Interlayer Expansion and Mechanisms of Anion Sorption of Na-montmorillonite Modified by Cetylpyridinium Chloride: A Monte Carlo Study

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To study the change of interlayer structure of a Wyoming-type Na-montmorillonite as a result of the replacement of interlayer Na^+ ions by cetylpyridinium (CP^+) ions, a series of NPT Monte Carlo simulations of the clay mineral with different contents of CP^+, Na^+, Cl^- ions and water in its interlayer space is carried out. In agreement with conclusions from experimental studies, the simulations show that the CP^+ ions form monomolecular, bimolecular, and pseudotrimolecular layers with increasing interlayer contents. Calculated potential energies reveal that clay−organic interactions are stronger than organic−organic interactions in CP^+-modified montmorillonite, which is in conformity with observations of earlier thermogravimetric experiments. The simulation results indicate that the pseudotrimolecular arrangement of CP^+ ions is a prerequisite for the experimentally observed interlayer sorption of inorganic anions. Furthermore, in the interlayer space with a pseudotrimolecular layer, chloride ions favor the formation of pairs with inorganic rather than organic cations. On the basis of these findings and available experimental data, we propose that the interlayer sorption of inorganic anions from the pore space of an organically modified montmorillonite may occur not only in pairs with organic cations, as suggested earlier, but also in pairs with inorganic cations, which represents a so-far unconsidered and maybe more important mechanism of anion sorption on clay minerals.

1. Introduction

Montmorillonite is a naturally occurring clay mineral characterized by relatively low negative charge of its aluminosilicate layers as a consequence of tetrahedral substitutions of Si by Al in two tetrahedral sheets and octahedral substitutions of Al by Mg in a central octahedral sheet. This negative charge is compensated by inorganic cations in the interlayer spaces between neighboring mineral layers. The interlayer space thickness can vary depending on the interlayer content. This thickness plus the constant thickness of one mineral layer represent the layer spacing of a montmorillonite. Extensive experimental studies[1−6] of montmorillonite modifications by cetylpyridinium (CP^+) or cetyltrimethylammonium (CTA^+) ions have shown that their uptake in the interlayer spaces occurs as a result of two mechanisms: (1) exchange of interlayer inorganic cations and (2) uptake in the form of an "organic cation−inorganic anion" (e.g. I^-, Br^-, or Cl^-) pair. As a result of the second mechanism, the total amount of the interlayer organic cations can even exceed the cation exchange capacity (CEC) of the natural clay mineral.[1,2,4,5] With increasing concentration, the CP^+ and CTA^+ ions build monomolecular, bimolecular, and pseudotrimolecular layers in the interlayer space of a montmorillonite, as deduced in experimental studies[1,5,7,8] on the basis of considerations of the van der Waals dimensions of these cations, the charge distribution in mineral layers, and the observed values of layer spacing. It was suggested by Lagaly[8] that in case of the pseudotrimolecular arrangement of the interlayer organic cations, their headgroups are actually located in the two molecular layers covering the mineral surface, whereas their chains bend in such a way that they build a third molecular layer between the first two layers. The layer spacing

of a montmorillonite changes according to the increasing interlayer content of CP^+ ions and assumes values of ∼14.4 Å, ∼17.9 Å, and ∼21.8 Å for the monomolecular, bimolecular, and pseudotrimolecular arrangement, respectively.[1,4] Contrary to montmorillonite, in vermiculite, a clay mineral with a similar structure but a higher negative charge of aluminosilicate layers, a paraffin-like arrangement of CP^+ ions with the chains directed upright from the mineral surface is favored.[9] The layer spacing amounts to ∼30−50 Å in this case.[3,9,10]

Experimental studies[1,4] have also shown that an interlayer uptake of CP^+ ions by a Na-montmorillonite in amounts above 100% of its CEC does not lead to a complete exchange of all Na^+ cations, but an amount equivalent to ∼30% CEC still remains in the interlayer spaces. After the CP^+ uptake, the organic and inorganic cations are located in the same interlayer spaces of a montmorillonite particle and no demixing into organically modified and nonmodified interlayer spaces occurs.[3,5] During the CP^+ uptake, interlayer inorganic cations together with their hydration shells are replaced by organic cations, so that the interlayer water content decreases. However, water molecules, which hydrate inorganic cations and/or mineral layers in a natural montmorillonite, are not completely removed from the interlayer space of an organically modified montmorillonite.[2,4−7,10] After a CP^+ uptake to 100% CEC, the water contribution to the total weight of a montmorillonite amounts to ∼2%.[4,10] The structure of interlayer water and its function in an organically modified montmorillonite are as yet largely unknown.[5] Furthermore, the location and the hydration state of inorganic ions as well as the arrangement of organic cations in the interlayer space of an organically modified montmorillonite have not been determined experimentally yet because of the low crystallinity of a montmorillonite preventing an extensive

TABLE 1: Partial Atomic Charges for the Pyridinium Ring (C$_5$H$_5$N), the First Methylene Group (α-CH$_2$), and the Remaining Chain Groups (C$_{15}$H$_{31}$) of the CP$^+$ Ion

	N (C$_5$H$_5$N)	C (C$_5$H$_5$N)	H (C$_5$H$_5$N)	C (α-CH$_2$)	H (α-CH$_2$)	C (C$_{15}$H$_{31}$)	H (C$_{15}$H$_{31}$)
total	−0.13	0.38	0.37	0.11	0.12	0.23	−0.08
(*min, max*) charge		(0.02, 0.12)	(0.07, 0.08)		(0.06, 0.06)	(−0.01, 0.02)	(−0.01, 0.02)

study of its interlayer structure by experimental methods.[11] Hence, the application of molecular simulations was stimulated to study this complex system.

