

Molecular modeling of surface modification of Wyoming and Cheto montmorillonite by methylene blue

Petr Kovář · Miroslav Pospíšil · Petr Malý ·
Zdeněk Klika · Pavla Čapková · Petra Horáková ·
Marta Valášková

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Abstract The surface area of various types of montmorillonites (MMT) with different values of layer charge plays a very important role in surface arrangement of methylene blue cations (MB). Photoluminescence measurements can be strongly or partially influenced by this surface arrangement of cations. For these reasons and on the basis of our previous results, molecular simulations were performed for various types of montmorillonites covered with methylene blue cations. Adsorption of methylene blue cations on Na-Wyoming MMT surface is different from Ca-Cheto MMT. In the case of Wyoming with a lower layer charge, MB cations lie parallel to the silicate layer for all investigated samples. On the other hand, Cheto surface is covered with a higher amount of MB cations. The results obtained from molecular modeling indicate that MB lies parallel to low loading case and become tilted with respect to layer for a higher loading. Moreover, a higher amount of MB cations covering the silicate layer are much less energy-stable. A higher loading of MB cations leads to aggregates but at low loading MB cations degrade to monomers.

Keywords Intercalation · Methylene blue · Surface · Molecular simulations · Montmorillonite · Sorption

Introduction

The techniques of molecular mechanics and classical molecular dynamics have been intensely used to study the interlayer arrangement of species in layer silicates, both cations (Keggin, ammonium, dyes) and neutral molecules (different types of amine). A review about this type of structure analysis using molecular simulations was given by Čapková *et al.* [1]. This technique is very useful for studying the arrangement of organic molecules on the surface of layer silicates because different arrangements with respect to the minimum energy can be studied. The disadvantages of molecular simulations are usually the simplification of the modeled structure, difficulty in obtaining correct description of energy potential, and difficulty in finding an adequate method for validation of calculated and experimental results. On the other hand, the advantages include: (i) detailed description of the probable structural arrangement, (ii) understanding of mutual interactions, (iii) better and more precise explanation of experimental results.

Klika *et al.* [2] gave a detailed description of preparation and many related experimental results of methylene blue cations intercalated into two different types of montmorillonites (Na-Wyoming and Ca-Cheto) together with molecular modeling of interlayer space of these intercalates. A lot of works focused on studying the arrangement and position of methylene blue cations [3] and other organic dyes [4, 5] with respect to various silicate layers [6] in the interlayer and on the surface. We focused directly on studying MB interactions within the interlayer or surface for different types of silicates in solid, colloid or liquid

P. Kovář (✉) · M. Pospíšil · P. Malý
Charles University in Prague,
Faculty of Mathematics and Physics,
Ke Karlovu 3,
121 16 Prague, Czech Republic
e-mail: kovar@karlov.mff.cuni.cz

Z. Klika · P. Čapková · P. Horáková · M. Valášková
VŠB-Technical University Ostrava,
708 33 Ostrava-Poruba, Czech Republic

states. Various influences impacting MB arrangements were studied like the effect of various exchangeable cations [7], layer charge density of smectites [8, 9] or ageing [10] mentioned in previous work [6].

Let's investigate the influence of the layer charge on MB arrangement. It has been confirmed by experimental measurements that MB cations form aggregates in case of higher layer charge and mutual distances between MB are short. On the other hand, layers with low layer charge with active sites far between each other result in longer distances between MB cations, which suppress the aggregation. The position of layer charge in octahedral or in tetrahedral sheets plays an important role in MB arrangement. Tetrahedral charge is not able to aggregate MB cations due to repulsions in contrast to octahedral charge, which allows the agglomeration of MB on the silicate surface [9].

In the present work we calculated the arrangement of different amounts of methylene blue cations on the surface of Wyoming and Cheto MMT reported earlier by Klika *et al.* [2]. Various types of structural arrangement could better explain the influence on photoluminescence properties of intercalates. We also compare our results with previous predictions concerning MB positions on MMT surface derived from experimental results and stoichiometry presumptions. There is a number of publications describing measurements of methylene blue cations on silicate surfaces in colloid liquids and predicting the existence of a silicate monolayer with adsorbed methylene blue cations. On their basis we calculate models with a specific amount of water molecules to compare them with the ones without presence of water molecules.

