloids of RCMs and the changes of the spectra with time are in agreement with the results obtained with similar reaction systems, which have been studied previously [10,11,13,19]. The spectral changes with layer charge are in accordance with the theory of layer charge influence on the MB molecular aggregation [11].

Derivative spectroscopy is able to distinguish between broad and narrow absorbance bands and is often used to minimize signal contribution from light scattering. This method is a good analysis tool for quantification of chromophores [18]. From broad band spectra, the 2DS often provides well-distinguished narrow bands of resolvable components. Therefore, it could be used to identify the position of the bands, that in the original absorption spectra are very broad and/or overlapped. We used second-derivative spectroscopy to enhance the resolution of the individual bands in our dye absorption spectra, to estimate the monomer's and *H*-aggregates' peak positions, and to compare the amounts of the species in comparable reaction systems. The 2DS identifies maxima in absorption spectra bands as the minima of the negative value bands. A complete series of second derivative spectra are provided as supplementary data.

The 2DS could identify four bands for MB/RCM systems: at about 570 (*H*-aggregates), 675 (monomers), 765 (*J*-aggregates) and a small intensity band at 605-610 nm (Fig. 2b). The band with the maximum at 610 nm, which is attributed to *H*-dimers including the vibronic component of monomers, was not clearly detectable in the absorption spectra. Spectral changes with charge reduction were similar to those observed in the absorption spectra: The band assigned to the *H*-aggregates increased with the layer charge. An opposite trend was observed for the bands assigned to monomers and *H*-dimers, which increased with the charge reduction. Relatively higher intensities of bands of the H-dimers, monomers and J-aggregates were observed for the systems with lowest charge RCms.

After 24 hours, the 2DS of MB were significantly changed in some cases. In the case of the dispersions with low charge RCMs, rearrangement of the *H*-aggregates in favour of monomers, *H*-dimers and *J*-aggregates took place. The fraction of monomers and various types of the *H*-aggregates indicated by analysis of the spectra of the dispersions was increased with low charge RCMs. The 2DS of MB/N140 confirmed the presence of the dye in the forms of *H*-dimers (605 nm), monomers (575 nm) and *J*-aggregates (765 nm). A double band attributed to monomers in 2DS for MB/N140 indicates the presence of two types of this species (Fig. 2b). This interpretation is consistent with previous reports of two bands for MB monomers, having been assigned to those bound on the surface of clay particles or ones trapped between clay layers inside clay particle flocs [20].

3.2.4 Azine A and azine B aggregation

Cationic dyes Th, AzA, AzB and MB are structurally very similar; the only difference is the number of methyl groups bound to nitrogen atoms of amino-groups (Fig. 1). The amino-groups in MB cations are fully substituted with methyl groups. AzA and AzB contain two and three methyl groups, respectively, which are bound to amine nitrogen atoms in the structure,. Representative absorption spectra of AzA and AzB in the aqueous solutions and in reduced-charge montmorillonite colloidal dispersions are shown in Fig. 3a.

The trends in the absorption spectra of AzA and AzB in presence of RCMs were very similar to those observed for MB spectra: 1. *H*-Aggregates dominated in the colloids based on RCMs with highest charge densities. The positions of the *H*-aggregate bands were at lower wavelengths (near 550 nm). 2. With decreasing

layer charge, the fraction of *H*-aggregates decreased in favour of monomers and *J*-aggregates. *J*-aggregates of AzA and AzB, had maxima at 720 and 742 nm, respectively.

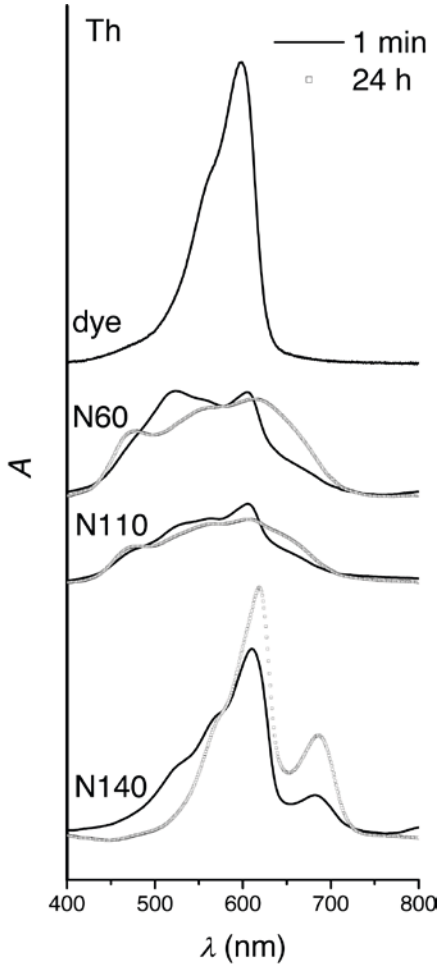

Figure 4. Absorption spectra of thionine/reduced-charge montmorillonite colloidal dispersions