Pospíšil et al.[12] have simulated CP$^+$- and CTA$^+$-saturated montmorillonites in the dehydrated state, applying a combination of the energy minimization and the NVE molecular dynamics methods. Methyl-, methylene-, and headgroups of the organic cations were represented as single interaction points in this study. Contrary to the interpretations of experimental studies,[1−8] Pospíšil et al. have concluded that the CP$^+$ and CTA$^+$ ions have a monomolecular interlayer arrangement at the simulated layer spacings of ∼20.6 Å and ∼18.1 Å, respectively. Using a similar approach for the representation of organic cations, Hackett et al.[13] have carried out the NVT molecular dynamics simulation of a dehydrated montmorillonite saturated with hexadecylammonium cations. They suggest a monomolecular arrangement at the preset layer spacing of ∼15.5 Å, which agrees well with the experiments.[1−8] The agreement of the relation between the type of simulated arrangement and the preset values of the layer spacing with experimental suggestions has also been reported by He et al.[14] in their NVT molecular dynamics study of a dehydrated, CTA$^+$-saturated montmorillonite. Still, an important drawback of the application of simulations in the NVT ensemble for the study of the experimentally observed expansion of montmorillonite is that in this ensemble the layer spacing of the simulated system cannot accommodate to the interlayer content. The situation is very different in the real system, where such an accommodation actually takes place.[6] Therefore, the correspondence between the simulator-guessed value of the layer spacing and the simulator-assumed interlayer content is highly questionable. A guess of the value of the layer spacing based on an experimental value does not really help in this case, as generally only the contents of the major interlayer species are reported experimentally, so that some simplifying assumptions about the interlayer chemical composition should be made in a simulation (as was also made in the studies of refs 12−14). The use of the NPT ensemble instead eliminates such a drawback and can be considered as the most appropriate one for studies of montmorillonite expansion. Zeng et al.[15] have carried out a NPT molecular dynamics study of dehydrated, CTA$^+$-saturated montmorillonites with different layer charges. In support of experimental observations, these simulations have shown that CTA$^+$ ions form monomolecular or bimolecular interlayer arrangements in low-charge or medium- and high-charge montmorillonites, respectively.

Differently from previous simulation studies, we consider a montmorillonite, which contains not only organic cations but also inorganic ions and water in the interlayer space. Such an interlayer coexistence of organic and inorganic ions and water seems to be the common case following the experimental studies,[1−7,10] rather than the case with only organic cations in the interlayer space of a montmorillonite, which should be referred to as a hypothetical case. Furthermore, the experimental equilibration during the organic modification of a montmorillonite takes at least 16 h and up to 5 days.[1−8] Since the application of the molecular dynamics method to the studied system is restricted to one nanosecond,[12−15] we have chosen to

use the Monte Carlo method instead in our study. As only limited information is available as yet about the interlayer structure and properties of such a mixed system, our study aims at improving the knowledge about it and suggesting possible mechanisms of the interlayer sorption of inorganic anions observed in experimental studies with this system. For this purpose, we have carried out a series of isothermal−isobaric Monte Carlo simulations of a Wyoming-type montmorillonite with varying interlayer contents of CP$^+$, Na$^+$, Cl$^-$ ions and water molecules utilizing the OPLS-AA force field[16] and the TIP4P water model[17] as described in the next section.

2. Simulation Details

To model a montmorillonite particle, three-dimensional periodic boundary conditions were applied to a simulation box composed of 20 unit cells, having horizontal dimensions of ∼26 Å by ∼36 Å and representing halves of two montmorillonite layers with an interlayer space in between. The unit cell of a simulated CP$^+$- or CPCl-modified Wyoming-type Na-montmorillonite has the formula X$_y$(Si$_{7.9}$Al$_{0.1}$)(Al$_{3.1}$Fe$^{3+}_{0.4}$Mg$_{0.5}$)O$_{20}$-(OH)$_4$, where X$_y$≡Na$_{k/20}$CP$_{l/20}$Cl$_{m/20}$ with $k\in[3,11]$, $l\in[1,13]$, $m\in[0,4]$ in a total of 13 simulation runs. The numbers k, l, and m satisfy the condition $k + l - m = 12$ in each simulation run, ensuring that the total interlayer charge compensates the total mineral layer charge ($-12e$) in the simulation box. Thus the l-values of, for example, 6 and 12 correspond to the interlayer CP$^+$ contents of 50 and 100% CEC, respectively. The number of water molecules in the simulation box decreases in steps of 10 from 80 (for $k = 11$) to 20 (for $k = 5$), whereas for $k < 5$ it is defined as $3k$, if $m = 0$, or $(k + m)2$, if $m > 0$. The resulting water content of the montmorillonites, modified by CP$^+$ ions from 50 up to 108% CEC, varies in the range between 3.1 and 1.0 mass percents, in agreement with the experimental values.[4,10] Coordinates of layer atoms were calculated according to the method of Smoliar-Zviagina.[18] The planes of octahedral substitutions were on the external, upper, and lower sides of the simulation box.[19] Two tetrahedral substitutions were positioned in the two opposite mineral half-layers according to the requirement of a uniform distribution of tetrahedral substitutions in the modeled particle. Charges arising due to substitutions were delocalized between oxygens of substituted tetrahedrons and octahedrons following the methodology of Skipper and coworkers.[19] No flexibility in the clay lattice was allowed.[19]

For the development of a model of the CP$^+$ ion, its bond lengths and angles were taken as estimated at 158 K in the experimental study of CPCl-monohydrate.[20] At this temperature, CP$^+$ ions are characterized by an all-trans conformation of the alkyl chains, which was assumed to be representative of the modeled system based on the results of experimental studies of organically modified montmorillonites.[21−23] The results of a further refinement of the structure of the CP$^+$ ion with an all-trans conformation of its alkyl chain and the results of a calculation of its atomic charges using the B3LYP quantum-chemical method and the SVP basis set were made available to the authors by D. Tunega (Institute for Theoretical Chemistry and Structural Biology, University of Vienna). The calculated partial atomic charges are presented in Table 1, which shows

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that the bulk of the positive charge of a CP^+ ion ($\sim$85%) resides on the pyridinium ring and the first CH_2 group, with the rest ($\sim$15%) being on the remaining groups of the alkyl chain. This supports the suggestion[24] that the first CH_2 group should be attributed to the headgroup in an ionic surfactant.