Experimental

Na-montmorillonite SWy-2 (Na-SWy) and Ca-montmorillonite SAz-2 (Ca-Cheto) samples were used as the hosts for the intercalation and sorption with methylene blue cations (MB). The first sample is from Wyoming, USA, the second one from Arizona, USA. The preparation and measurement of samples is described in detail in our previous work [2]. For this reason we focus directly on the description of the molecular modeling strategy used.

Table 1 Energy characteristics of SWy montmorillonite at various loading of MB cations

Loading/%	$E_{total}/\text{kcal/mol}$	$vdW/\text{kcal/mol}$	$elst/\text{kcal/mol}$
25	-209	-34	-175
50	-236	-86	-150
75	-263	-122	-141
100	-288	-175	-113

Table 2 Effect of water at different loading of MB cations on the surface of SWy montmorillonite

Loading/%	$E_{total}/\text{kcal/mol}$	$vdW/\text{kcal/mol}$	$elst/\text{kcal/mol}$
25	-460	-124	-335
50	-507	-173	-334
75	-495	-224	-270
100	-304	-182	-121

Modeling strategy

The initial model of the surface structure was built in Surface builder in *Cerius²* modeling environment [11]. The constructing of the host framework was done according to the following structure data published in [12, 13]: $a=5.208 \text{ \AA}$, $b=9.020 \text{ \AA}$. We created a $3a \times 4b$ two-dimensional supercell with the following dimensions: $A=15.624 \text{ \AA}$, $B=36.080 \text{ \AA}$. The composition of the layer was: $(\text{Al}_{36} \text{Mg}_6 \text{Fe}_6^{3+})(\text{Si}_{94} \text{Al}_2)\text{O}_{240}(\text{OH})_{48}$ with the layer charge of -8 el for Swy montmorillonite and $(\text{Al}_{34} \text{Mg}_{12} \text{Fe}_2^{3+})(\text{Si}_{94} \text{Al}_2)\text{O}_{240}(\text{OH})_{48}$ with the layer charge of -14 el for Cheto montmorillonite, respectively. Methylene blue (MB) as a cation with the charge of +1 was placed on the host surface. The model consisted of the host layer, one adjacent surface guest layer, and of the sheet layer of charge balancing cations on the opposite site of the surface. In the case of modeling of fully exchanged montmorillonite, the surface guest layer contained four MB cations for Wyoming and 7 MB cations for Cheto. In the case of partially exchanged montmorillonite the charge compensating cations (Na^+ or Ca^{2+}) were placed on the upper side of the host supercell between MB cations. We built a set of initial models with various loadings of methylene blue cations on the surface and with various positions of methylene blue cations with respect to the host surface layer and with respect to each other. The effect of water on the arrangement of the guests and on the energy was simulated by adding 42 water molecules above the guest layer.

The modeling of the molecular mechanics and of the classical molecular dynamics was performed in *Cerius²* and *Materials Studio* modeling environment [11, 14]. Universal

Table 3 Energy characteristics of Cheto montmorillonite at various loading of MB cations

Loading/%	$E_{total}/\text{kcal/mol}$	$vdW/\text{kcal/mol}$	$elst/\text{kcal/mol}$
14	-658	-29	-629
43	-660	-96	-564
71	-640	-191	-449
100	-570	-271	-299

Table 4 Effect of water at different loading of MB cations on the surface of Cheto montmorillonite

Loading/%	E_{total} /kcal/mol	vdW /kcal/mol	$elst$ /kcal/mol
14	-1021	-112	-909
43	-955	-207	-748
71	-769	-277	-492
100	-733	-364	-369

field of force was used to describe the potential energy of the models [15]. During energy minimization the host layers and the sheet layer of charge-balancing cations were kept fixed. Charges were calculated by Gasteiger method [16]. All atoms of the surface guest layer with cations were variable. After energy minimization, molecular dynamics simulations were carried out. The quench dynamics was simulated using the NVT statistical ensemble (constant number of atoms, volume and temperature) at 300 K. In quench dynamics, periods of dynamics simulations are followed by a quench period, in which the model is minimized (in our case 100 steps of dynamics between quenches and 500 steps of minimization in quenches). The dynamics time step was set up to 0.001 ps. The silicate layers were kept frozen (fixed) during the dynamics simulations and the total length of the dynamics trajectory was 50 ps.

