Molecular Dynamics Simulation of Organic−Inorganic Nanocomposites: Layering Behavior and Interlayer Structure of Organoclays

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Isothermal−isobaric (NPT) molecular dynamics simulation has been performed to investigate the layering behavior and structure of nanoconfined quaternary alkylammoniums in organoclays. This work is focused on systems consisting of two clay layers and a number of alkylammoniums, and involves the use of modified Dreiding force field. The simulated basal spacings of organoclays agree satisfactorily with the experimental results in the literature. The atomic density profiles in the direction normal to the clay surface indicate that the alkyl chains within the interlayer space of montmorillonite exhibit an obvious layering behavior. The headgroups of long alkyl chains are distributed within two layers close to the clay surface, whereas the distributions of methyl and methylene groups are strongly dependent on the alkyl chain length and clay layer charge. Monolayer, bilayer, and pseudo-trilayer structures are found in organoclays modified with single long alkyl chains, which are identical to the structural models based on the measured basal spacings. A pseudo-quadrilayer structure, for the first time to our knowledge, is also identified in organoclays with double long alkyl chains. In the mixture structure of paraffin-type and multilayer, alkyl chains do not lie flat within a single layer but interlace, and also jump to the next layer in pseudo-trilayer as well as next nearest layer in pseudo-quadrilayer.

Introduction

Layered solids such as graphite, clay minerals, layered double hydroxides, transition metal dichalcogenides, metal phosphates, and phosphonates can form organic−inorganic nanocomposites through incorporating organic guest species in their interlayer space, including neutral molecules, organic cations, or anions.[1,2] Among them, smectite groups of layered clay minerals have been investigated extensively as hosts because of their attractive features of swelling behavior, cationic exchangeability, adsorption properties, and large surface area. Organic modified clays, also called organoclays, are widely applied in various industries, including the rheological controlling of paints and greases, selective adsorption of toxic compounds, and immobilization of photo- and electroactive materials.[3,4] More recently, clay minerals have been used to make polymer nanocomposites with enhanced physical, chemical, and mechanical properties.[5−8]

Montmorillonite, a smectite clay, is a hydrophilic mineral that consists of nanometer-thick layers formed by sandwiching an aluminum octahedron sheet between two silicon tetrahedron sheets. Stacking of the layers leads to a van der Waals gap between the layers. Substitution of aluminum ions with magnesium ions in the octahedron sheet gives each three-sheet layer an overall negative charge, which is counterbalanced by exchangeable metal cations residing in the interlayer space. The interlayer cations hold the individual silicate layer through electrostatic forces. To improve the miscibility with polymers, clay minerals are usually modulated with alkylammoniums through cationic exchange reaction, which results in the transition of clay surface from hydrophilic to organophilic.

Understanding the structure of organoclays and the interactions of surfactant−clay and surfactant−surfactant is of importance in design and characterization of polymer nanocomposites. However, such information is rarely available from experimental measurements be-

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cause of the low crystallizability of clays. So far, X-ray diffraction (XRD) is the most widely used technique to determine the structure of organoclays and polymer clay nanocomposites because it gives the basal spacings of the materials. On the basis of the measured basal spacings as well as the length of alkyl chains, various structural models have been proposed for the interlayer alkyl chains, including monolayers, bilayers, pseudotrilayers, and paraffin-type monolayers and bilayers.[9] In a paraffin-type structure, the alkyl chains are considered to radiate away from the clay surface. These idealized structures are almost exclusively based on all-trans conformation and do not directly reveal the significant structural characteristics of alkyl chains. To overcome this problem, other techniques have been employed, including Fourier transform infrared spectroscopy (FTIR)[10] and nuclear magnetic resonance spectroscopy (NMR),[11] to probe the interlayer structure and molecular conformation with limited success. To date, the molecular arrangements and layering structure of organoclays is still difficult to quantify experimentally.

In this study, molecular dynamics (MD) simulation is used to probe the layering behavior and interlayer structure of quaternary alkylammonium modified montmorillonites at a molecular level. We have chosen specifically the quaternary alkylammoniums as the guests because there is a wealth of experimental XRD data on these organoclays and they are widely used as precursors in the preparation of polymer nanocomposites.[6,7,12,13] Comparison will be made between the simulated and experimental results mainly in terms of the basal spacings. These results will be used to examine the validity of our MD approach to the organoclay systems. The atomic density profiles and arrangement of alkyl chains will also be produced and discussed.