All bond lengths within a CP^+ ion as well as the bond angles within its headgroup, consisting of the pyridinium ring and α-methylene, and within the other fourteen CH_2 groups, and the terminal CH_3 group were not allowed to change during the simulations. This approximation was made in assumption that the corresponding changes can be neglected when studying the dependence of the layer spacing and the interlayer arrangement of CP^+ ions on the interlayer CP^+ content. Conformational changes of a simulated CP^+ ion, consisting consequently of the sixteen segments, take place only due to the changes in bond and torsion angles formed by the atoms of at least two segments.

Monte Carlo (MC) simulations of a CP^+-modified montmorillonite were carried out in the isothermal-constant stress ensemble according to the methodology of Skipper et al.[19] with additional consideration of conformational changes of CP^+ ions. During the simulations, displacement and rotation MC moves for water molecules and displacement MC moves for interlayer inorganic and organic ions were allowed. To simulate the conformational changes of CP^+ ions, the configurational-bias Monte Carlo (CBMC) method[25,26] was applied. In a CBMC move, a randomly chosen CP^+ ion was regrown segment by segment starting from a randomly chosen segment and proceeding in the headgroup ($C_5H_5NCH_2$) or terminal group (CH_3) direction. Trial orientations of grown segments were generated according to the algorithm described by Vlugt et al.[26] The number of trial orientations was set to 10 for a CH_2 or CH_3 group and to 30 for the headgroup of the CP^+ ion. Thus, within one MC cycle each interlayer molecule or ion was tried to be moved (by MC or CBMC move) once on average. Mineral layers were allowed to move perpendicular or parallel to the midplane of the simulation box once per 20 MC cycles on average.

The potential energy of interactions between interlayer ions, water molecules, and mineral layers was calculated with help of the OPLS-AA force field and consists of bending, torsion, and nonbonded terms $k_{\theta,i}(\theta_i - \theta_{0,i})^2$, $\sum_{n=1}^{3}V_{n,i}(1 + (-1)^{n+1}\cos l\phi_i)/2$, and $a_{ij}(q_iq_j/r_{ij} + 4\epsilon_{ij}[(\sigma_{ij}/r_{ij})^{12} - (\sigma_{ij}/r_{ij})^6])$, respectively.[16] In the third term, a_{ij} equals 0 ($j=i+1$, $j=i+2$) or 1/2 ($j=i+3$) when atoms i, j belong to the same CP^+ ion, or 1 otherwise. Intramolecular bending, torsion, and nonbonded interactions were accounted only for CP^+ ions and only if the participating atoms belonged to at least two segments of the CP^+ ion. The parameters $k_{q,i}$, $\theta_{0,i}$, $V_{n,i}$, ϵ_{ij}, σ_{ij} for the CP^+ ion and ϵ_{ij}, σ_{ij} for TIP4P water, Cl^-, and Na^+ ions were taken from the literature.[16,17,27] The missing $V_{n,i}$ parameters for the torsional angle $C-C-N-C_{aromatic}$ were extrapolated from related types and had values of -11.422, 5.768, and 7.841 kJ/mol for $n = 1$, 2, and 3, respectively. The values of the $V_{n,i}$ parameters for a $C-C-C-C$ torsion angle formed by four carbons of the alkyl chain, as in the work of ref 16, define a torsional potential with only one minimum corresponding to the trans conformation (torsion angle of 180±60°) of these carbons. Such a torsional potential deviates significantly from the torsional potential for isolated alkyl chains[28] characterized by the additional local minima corresponding to the two gauche conformations (torsion angles of 60±60° and 300±60°), which are separated by a rotational barrier of $\sim$3.6 kcal/mol from the trans conformation. Therefore, the optimized parameters $V_{n,i}$ with values of 7.588, -3.845, and 16.010 kJ/mol for $n = 1$, 2, and 3, respectively,
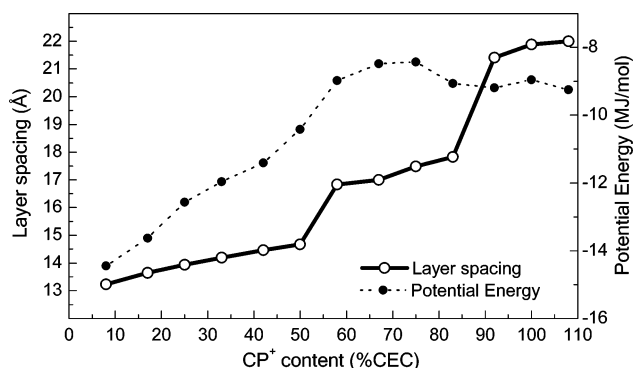

Figure 1. Simulated layer spacings (Å) and total potential energies (kJ/mol per simulation box) as functions of interlayer CP^+ content in montmorillonite. Error bars associated with simulated data do not exceed the size of the symbols and are not shown.

were applied in the simulations for this torsion angle to provide an agreement with the torsional potential.[28] In the simulated system, the cutoff distance of 9 Å and the all-image convention[19] were adopted for the short-range interactions, and the Ewald technique[29] was applied to handle the long-range Coulomb interactions. Temperature and stress were fixed at 298 K and 10^5 Pa, respectively.