The changes detected at 24 hours were similar to those observed for MB spectra. In the case of high charge RCMs, almost no changes were detected (not shown). The intensities of the bands assigned to monomers and *J*-aggregates gradually increased with the layer charge reduction. *J*-aggregates were predominantly formed on surfaces with low charge densities (*e.g.* N140).

No principal and only negligible differences in the trends with respect to MB spectra were observable using absorption spectroscopy for AzA and AzB systems. Spectra of AzA in the dispersions of RCMs exhibited broader bands (*e.g.* AzA monomers absorbing near 650 nm). AzA cations have one primary amino-group without any methyl substituents (similar to Th cation) and the second one is dimethylated (similar to MB cation). Therefore, the AzA cation exhibits an asymmetry with two non-equivalent amino-groups of different chemical properties. For example, the dimensions of the primary $-NH_2$ group, similar to ammonia or ammonium cations, allows its keying into the ditrigonal cavities of tetrahedral sheets of clay mineral layers [21]. The tertiary dimethyl amine group has lower reactivity than the non-substituted one. The asymmetry of the AzA cation may induce two different orientations of adsorption of the dye cations the surface either with the substituted or non-substituted amino-group of the molecule. The bands assigned to the *J*-aggregates absorbing at > 700 nm were also relatively broad and likely composed of two or more components (Fig. 3a). This trend can be explained in terms of the variation of possible assemblies due to the molecular asymmetry of the cations of this dye. For example, the *J*-dimer based on AzA cations can be formed from three possible assemblies by combining possible interactions of the molecules: 1. Head-to-tail interaction *via* the molecules' parts with non-substituted amino-groups. 2. Combination of the parts with substituted and non-substituted amino-groups. 3. Combination of the parts with dimethyl-substituted amino-groups. The spectra of both AzA and AzB did not significantly change in the case of high charge RCMs after 24 h. More significant changes were observed for the systems with lowest charge RCMs. The amount of monomers and the species absorbing at higher wavelengths, being assigned to the *J*-aggregates, increased significantly.

Second derivative spectroscopy was needed to identify the differences between the spectra of MB, AzA and AzB. The second derivative spectra of AzA/RCM dispersions (Fig. 3b) were significantly different from those of MB/RCM ones (Fig. 2b). For the fresh dispersions, the *H*-dimers were not clearly detected in the absorption spectra for almost any system. The *H*-aggregates were dominant in the dispersion of the highest charge RCM, N60. With the reduction of the layer charge, the bands of two types of monomeric species appeared in the spectra with minima around 635 and 665 nm. The 2DS was sensitive enough to resolve these species, which appeared as a single broad band in the absorption spectra. Concerning the fresh AzA/RCM dispersions, the presence of *J*-aggregates was only indicated for the lowest charge N140. Two types of *J*-aggregate species were observed in 2DS, which were detected only as a broad band in the absorption spectra. Various types of the species could be due to the molecular asymmetry of AzA, which introduces the possibility of variable interactions of the dye molecules at the clay mineral surface as discussed above.

The trends in the second derivative spectra of AzB/RCM dispersions were relatively similar to those of MB. The evolution of the bands assigned to the *H*-aggregates (550 nm) and monomers (655 nm) followed the changes of the layer charge. The high energy shoulder of the band assigned to monomers at about 640 nm indicates the presence of two monomeric species, similar to MB or AzA. The amount of *H*-dimers (600 nm) increased with the charge reduction. *J*-aggregates were not clearly identified for any fresh AzB/RCM colloidal dispersions. However, *J*-aggregates were formed in equilibrated systems of N130 and N140 (measured after 24 h). In the spectra measured after 24 h, similar amounts of *H*-aggregates were identified in the dispersions of high and medium charge RCMs, *e.g*. N60 and N110 (Fig. 3b). Significant amounts of the monomers, *H*-dimers and *J*-aggregates were only formed in the dispersions with lowest charge RCMs (*e.g*. N140).