Methodology

Initial Configuration. The model construction was carried out using the Crystal Builder of the Cerius2 package (MSI)[14] on a SGI supercomputer. The first step in preparing the initial organoclay configuration for MD simulations is to create a negatively charged montmorillonite framework. However, complete crystal structure information is not available because of the microcrystalline and poor ordering of smectite clays. Therefore, the atomic coordinates for montmorillonite in this study are derived from a simulated structural model proposed by Viani et al.[15] The thickness of silicate layer is 6.5 Å. The model unit cell parameters are $a = 5.18$ Å, $b = 8.95$ Å, $c = 15.0$ Å, and $\alpha = \beta = \gamma = 90°$. This model does not include coordinates for the hydroxyl hydrogen in the octahedral sheet, nor does it address the isomorphous substitution and its location in octahedral sheet. Therefore, hydroxyl groups are created by adding one hydrogen to each octahedral oxygen that does not connect with tetrahedral silicon. The OH bond length is assigned to be 0.96 Å as recommended by Skipper et al.[16] in which the hydrogen is located vertically away from the octahedral sheet. In natural montmorillonite, the layer charge arises primarily from the substitution of aluminum by magnesium ions in the octahedral sheets, although a small amount (less than 5% on the average) comes from the substitution of silicon by aluminum ions in the tetrahedral sheets.[17,18] Thus, in our idealized clay model we assume that all layer charge comes from the substitution of silicon by aluminum ions in octahedral sheets. Moreover, aluminum ions are substituted randomly by magnesium ions, but as suggested by Newman et al.,[19] to avoid a high local deficiency of charge, the magnesium ions are not allowed to occupy adjacent hydroxide octahedrals.

Three types of montmorillonites with different layer charge are studied, with their unit cell formula given by

$$M_xSi_8(Al_{4-x}Mg_x)O_{20}(OH)_4$$

where M represents a monovalent cation and x is the layer charge. The cation exchange capacity (CEC, milliequivalent of positive charge per 100 g of clay, or meq/100 g), which is defined as the amount of the exchangeable cations retained by the clay to neutralize the negative charge, can be calculated from the layer charge. For example, with the basic unit cell formula of $M_{0.75}Si_8(Al_{3.25}Mg_{0.75})O_{20}(OH)_4$, the net charge per unit cell is -0.75 and the calculated formula weight per unit cell of a Na clay is 733 g. Thus, the CEC of this montmorillonite is 102 meq/100 g. In this study, montmorillonite clays with various layer charges ($x = 0.625$, 0.75, or 0.875) have been constructed which correspond to various cation exchange capacities (CEC = 85, 102, or 119 meq/100 g). Our periodic MD simulation cell consists of 64 unit cells ($8 \times 4 \times 2$), resulting in an overall size of $a = 41.44$ Å, $b = 35.92$ Å. The third dimension is chosen close to the experimental results, which can avoid a significant contraction or expansion of the clay framework during the simulations.

We then constructed our systems by substituting all interlayer inorganic cations with alkylammoniums. In each case, the alkylammoniums are placed in the interlayer spaces with their longest chains oriented in a direction approximately parallel to the plane of the clay layers. The number of alkylammoniums included in the MD simulation cell varies from 40 to 56, depending on the layer charge of the simulated organoclays. The alkyl chains are built using the united atoms in which carbon atoms are made to adsorb the hydrogen in methyl and methylene groups.

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Force Field. The generic Dreiding force field is used for all simulations. This force field can predict the structures and dynamics of organic, biologic, and main-group inorganic molecules.[20] It is the sum of the following potential energy terms:

$$E = E_{\text{bond}} + E_{\text{angle}} + E_{\text{torsion}} + E_{\text{vdW}} + E_{\text{electrostatic}}$$

The first three terms are valence interactions including bond stretching (E_{bond}), bond-angle bend (E_{angle}), and dihedral angle torsion (E_{torsion}), whereas the nonbonded interactions consist of the van der Waals energy (E_{vdW}) and the electrostatic energy ($E_{\text{electrostatic}}$). The bond energy, E_{bond}, is in the harmonic form

$$E_{\text{bond}} = \frac{1}{2} k_{\text{b}}(R - R_0)^2$$

where k_{b} is the force constant of the bond, R is the length of the bond, and R_0 is the equilibrium length of the bond. The bond angle energy, E_{angle}, formed by two adjacent bonds is in the harmonic angle form