At the start of each simulation run, interlayer inorganic ions were positioned in the midplane of the simulation box, whereas water molecules were positioned randomly throughout the interlayer space. CP^+ ions were positioned in the mid plane of the simulation box or in two planes on both sides of it for interlayer CP^+ contents of 8 up to 17% CEC or 25 up to 108% CEC, respectively. The initial layer spacing was set to 22, 24, or 28 Å for the interlayer CP^+ contents of 8 up to 75% CEC, 83% CEC or 92 up to 108% CEC, respectively. During the first $\sim$1.6×10^4 MC moves of a simulation run, only water molecules were allowed to move,[19] so that interlayer inorganic ions become hydrated before they start to move. A mean of $\sim$7.8×10^6 MC moves were made in a simulation run, and a mean of $\sim$4.8×10^5 MC moves were taken for sampling of layer spacings, total potential energies, energies of interaction between components of the system and radial distribution functions.

3. Results and Discussion

3.1. Interlayer Arrangement and Conformation of CP^+ Ions. The expansion curve of the simulated CP^+-modified Na-montmorillonite as a function of interlayer CP^+ content is presented in Figure 1. The pattern of this curve can be clearly divided into three ranges: (1) $\sim$13.2 Å up to $\sim$14.7 Å for CP^+ contents of $\sim$10 up to 50% CEC, (2) $\sim$16.8 Å up to $\sim$17.8 Å for CP^+ contents of $\sim$60 up to $\sim$80% CEC, and (3) $\sim$21.4 Å up to $\sim$22.0 Å for CP^+ contents of $\sim$90 up to $\sim$110% CEC. In experimental studies, montmorillonite exhibits layer spacings of $\sim$14.4 Å, $\sim$17.9 Å, and $\sim$21.8 Å at CP^+ contents of $\sim$37, $\sim$70 up to $\sim$90 and $\sim$100% CEC, respectively.[1,4] The calculated layer spacings of 14.46±0.05 Å, 17.83±0.07 Å, and 21.88±0.12 Å at the very similar CP^+ contents of 42, 83, and 100% CEC, respectively, show very good agreement with the experimental values.

The characteristic interlayer structures for the ranges (1), (2), and (3) are presented in Figures 2a, 2b, and 2c, respectively. The suggestions about the arrangement of long-chain organic cations in the interlayer space of montmorillonite were derived so far on the basis of experimentally observed layer spacings and with help of geometrical considerations.[1–8] As can be clearly seen in Figure 2, CP^+ ions build monomolecular, bimolecular,
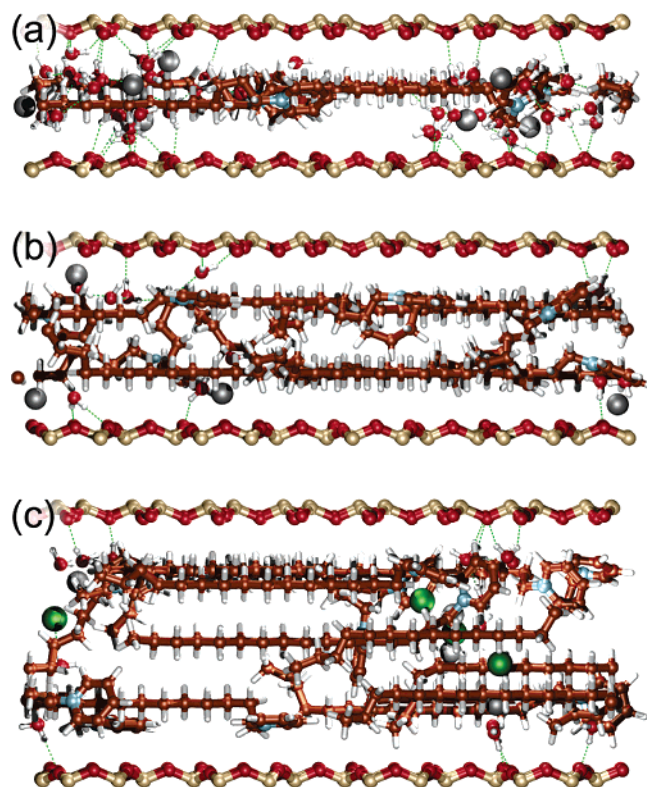
Figure 2. (a) Monomolecular ($\sim$14.2 Å), (b) bimolecular (17.0 Å), and (c) pseudotrimolecular ($\sim$21.9 Å) arrangements of interlayer CP^+ ions in montmorillonite (side view). Ball and stick colors: gray (Na^+), green (Cl^- and hydrogen bonds), red (O), white (H), brown (C), turquoise (N), gold (Si). Out of the mineral layer atoms, only basal oxygens and silicon atoms are shown. Water oxygen, basal oxygen, or chloride is considered as an acceptor A of a hydrogen bond from a water molecule when the separation between the water oxygen O and the acceptor A is less than 3.5, 3.5, or 3.7 Å, respectively, and the O−H···A angle is less than 30°.

and pseudotrimolecular layers in the layer spacing ranges (1), (2), and (3), respectively, in the simulated montmorillonite, which is in excellent agreement with the above suggestions. The transformations from monomolecular into bimolecular and from bimolecular into pseudotrimolecular arrangements occur at the CP^+ contents of 58 and 92% CEC, respectively, as is explicitly manifested by the corresponding stepwise increases of the layer spacing (Figure 1). In agreement with the assumption of Lagaly,[8] only parts of the CP^+ alkyl chains are located near the midplane of the interlayer space and build a middle "pseudo" layer, whereas the pyridinium rings are positioned in the other two molecular layers covering the mineral surfaces (Figure 2c). This is the common observation for the three simulated states with pseudotrimolecular arrangements of CP^+ ions (Figure 1). In those states, only one out of 36 CP^+ ions deviates from the rule having its pyridinium ring located in the middle layer and a greater part of its chain located in another molecular layer (Figure 2c).