Results and discussion

The results of molecular simulations are summarized in Tables 1, 2, 3, 4. Tables 1 and 3 describe energy characteristics of the models with varying loading of MB cations on the host surfaces. The tables show total sublimation energy (E_{total}) and its components - electrostatic energy ($elst$) and van der Waals energy contributions (vdW). The effect of water on the surface is summarized in Tables 2 and 4.

Wyoming Montmorillonite covered with different amounts of methylene blue cations

Table 1 shows the energy characteristics for 25%, 50%, 75%, and 100% loading of MB cations on the host surface of SWy-montmorillonite. We can see that the total sublimation energy decreases with the increasing loading of MB cations. The increasing loading of the guests leads to a rapid decrease of the values of van der Waals energy contributions; on the other hand the increasing guest loading leads to the slow increase of the value of electrostatic energy contributions and in the case of the full cation exchange the value of van der Waals contribution is a dominant component in the total sublimation energy. As shown in Table 1, the total sublimation energy has no local minimum with respect to the guest loading, so the charge balancing cations on the host surface of Wyoming montmorillonite can be exchanged for MB cations up to 100%. Figure 1 shows the top view of the arrangement of

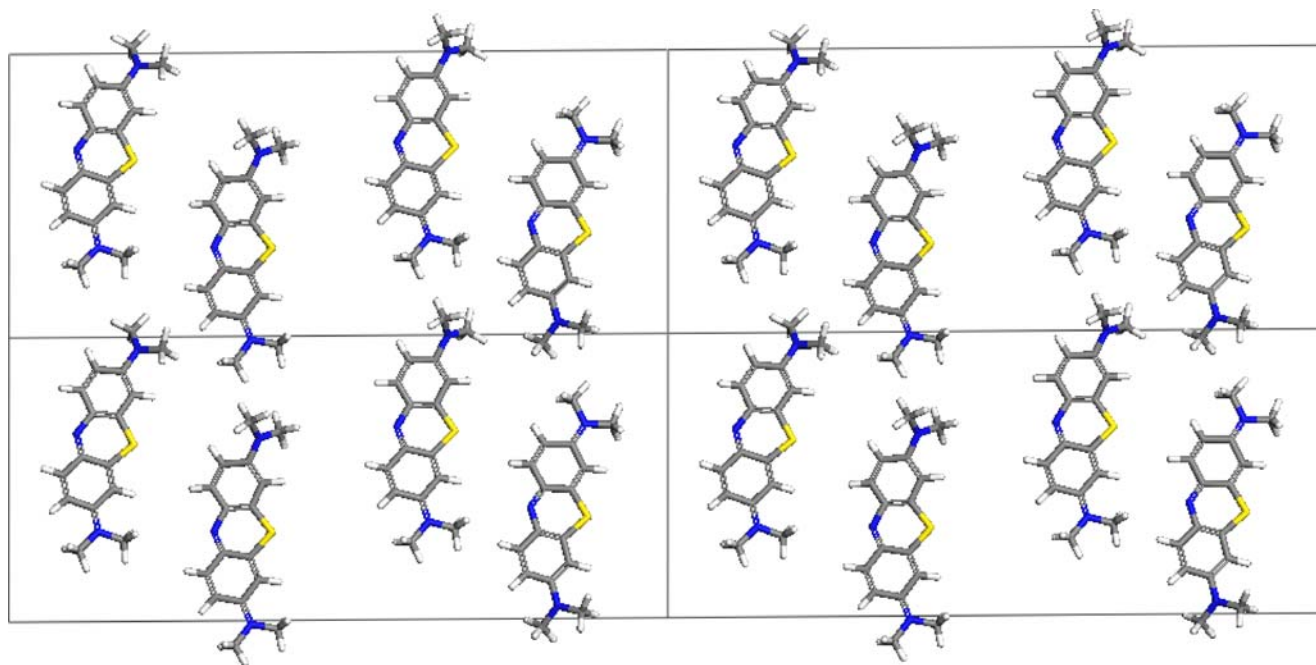
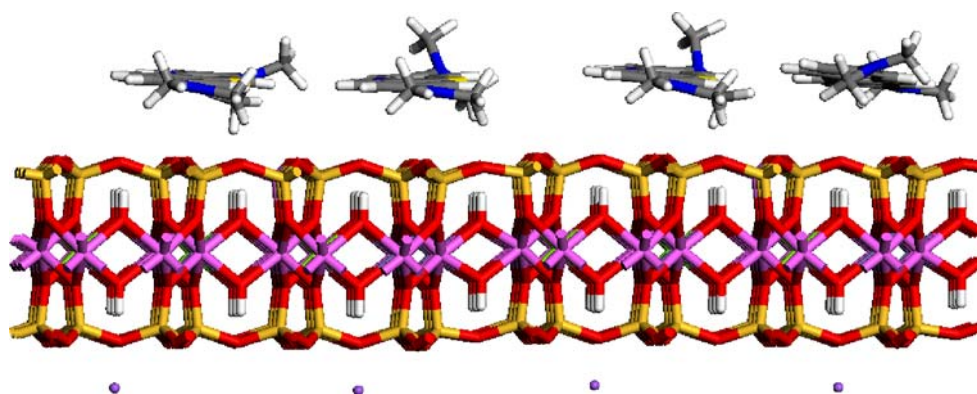