3.2.5 Thionine aggregation

Absorption spectra of Th in presence of RCMs are shown in Fig. 4. Th is a cationic, phenothiazine dye structurally similar to MB, but having primary amino groups in place of the dimethyl amines of MB. Th cations in the form of aqueous solutions absorb light at lower wavelengths compared to MB (Fig. 2a, Table 2). However, the absorption spectra of Th in RCM dispersions shown in Fig. 4 are significantly different from those of MB for identical systems (Fig. 2a). Th aggregates absorbing at 521 nm were clearly detected only in the presence of N60. The intensity of this band in comparison with MB aggregates was much lower, suggesting that side-reactions may be taking place. Some of the Th cations seemed to remain in a monomeric form absorbing light at 605 nm even in the systems of relatively high charge RCMs (N110). The intensity of the monomeric band increased significantly with charge reduction. *J*-aggregate absorptions were detected at about 680 nm in the presence of low charge RCMs (Fig. 4).

Absorption spectra of Th measured after 24 h (Fig. 4) are significantly different from the spectra of other phenothiazine dyes. The spectral bands of Th are much broader, especially in the systems with high charge RCMs (N60-N110). A new band appeared with a maximal absorbance at 472 nm (Fig. 4), which is a significant spectral shift with respect to the band present in aqueous solution. In addition, very broad bands were hardly identified in the envelope of broad absorption with maxima approximately at 550 and 620 nm. These observations indicate that additional reaction(s) took place besides the molecular aggregation. We assume that the low wavelength band could be assigned to a new type of molecular aggregate or more likely (taking into account the structural difference between MB and Th, Fig. 1) to a non-specific product of Th decomposition. The decomposition of aromatic primary amines in clay mineral colloids is a relatively common phenomenon [23]. The high reactivity of Th is attributed to the presence of the primary -NH_2 groups. Radical species at nitrogen atoms are likely formed in these reactions as has been observed in numerous cases of other aromatic amines. For example, aromatic primary amines absorbing light in a UV region turn in clay mineral dispersions, due to radicals formation, to dark chromophores [23]. We assume that radical formation may initiate further series of reactions such as polymerization and other types of decomposition reactions. A remarkable property of the Th decomposition is the effect of the layer charge: High charge densities promoted the decomposition of the Th cations. On the other hand, non-decomposed dye remained in significant amounts in the dispersions with low charge RCMs (Fig. 4). The phenomenon of clay template-induced decomposition of Th or other dyes could be very important for environmental chemistry. Interestingly, the basic trends are the same as have been observed for some reactive cyanine dyes [24]. There is no evidence of similar reactions taking place in the case of AzA, which has only one non-substituted amino-group.

3.2.6 Pyronin G aggregation

The main difference between the molecular structure of phenothiazine dyes and Pyr is the structure of heteroaromatic skeleton. There is only one heteroatom, oxygen, in an aromatic ring of the Pyr cation (Fig. 1), whereby MB cation contains nitrogen and sulphur atoms. Absorption spectra of Pyr measured 1 minute after mixing the RCM colloidal dispersion and solution of the dye are shown in Fig. 5a. The spectrum of Pyr in the presence of N60 shows a band at 475 nm assigned to *H*-aggregates. The intensity of this band gradually decreased with reduction of the layer charge in favour of a band at 550 nm, assigned to the absorption of monomers. Only small shoulders from *H*-aggregates were observed in the presence of the sample with the lowest charge (Fig. 5a). A small band was detected at approximately 510 nm for the Pyr/N110 system, probably related to *H*-dimers. The intensity of this band increased with the layer charge reduction.

There are remarkable differences between the spectra of MB and Pyr, measured for identical RCM dispersions. Generally, there are fewer molecular aggregates of Pyr in the RCM dispersions. Although