Figure 2 also points out the existence of a number of trans conformers of alkyl chains, but the full stretching (all-trans conformation) is obviously not characteristic for CP^+ chains in the interlayer space of montmorillonite. Data on the fraction of gauche conformers in the total conformer population, calculated for 12 conformers composed of 15 interior methylene carbons of each CP^+ alkyl chain, demonstrate this quantitatively in Figure 3. According to these data, the total content of gauche conformation varies from 8 to 30% depending on the CP^+ content and has an average value of 20±8% over the whole
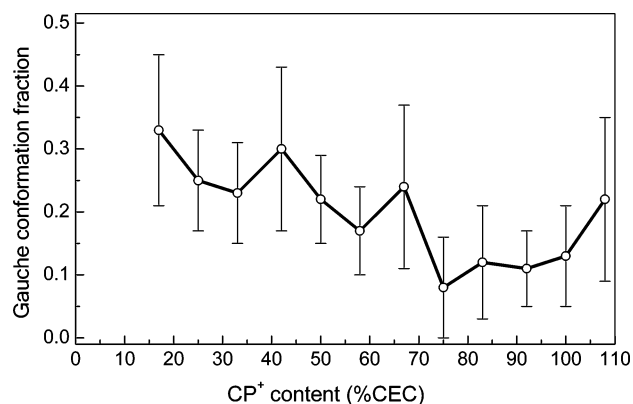

Figure 3. Fraction of gauche conformations as a function of interlayer CP^+ content in montmorillonite.

simulated CP^+ content range. This value agrees well with the corresponding value of 18% obtained in experiment[21] with octadecylamine-modified montmorillonite and is in line with the all-trans to mixed trans/gauche ratios estimated in experiments[22,23] with CTA^+- and octadecylammonium-modified montmorillonites. Based on the information of Figures 2 and 3, the following interpretation can then be given for the reasons of the gradual as well as the stepwise changes in the layer spacing occurring as a result of the gradual increase of interlayer CP^+ content (Figure 1). An increase of the number of CP^+ ions in the interlayer space apparently leads to a decrease of the lateral separations between CP^+ ions in the midplane of a molecular layer being in the process of formation. To accommodate this shortage of space, CP^+ ions change their conformation through bends and torsions in alkyl chains as well as rotations of pyridinium rings, which may push some of their constituents out of the molecular layer. As the interlayer CP^+ content increases, such conformational changes result in a gradual increase of the thickness of the molecular layer under formation and thus of the layer spacing. This gradual increase proceeds till the formation of the molecular layer is completed, so that the formation of an additional layer can start accompanied by a stepwise increase of the layer spacing.

3.2. Energies of the Interactions in CP^+-Modified Montmorillonite. The dependence of the calculated total potential energies on the interlayer CP^+ content for the simulated CP^+-modified montmorillonite is presented in Figure 1. In a natural montmorillonite, an increase of interlayer water content in the course of swelling results in a decrease of the total potential energy and is thus energetically favorable.[30,31] Quite differently, the interlayer uptake of CP^+ ions is energetically unfavorable until they reach a bimolecular arrangement (CP^+ content of 58% CEC). This finding suggests that, at least in the beginning of the modification of a Na-montmorillonite with CP^+ ions, their interlayer uptake is an entropy-driven and not enthalpy-driven process.

The reasons for this positive energy change can be investigated in detail considering calculated energies of interactions between the components of the CP^+-modified montmorillonite, as presented in Figure 4. It shows that the initial increase in the total potential energy occurs mainly due to two energy contributions: (1) an increase in the interaction energy between interlayer Na^+ ions and clay as a result of their replacement by CP^+ ions and (2) an increase in the interaction energy between water molecules and Na^+ ions as a result of the partial dehydration of the remaining interlayer Na^+ ions and of the water loss during the replacement of hydrated Na^+ ions by CP^+ ions. The water−water and water−clay energies are also

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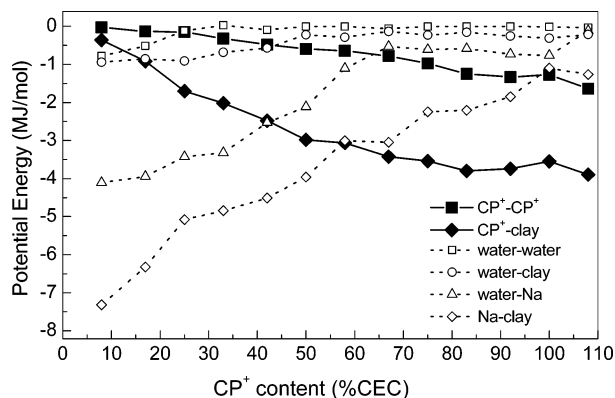*J. Phys. Chem. B, Vol. 110, No. 5, 2006* **2275**

Figure 4. Potential energies of interactions (kJ/mol per simulation box) as functions of interlayer CP$^+$ content in montmorillonite. Error bars associated with simulated data do not exceed the size of the symbols and are not shown.
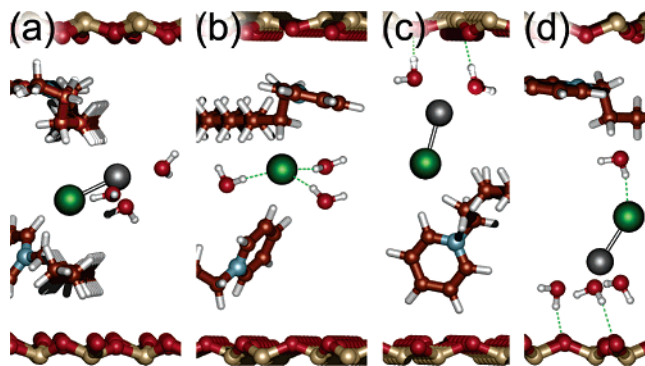