Fig. 1 Top view on the arrangement at 100% loading of MB cations on the host surface of SWy montmorillonite

Fig. 2 Side view on the arrangement at 100% loading of MB cations on the surface of SWy montmorillonite

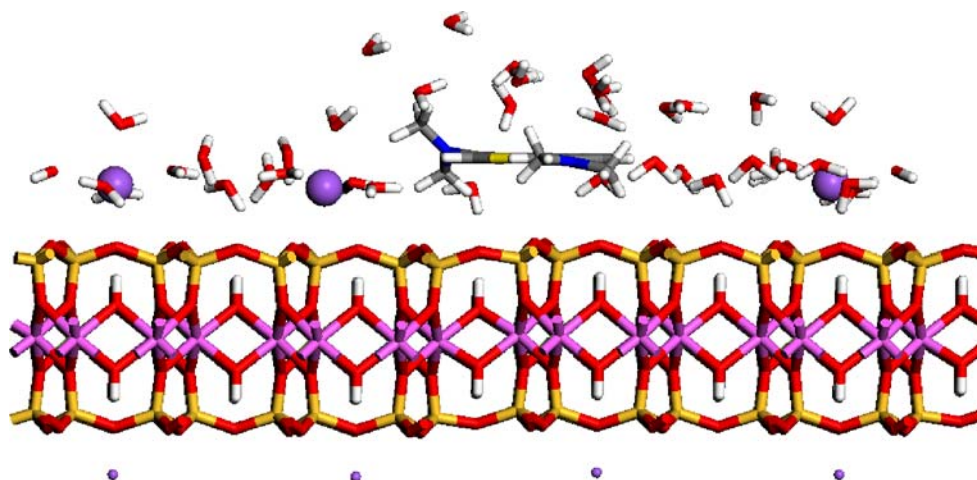


MB cations on the fully exchanged surface. In this case, MB cations form a dimeric-like arrangement as the one with the lowest total sublimation energy. The calculations showed a very similar value for the monomer arrangement of the guests; therefore both of these arrangements can be expected in the real sample.