$$E_{\text{angle}} = \frac{1}{2} k_{\theta}(\theta - \theta_0)^2$$

where k_θ is the force constant, θ is the bond angle, and θ_0 is the equilibrium bond angle. The torsion energy, E_{torsion}, takes the form

$$E_{\text{torsion}} = \frac{1}{2} k_{\varphi}\{1 - \cos[n(\varphi - \varphi_0)]\}$$

where k_φ is the barrier to rotation, φ is the torsion angle, φ_0 is the equilibrium torsion angle, and n is the periodicity of the rotational potential and determines the number of minima in the rotational potential. The van der Waals interaction energy, E_{vdW}, is in the form of the well-established Lennard−Jones potential

$$E_{\text{vdW}} = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

where σ is the collision diameter and ϵ is the energy well depth. The standard combination rules of geometric mean are used for parameters of cross interactions, i.e.,

$$\sigma_{ij} = (\sigma_i\sigma_j)^{1/2} \quad \text{and} \quad \epsilon_{ij} = (\epsilon_i\epsilon_j)^{1/2}$$

The electrostatic energy, $E_{\text{electrostatic}}$, is given by

$$E_{\text{electrostatic}} = \frac{q_i q_j}{4\pi\epsilon_0 r}$$

where q_i and q_j are the partial charges on the ith and jth atoms, respectively; ϵ_0 is the dielectric constant, and r is the separation between the ith and jth atoms.

Because Dreiding does not contain parameters for Mg atoms, modification has been made according to Aikin et al.[21] We assign Mg the same parameters (bond, angle, torsion, and van der Waals) as Al except the formal charges and its equilibrium bond length with oxygen (2.100 Å). In addition, the parameters for quaternary nitrogen are equal to those of N_3 in Dreiding, which has been successfully used in the study done by Tanaka et al.[22]

The mixture of formal and partial charges, or simply the partial charges, of clay have been successfully used in a few studies.[23−27] In this work, the charges of atoms in montmorillonite framework are directly adopted from the studies done by Skipper et al.[23] Thus, octahedral Mg and Al are assigned +2 and +3, respectively, tetrahedral Si +1.2, surface O in the SiO_4 tetrahedron is −0.8, apical O in the SiO_4 tetrahedron is −1.0, H and O in structural OH groups are assigned 0.7175 and −1.7175, respectively. These charge parameters proved to work well with the systems of hydrated clays.[23−26] The atomic charges of quaternary alkylammonium are assigned by a charge equilibration method.[28] The charge equilibration calculation shows that the positive charge is not localized on the nitrogen atom but around the nitrogen atom and its adjacent carbons. Therefore, in the present model, the positive charge of one (esu) is assigned to the headgroup containing one nitrogen and its adjacent carbons, followed by the charge equilibration method.

Simulation Methods. MD simulations are performed using DL_POLY (version 2.13) program[29] on a SGI supercomputer. The MD algorithm is in the form of the Verlet leapfrog integration algorithm. Periodic boundary conditions are applied in three dimensions. To relax the model structures, simulations are first performed in the canonical (NVT) ensembles for 200 ps at 10 or 300 K with a time step of 0.001 ps to obtain the initial configuration for the isothermal−isobaric (NPT) simulation. The NPT simulations are then performed for 800 ps at 300 K and 10^5 Pa (1 atm) with a time step of 0.001 ps. The first 400-ps run is chosen to ensure that the system reaches its equilibrium, and the last 400-ps run is used to collect data for later analysis. The electrostatic interaction is calculated by the Ewald sum method.[30] The equilibrium of the system is reached if the thermodynamic quantities stabilize around their average values. Temperature and pressure are maintained respectively by using the Hoover thermostat and barostat with a relaxation time of 0.5 ps.[31] For each simulation, the data, including coordinates, velocity, force, and statistic quantities, are collected every 5 ps. The basal spacings of the clay systems are averaged over the final 400 ps. During the simulations the atom positions of montmorillonite are fixed in the MD cell. The reference positions of the atoms are scaled with the cell vectors in NPT simulations. Thus, the interaction

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Table 1. Basal Spacings on Organically Modified Montmorillonites (Å)

	alkylammonium		simulation with different CEC[a]			
no.	chemical formula	abbreviation	85	102	119	experimental
1	tetramethyl	TMA	13.0	13.2	13.3	13.8[b]
2	hexyltrimethyl	HTMA	14.2	15.1	15.9	N/A
3	dodecyltrimethyl	DDTMA	16.7	17.8	18.7	18.3[c]
4	octadecyltrimethyl	ODTMA	19.6	20.8	21.9	22.0[c]
5	dioctadecyldimethyl	DODDMA	25.6	27.3	28.8	30.0[c]
6	octadecylethylhexyldimethyl	ODEHDMA	21.3	22.9	24.0	20.4[d]
7	octadecyldihydroxylethylmethyl	ODDHEMA	18.1	19.2	20.2	18.4[d]