Figure 5. (a), (b), (c) and (d) show four characteristic positions of chloride (green spheres) and sodium (grey spheres) ions in the interlayer space of CP$^+$-modified montmorillonite at CP$^+$ contents of 100% CEC (a, c, d) and 108% CEC (b). For clarity only the CP$^+$ ion(s) are shown, which are in the immediate vicinity of a chloride ion, and only the water molecules, which hydrate sodium or chloride ions. Sticks between Na$^+$ and Cl$^-$ denote the distances of ~2.6 Å. Ball and stick colors as in Figure 2.

increasing due to the water loss (Figure 4), which leads to a decrease of the number of hydrogen bonds of water oxygens among each other and with basal oxygens of the mineral surface (compare Figure 2a and 2b). The latter observation supports the experimentally derived suggestion[32] that the increase of water mobility in the organically modified montmorillonite as compared to the natural one occurs as a result of a deterioration of the hydrogen-bonded water network. Additionally, it points out that the strong decrease in the number of hydrogen bonds between water oxygens belonging to the hydration shells of interlayer inorganic cations and basal oxygens makes an important contribution to this increase.

The CP$^+$−clay energy decreases up to a CP$^+$ content of 83% CEC (Figure 4), until the bimolecular layer structure is formed and, consequently, the maximal coverage of the mineral surface with CP$^+$ ions is reached. As the uptake of CP$^+$ ions proceeds, this energy shows expectedly only minor changes, because the major structural effect of this uptake is the formation of the pseudo-layer, which has only minimal direct contact with the mineral surface. The decreasing CP$^+$−clay energy does not compensate the simultaneously increasing Na$^+$−clay energy, because differently from the point charge on a Na$^+$ ion, the positive charge on a CP$^+$ ion is smeared between its atoms and cannot accommodate to the negatively charged mineral surface in a spatially optimal way.

The CP$^+$−CP$^+$ energy decreases with increasing CP$^+$ content and decreasing CP$^+$−CP$^+$ separations but has significantly higher values than the CP$^+$−clay energy (Figure 4). This explains why in thermogravimetric studies of a CP$^+$-modified montmorillonite with CP$^+$ contents $\geq$ 100% CEC, the weight loss due to the removal of interlayer organic material starts at a significantly lower temperature (190 °C) than with CP$^+$ contents of 50 and 70% CEC (at 280 °C and 240 °C, respectively).[4] With the latter two contents, CP$^+$ ions are in contact with the mineral surface (Figures 2a, 2b), whereas with CP$^+$ contents $\geq$ 100% CEC, the CP$^+$ ions in the pseudolayer have much less contact with the mineral surface (Figure 2c). As compared to the CP$^+$ ions covering mineral layers, the pseudolayer CP$^+$ ions need significantly lower energy input to be removed from the interlayer space. This follows from the difference between the CP$^+$−clay and CP$^+$−CP$^+$ energies and the above-discussed pattern of the CP$^+$−clay energy (Figure 4). Analogously, a montmorillonite with a CP$^+$ content of 50% CEC and the corresponding monomolecular CP$^+$ arrangement is more thermostable than that with a CP$^+$ content of 70% CEC and the bimolecular CP$^+$ arrangement (Figure 2), because CP$^+$ ions in the monomolecular arrangement are in maximal contact

with both mineral surfaces and not only with one of them, as in case of the bimolecular arrangement. This conclusion is further supported by the experimental observation[10] that when heating a montmorillonite modified by CP$^+$ ions above 100% CEC, its layer spacing changes from an initial ~22 Å to ~18 Å (at ~190 °C) and then to ~15 Å (at ~210 °C), which persists up to 280 °C. These layer spacings are characteristic for the pseudotrimolecular, bimolecular, and monomolecular CP$^+$ arrangements, respectively.

3.3. Interlayer Chloride Ions: Location and Possible Sorption Mechanisms. Experiments[1,4] have revealed that the interlayer sorption of chloride, bromide, or iodide ions on a montmorillonite occurs only when it has been modified by CP$^+$ ions to ~100% CEC and higher. Such a modified montmorillonite is characterized by layer spacings in the range between 21 and 22 Å (Figure 1, refs 1, 4) and, consequently, by the pseudotrimolecular arrangement of interlayer CP$^+$ ions (Figure 2c, refs 1, 8). Figure 2c clearly shows that the middle, pseudolayer in the interlayer space is not completely occupied even at a CP$^+$ content of 100% CEC. Therefore, it provides enough place for inorganic anions between the two neighboring molecular layers, which would screen the anions from the negatively charged mineral layers. It is obvious then that the formation of the pseudotrimolecular arrangement is a prerequisite for the interlayer sorption of inorganic anions on an organically modified montmorillonite. This conclusion is further supported by the experimental observation[4] that the interlayer sorption of chloride ions does not occur at interlayer CP$^+$ contents $\leq$ 80% CEC and layer spacings $\leq$ 17.9 Å. These values correspond exactly to the upper boundaries of the ranges of interlayer CP$^+$ contents and layer spacings characterized by a bimolecular arrangement of CP$^+$ ions, as identified with help of Figure 1.