Figure 2 shows a side view of the fully exchanged sample. Since the charge of the surface layer of Wyoming montmorillonite is much lower (-8 e) than in the case of Cheto montmorillonite (-14 e) the guests are able to adopt a parallel arrangement with respect to the host surface even in the case of full exchange, which can be important for the observed photoluminescence properties.

The simulations showed a significant influence of water in the sample. The results are summarized in Table 2. It can be seen that in all cases water stabilizes the structure that is accompanied by a significant decrease of the total sublimation energy with respect to the values of the total sublimation energy presented in Table 1. The highest decrease of the energy occurs in the case of 25% and 50% exchange and, due to relatively low loading of MB cations, most of the water molecules tend to form a monolayer arrangement with respect to the host surface as can be seen in Fig. 3. In the case of 75% and 100% exchange the decrease of the total sublimation energy is lower than in the previous cases

Fig. 3 Side view on the model with 25% loading of MB cations and water molecules on the host surface of SWy montmorillonite



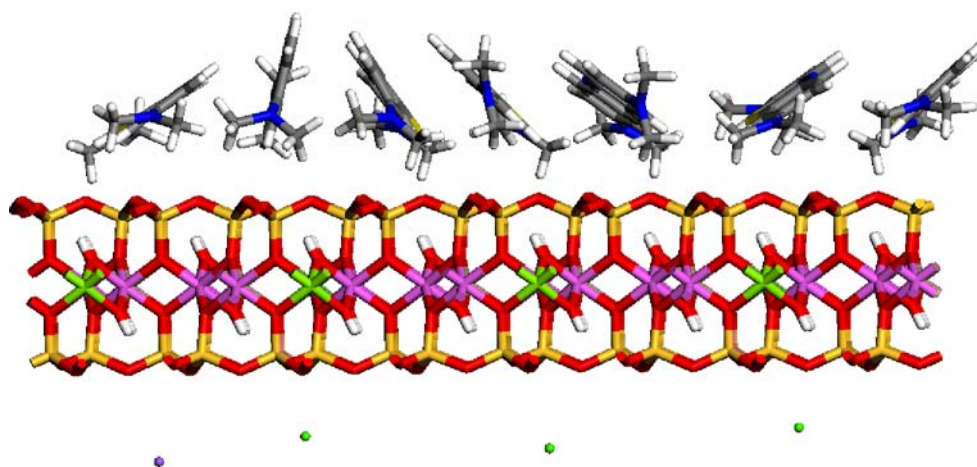
because the hydrophobic guest layer covers the majority of the host surface. In general, surface water has no influence on mutual orientation of the guests or on their orientation with respect to the host surface.

Cheto Montmorillonite covered with different amounts of methylene blue cations

The results for Cheto montmorillonite are summarized in Table 3. It shows energy characteristics for 14%, 43%, 71%, and 100% loading of MB cations. In comparison to Table 1 we can see that Cheto montmorillonite shows the following differences:

- 1/ The total sublimation energy reaches its lowest value in the case of 14% and 42% cationic exchange and both these models also show very similar sublimation energies. Higher loading of the guests leads to an increase of the total sublimation energy indicating that in comparison to Wyoming the guest anions prefer to be accommodated on the host surface in a lower loading. On the other hand, the increasing loading of the guests leads to their tilted orientation with respect to the host surface. In the case when 5 MB cations are accommodated on the host surface we still obtain their

Fig. 4 Side view of the tilted orientation of 100% loading of MB cations on the surface of SAz montmorillonite



parallel arrangement, but in the case of a higher loading the orientation of the guests becomes tilted as can be seen in Fig. 4.

- 2/ Due to a higher layer charge in the case of Cheto montmorillonite electrostatic contributions are dominant in comparison to Wyoming where in the case of full cationic exchange the electrostatic contribution is lower in comparison to the van der Waals contribution. The effect of high loading accompanied by the tilted orientation and stronger electrostatic interactions in comparison to SWy montmorillonite results in differences between the optical properties of these two samples and causes quenching of photoluminescence.