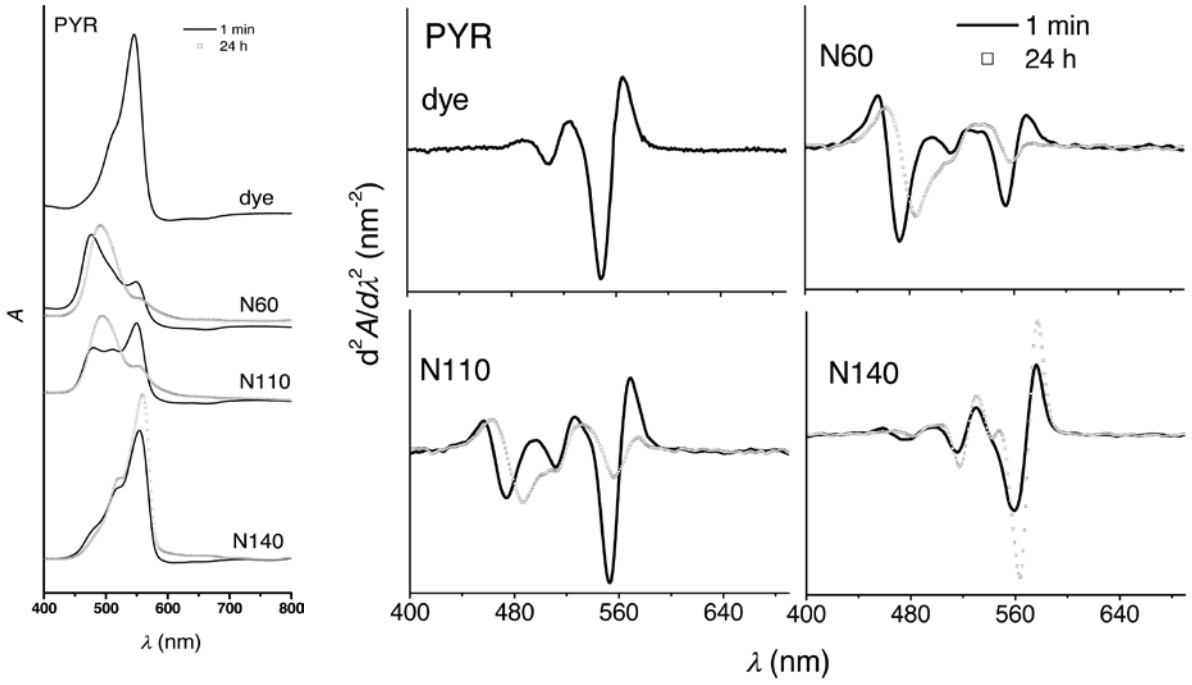

Figure 5. a) Absorption spectra of pyronin G/reduced-charge montmorillonite colloidal dispersions; b) Second-derivative spectra of pyronin G/reduced-charge montmorillonite colloidal dispersions

N60 induced an extensive molecular aggregation of Pyr, relatively large amounts of Pyr monomers were present in N110 dispersions. The sample of the lowest charge N140 was predominantly occupied with adsorbed Pyr monomers. In contrast, identical systems with MB measured under the identical conditions contained almost equal amounts of monomers and *H*-aggregates (Fig. 2a).

Another difference is the absence of Pyr *J*-aggregates, which were not detected even in equilibrated systems measured after 24 h. Hence the presence of *J*-aggregates might be the result of the properties of the phenothiazine skeleton. Spectra of Pyr measured 24 hours after mixing the components are different from those obtained for fresh dispersions (Fig. 5a). The Band assigned to the *H*-aggregates was shifted from 475 to longer wavelengths and its absorbance increased with time for high-charge RCMs. Additionally, the amount of monomer decreased with time in such cases (see Pyr/N110 spectrum in Fig. 5a), which is opposite to the trend observed for MB or other phenothiazine dyes. These changes with time have been also observed for other xanthene dyes and rhodamines [11,18]. The band attributed to monomeric species gradually increased for the systems based on RCMs with the lowest charge (Fig. 5a). In general, the difference between the molecular aggregation of phenothiazine dyes and Pyr could be explained in terms of the structures of the heteroaromatic skeletons of these dyes. Greater hydrophobicity of Pyr cations is expected due to the presence of only one heteroatom in the aromatic rings, whereas the presence of nitrogen and sulphur atoms contributes to polar interactions between neighbouring cations in molecular assemblies.

The second derivative spectra of Pyr/RCMs are significantly different from those of phenothiazine dyes. There were no *J*-aggregates identified neither in fresh nor in equilibrated colloidal dispersions of RCMs (Fig. 5b). In the fresh dispersions, the *H*-aggregates (470 nm), *H*-dimers (511 nm) and monomers (553 nm) were clearly identified (Fig. 5b). The fraction of the *H*-aggregates decreased with the layer charge reduction in favour of monomers and *H*-dimers. Additionally, a slight shift to higher wavelengths with charge reduction was observed for the bands assigned to monomers and *H*-dimers. After 24 h, basic features of the spectra remain the same. The fraction of the *H*-aggregates decreased with the charge reduction, but less significantly than in the fresh dispersions. The fraction of the *H*-dimers and monomers was much higher in the dispersions of the lowest charge, *e.g.* N140 (Fig. 5b).