Simulation results presented in Figure 5 show that chloride ions are indeed located near the mid plane of the interlayer space. This figure reveals, however, that an interlayer chloride ion can be screened from negatively charged mineral layers not only by two CP$^+$ ions (Figures 5a, 5b), but also by one CP$^+$ ion and one hydrated Na$^+$ ion (Figures 5c, 5d). Moreover, it can be either in dehydrated (Figures 5a, 5c) or in partially hydrated (Figures 5b, 5d) state. In the latter case, the most probable distance between a chloride ion and a water hydrogen or oxygen equals to 2.27 or 3.20 Å, respectively (Figure 6). These values are in very good agreement with the corresponding
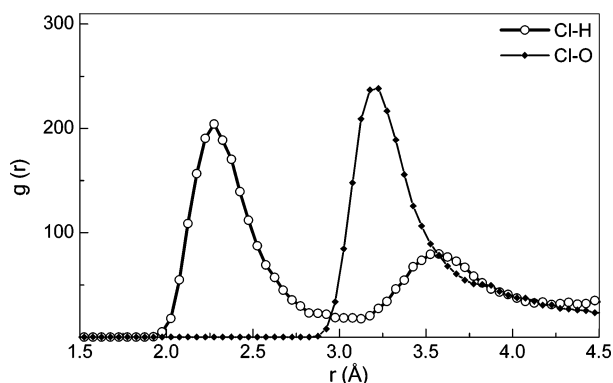
Figure 6. Radial distribution functions $g(r)$ for water hydrogens and oxygens around chloride ions in CP^+-modified montmorillonite at a CP^+ content of 108% CEC. $g(r)$ is a function of the distance r (Å) of a water hydrogen or oxygen from the central ion and is calculated according to the definition (ref 29).
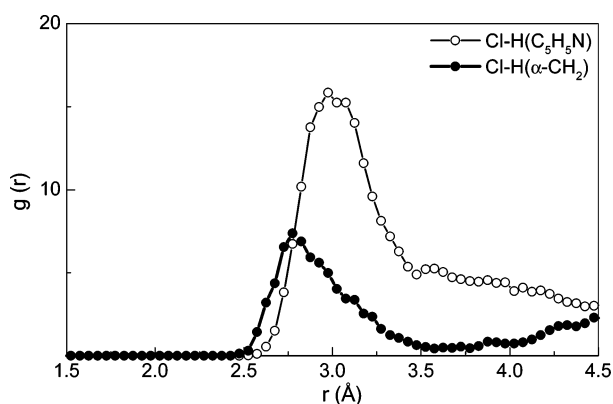

Figure 7. Radial distribution functions $g(r)$ for pyridinium and α-methylene hydrogens around chloride ions in CP^+-modified montmorillonite at a CP^+ content of 108% CEC.

Figure 8. Radial distribution functions $g(r)$ for sodium ions around chloride ions in CP^+-modified montmorillonite at a CP^+ content of 108% CEC.

experimental values of 2.26 or 3.15 Å, respectively, for the crystalline CPCl-monohydrate[20] as well as with the respective values of 2.25 or 3.20 Å obtained in a simulation with TIP4P water for an aqueous chloride solution.[27] When a chloride ion is screened from the mineral surface by the pyridinium ring of a CP^+ ion (Figures 5b, 5c), the most probable distance between it and a hydrogen of the first methylene group equals 2.77 Å (Figure 7), which is also in a very good agreement with the value of 2.74 Å obtained from the experiment with the crystalline CPCl-monohydrate.[20] On the other hand, the most probable distance between a chloride ion and a hydrogen of the pyridinium ring equals 2.97 Å (Figure 7), while the latter experiment[20] yields 2.75 Å. This disagreement must obviously be attributed to the presence of sodium cations and to the greater water content in the interlayer space of a CP^+-modified montmorillonite as compared to the crystalline CPCl-monohydrate.

Figures 5a, 5c, and 5d reveal furthermore that Na^+ and Cl^- ions can form Na^+-Cl^- contact pairs in the interlayer space of a CP^+-modified montmorillonite. Such a contact ion pair is hydrated by at most four water molecules in our simulations (Figure 5), so that its Na^+ ion is always partially hydrated. In this pair, the Cl^- ion can either be partially hydrated, too, and have no close contact with a CP^+ ion (Figure 5d) or be dehydrated and have close contact with the pyridinium ring of a CP^+ ion (Figure 5c) or with alkyl chains of two CP^+ ions (Figure 5a). It is well-known that alkali halide molecules dissolve in water, so that no contact ion pairs are likely to exist in a bulk aqueous solution.[33,34] The situation is very different,
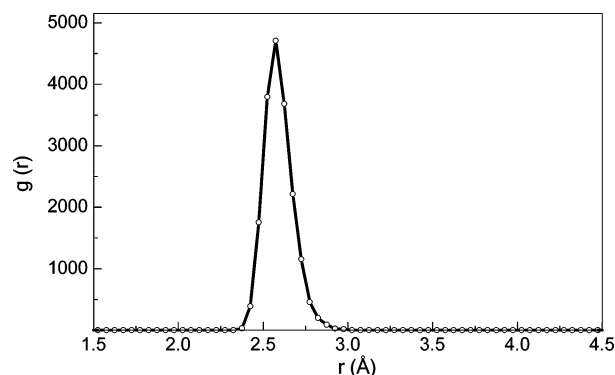
however, when a water cluster containing alkali and halide ions is considered, as was shown in experimental[33] and ab initio simulation[34,35] studies. It was found[34,35] that at least six water molecules are necessary, in order that a Na^+-Cl^- contact pair dissociates and becomes a solvent-separated one. This fact strongly supports our finding about the formation of interlayer Na^+-Cl^- contact pairs, since the water content in the interlayer space of a CP^+-modified montmorillonite is very low[4,10] and corresponds to about two water molecules per interlayer inorganic ion at CP^+ contents relevant for the interlayer sorption of inorganic anions (see section "Simulation Details"). As a further support, the distances between Na^+ and Cl^- ions in an interlayer ion pair vary between ~2.4 Å and ~2.8 Å (Figure 8), which correspond very well to the values of 2.41 Å up to 2.76 Å observed for contact ion pairs in water clusters of one up to six water molecules, respectively. Furthermore, the simulated most probable value of ~2.6 Å for this interionic distance (Figure 8) is in perfect agreement with the value of 2.59 Å for water clusters of three and four water molecules.[34,35]