Moreover, the models of Cheto montmorillonite exhibit very different repulsive interactions between the species in the guest layer (interactions between MB cations and the charge-balancing cations). Repulsive interactions in the guest layer for Cheto are 457 ± 30 kcal mol⁻¹, whereas for Wyoming montmorillonite the value is 138 ± 5 kcal mol⁻¹. The big difference between the interactions is due to the

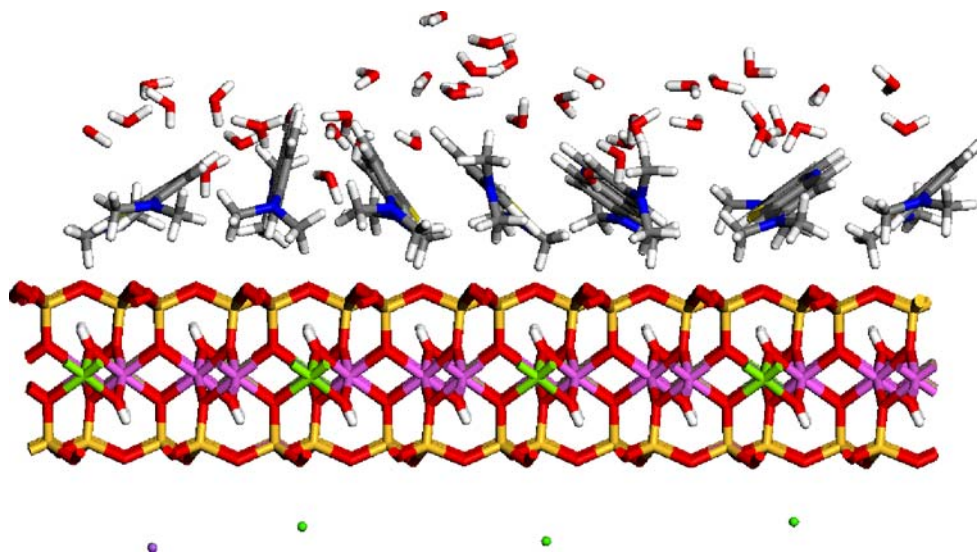
existence of different charge-balancing cations in the guest layer (Ca^{2+} in case of Cheto and Na^+ for Wyoming) and in the case of fully exchanged models due to the high loading of guests in Cheto. This difference between the interactions can also contribute to the explanation of the observed difference in photoluminescence properties [2].

The effect of water is similar as in the case of Wyoming, i.e., the decreasing of the absolute value of energy contributions with increasing intensity of the guests. The effects of surface water on the energy characteristics are summarized in Table 4. Figure 5 shows a side view of a fully exchanged sample where the majority of water molecules are located above the hydrophobic guest layer.

Conclusions

Two different types of MMT were investigated with respect to MB sorption. A different behavior depending on the layer charge of MMT was observed. In the case of lower

Fig. 5 Side view of the tilted orientation of 100% loading of MB cations on the surface of SAz montmorillonite and water molecules



amounts of adsorbed MB cations, the cations lie parallel with respect to the silicate layer for both types of MMT. In the case of Wyoming the charge value is not sufficient to obtain a tilted arrangement of the guests. We can conclude that due to lower value of charge the MB arrangement is always parallel and this investigated type of Wyoming MMT surface is covered just by a monolayer of guests with are oriented parallel to the surface. The parallel orientation of MB noticeably contributes to the photoluminescence of the samples. On the other hand, we obtained models of Cheto montmorillonite with parallel arrangement for a low loading of MB and a tilted irregular arrangement for a high sorption of MB on the silicate layer. A low photoluminescence value was detected for low MB sorption and it can be partially compared to MB arrangement in the case of Wyoming MMT. High sorption of MB cations and mutual interactions between the species strongly influences the photoluminescence and leads to its complete quenching. In this case MB has longitudinal axes parallel to the silicate layer but the transverse axis is tilted. This irregular arrangement completely quenches photoluminescence and strongly confirms the experimental measured values. It can be concluded that not only the interlayer space is important for increasing and quenching of the photoluminescence but also the surface arrangement can influence the photoluminescence results [2].

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