The ratios of the amplitudes of the bands assigned to monomeric forms (I_{mon}) and the *H*-aggregates (I_{agg}) were calculated from second-derivative spectra to estimate semi-quantitatively the relationship between layer charge and the molecular aggregation of the dyes. The

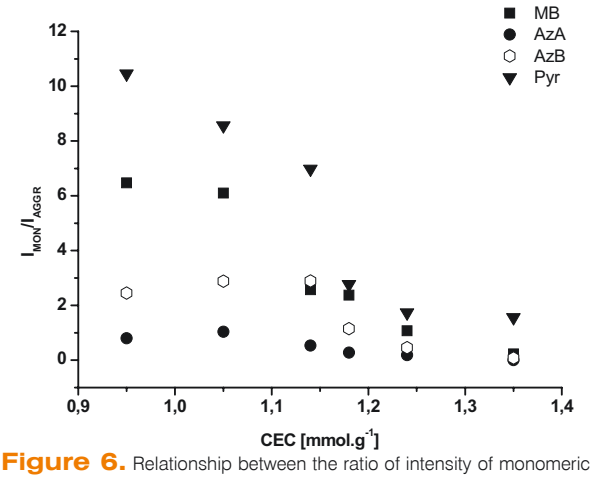

Figure 6. Relationship between the ratio of intensity of monomeric forms and intensity of H-aggregates calculated from second derivative spectra and cation exchange capacities of reduced-charge montmorillonites.

functional dependence between I_{mon}/I_{agg} ratios and cation exchange capacities of reduced-charge montmorillonites is shown in Fig. 6. The absolute values of the second derivative curves are linearly proportional to the amount of the analyte according to Lambert–Beer law [17].

It is obvious that the amount of *H*-aggregates gradually increased with the CEC values of smectites. Pyr cations tend to form the lowest amount of monomers. The ratio I_{mon}/I_{agg} was higher if compared to phenothiazine dyes. The ratio gradually decreased in order Pyr, MB, AzB, AzA, Th, especially for the RCMs of low layer charge. This trend could be assigned to the effect of the presence of bulky methyl substituents, which may prevent close sandwich-type interaction between dye chromophores. For Pyr, slow formation of the *H*-aggregates, which are in some cases formed after longer reaction times, contributes to higher amounts of monomers (Fig. 6).

The measurement of dye spectra in the presence of smectite suspension for characterization of layer charge density does not provide quantitative information on the layer charge of clay minerals, because molecular aggregate formation is a very complex process. The relationship (I_{mon}/I_{agg}) *vs*. CEC provides qualitative aspects of the correlation between the CEC and the amounts of monomers and *H*-aggregates. Various species of monomers and *H*-aggregates with different spectral properties can be formed depending on the chemical environment (interlayers, external surface, and particle edges). The spectral characteristics of *H*-aggregates depend very sensitively on the number of dye cations forming the molecular assembly and its specific structural aspects.

4. Conclusions

1. Methylene blue cation is a valuable analytical tool for fast, qualitative characterisation of the layer charge density of smectites. The distribution of the layer charge controls the distances between adsorbed dye cations. It was found out that reduced-charge montmorillonites with high layer charge induced the formation of *H*-aggregates, because of the short distances between adsorbed dye cations. The middle charge smectites were characterised by approximately equal formation of *H*-aggregates and monomers. Low charge smectite surface induced formation of the monomers, due to the longer distances between adsorbed dye cations.
2. Cationic dyes azure A and azure B are structurally very similar to methylene blue, differing only in the number of methyl substituents present on the exocyclic amines. The trends in absorption spectra of these dyes in the presence of reduced charge montmorillonites were similar to those of methylene blue. More significant differences were observed for the systems with azure A, probably because of the non-symmetrical molecular structure of this dye.
3. The difference of thionine molecular structure is related to the absence of methyl substituents bound to the nitrogen atoms of amino-groups. This difference was evident also on the absorption spectra in presence of smectite colloidal dispersions. Differences between MB and Th spectra were observed mainly for the colloids of high charge specimens. Th probably partially decomposed on the surfaces of high charge silicates, due to the presence of $-NH_2$ groups.
4. Pyronin G and MB have different heterocyclic aromatic skeletons. Pyronin demonstrated an increase in the amount of the molecular aggregates with the layer charge. However, the spectral changes with time and sensitivity of molecular aggregation to layer charge was minimally different from the trends observed with phenothiazine dyes. More Pyr monomers were present in the colloids compared to identical systems with phenothiazine dyes.

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