The fact that interlayer chloride ions form pairs with Na^+ ions rather than with CP^+ ions suggests that the intercalation of Na^+-Cl^- pairs may be a second mechanism of the interlayer sorption of inorganic anions in organically modified montmorillonites, which has not been considered so far. As concluded above, this anion sorption cannot take place before the formation of pseudotrimolecular structure in the interlayer space of a montmorillonite is initiated. It follows then that after the formation of the bimolecular layer is completed, two mechanisms of anion sorption are principally possible during the further organic modification of a montmorillonite.

In the first mechanism, implicitly suggested in the experimental studies,[1-6] no exchange of the "next-in-the-queue" interlayer inorganic cation occurs, but a neutral (not violating the balance between layer and interlayer charges) organic cation—inorganic anion pair intercalates into the interlayer space instead[1-6] and initiates the formation of the pseudolayer. The pseudotrimolecular arrangement requires further that the positively charged headgroup of the organic cation belonging to the newly intercalated pair should be placed near the mineral surface. The organic cation—inorganic anion pair should dissociate before or during this process, since the organic cation becomes associated with the negatively charged mineral surface. Subsequently, the dissociated inorganic anion either associates with an interlayer inorganic cation to form an "inorganic cation— inorganic anion" pair (Figures 5a, 5c, 5d) or it becomes hydrated with additional water molecules and resides near the organic cation to which it was associated before (Figure 5b). This mechanism requires then that a three-step, "intercalation—

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dissociation−association (or hydration)" process takes place in the interlayer space, preceded by the organic cation−inorganic anion pair association in the aqueous solution of the pore space.

In the second mechanism, an exchange of the next-in-the-queue interlayer inorganic cation with an organic cation does occur and leads to the formation of the pseudolayer. One or even several inorganic cation−inorganic anion pairs, formed in the aqueous solution of the pore space, intercalate then into the expanded interlayer space with the number of intercalated pairs depending on the free space available in the pseudolayer. This mechanism requires that a two-step "exchange−intercalation" process takes place in the interlayer space, and it sidesteps the following controversial implications of the first mechanism: (1) starting from a certain interlayer content of organic cations, the "next-to-come" pore-space organic cation cannot enter the interlayer space alone any more (by exchanging one of the remaining interlayer inorganic cations), but only in a pair with an inorganic anion; and (2) the dissociation of the organic cation−inorganic anion pair is favored after it has been intercalated and not before, when it is still in the pore space or on the interface between pore and interlayer space. This mechanism also solves the apparent contradiction in experimental observations[1,3−5] that, although organic cations are able to effectively exchange the interlayer inorganic cations, the latter are still not completely removed from the interlayer space, even if the interlayer content of organic cations exceeds 100% CEC of a nonmodified montmorillonite. With this mechanism, the interlayer inorganic cations are actually exchanged with organic cations, even after the formation of the pseudotrimolecular structure is initiated, but they return in the interlayer space as soon as they form pairs with inorganic anions in the pore space.

The second mechanism suggests also an explanation for the experimental observation[36] that iodide sorption in a CP^+-modified montmorillonite from a NaI solution is higher than that from a KI solution: Taking into account the van der Waals diameters of Na^+ and K^+ ions, a Na^+-I^- pair is about 0.7 Å smaller than a K^+-I^- pair.[37] Therefore, the attraction between the ions in a Na^+-I^- pair is stronger than in a K^+-I^- pair, so that the probability of the pair dissociation before completion of the process of intercalation in the interlayer space is lower for a Na^+-I^- pair than for a K^+-I^- pair. Considering further that during the intercalation process a smaller pair can accommodate more easily in the free space available in the pseudolayer of an organically modified montmorillonite, the intercalation of a Na^+-I^- pair should be favored as compared to that of a K^+-I^- pair.

4. Conclusions

This work supports previous experimentally derived suggestions that CP^+ ions build monomolecular, bimolecular, or pseudotrimolecular layers depending on their content in interlayer space of the CP^+-modified montmorillonite. These arrangements of CP^+ ions are characterized by three different ranges of layer spacings: (1) ~13.2 Å up to ~14.7 Å, (2) ~16.8 Å up to ~17.8 Å, and (3) ~21.4 Å up to ~22.0 Å.

Calculated potential energies of the interactions between the components of the CP^+-modified montmorillonite reveal that the interaction of CP^+ ions with mineral layers is significantly stronger than the interaction of CP^+ ions among each other. Correspondingly, the thermal stability of CP^+-modified montmorillonites depends on the formed interlayer structures. It decreases in the order "monomolecular arrangement−bimolecular arrangement−pseudotrimolecular arrangement" of the CP^+ ions.

This simulation study allows to draw the conclusion that interlayer sorption of inorganic anions on CP^+-modified montmorillonite requires that CP^+ ions have a pseudotrimolecular arrangement in its interlayer space. Furthermore, the results of this work and available experimental information suggest a previously unconsidered and maybe more important mechanism of the interlayer sorption of inorganic anions on organically modified clay minerals, which takes place as a result of the formation of partially hydrated "inorganic cation-inorganic anion" pairs in the clay pore space and their subsequent uptake in the interlayer space.

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