[a] Cation exchangeable capacity (CEC), meq/100 g. [b] CEC = 89.7 meq/100 g.[6] [c] CEC = 119.0 meq/100 g.[33,34] [d] CEC = 92.6 meq/100 g.[35]

potentials within clay layer are actually neglected in our simulations, but all atoms of alkylammoniums are allowed to move.

Results and Discussion

Basal Spacings. To validate the force field and our simulation methods, we choose an initial spacing close to the corresponding experimental measurement for each organoclay system. All the initial basal spacings are allowed to vary during the simulations. This is different from the previous work where the basal spacings were constant, determined from experimental measurements.[32] The dependence of the basal spacings on chain length and layer charge has been investigated. Table 1 lists the experimental and simulated basal spacings for montmorillonites with three different layer charges and modified by quaternary alkylammoniums with different chain lengths and numbers of long alkyl chains. The first two columns represent Wyoming-type montmorillonites whereas the third column represents Otay-type montmorillonite. The simulated values of basal spacings are obtained by averaging over the time of production stage (the last 400 ps) whose standard deviation is within 0.1 Å in all cases. Comparison between simulated and experimental results has been made to the averaged basal spacings as the standard deviation for the experimental values is not available in the literature.

The simulated basal spacings agree well with the experimental results with similar CEC (Table 1), suggesting that the simulation method developed is valid. In all cases, the basal spacings increase with increasing layer charge, which indicates that increasing the packing density of alkyl chains results in further swelling of organoclays. For a given cation exchange capacity, a distinct trend of increasing basal spacings with an increase in alkyl chain length is demonstrated from the first four alkylammonium (n = 1, 6, 12, 18) modified montmorillonites. In general, the basal spacing of alkylammonium smectites is considered to increase in steps with the alkyl chain length. Considering the gyration diameter of a single alkyl chain, a monolayer structure is formed at a basal spacing of 13.2 Å, and a bilayer and a pseudo-trilayer structure correspond to a basal spacing of about 18.0 and 22.7 Å, respectively. Thus, the values of simulated basal spacings of TMA−, HTMA−, DDTMA−, and ODTMA−montmorillonites present all structural types (monolayer, bilayer, and pseudo-trilayer) proposed from structural models.[9] The basal spacings for double alkyl chains, DODDMA−montmorillonite, exceed the value of pseudo-trilayer structure. Additionally, basal spacings with values between those of monolayer and bilayer are also observed, for instance, in the case of HTMA−montmorillonite. This simulation result is consistent with the previous experimental observation that a monolayer/bilayer transition exists when the area of the alkylammonium cation is equal to the equivalent area (the area available for a monolayer cation in the interlayer area).[36,37] Moreover, the experimental basal spacings of organoclays were also observed to increase progressively with the chain length.[36,37] Note that in our simulations the basal spacings are averaged over the time of data collection stage and the layer charge is an average value. The random substitution in our models may cause heterogeneous charge distribution, which probably broadens the transition between monolayer and bilayer and results in the basal spacing between as obtained in HTMA−montmorillonite.

Interlayer Density Profiles. To establish the interlayer structure in organoclays, the density distributions of various components in the systems in the direction normal to the clay surface are calculated. The density profiles for headgroups (nitrogen), methyl, and methylene groups in various organoclays under different layer charges and alkyl chain lengths are shown in Figures 1−3. The atomic density profiles for all cases reveal strong layering behavior, which agrees well with the monolayer, bilayer, and pseudo-trilayer structures proposed for organoclays with various chain lengths.[9] In our simulations, the asymmetric nature of some density distributions is probably due to the random substitution and hence the heterogeneous charge distribution in both clay layers of the MD cell.

All headgroups in organoclay except for TMA−montmorillonite are distributed within two layers close to the surface of silicate layers, as seen from the two sharp peaks in Figure 1. These density profiles are due to the strong electrostatic interactions between the negative clay surface and the positive headgroups of the alkyl chains. In addition to both sharp peaks, some headgroups are also present throughout the whole accessible interlayer spaces in the systems of ODTMA− and DODDMA−montmorillonites. Although the basal spacings increase with the increase of chain length and layer

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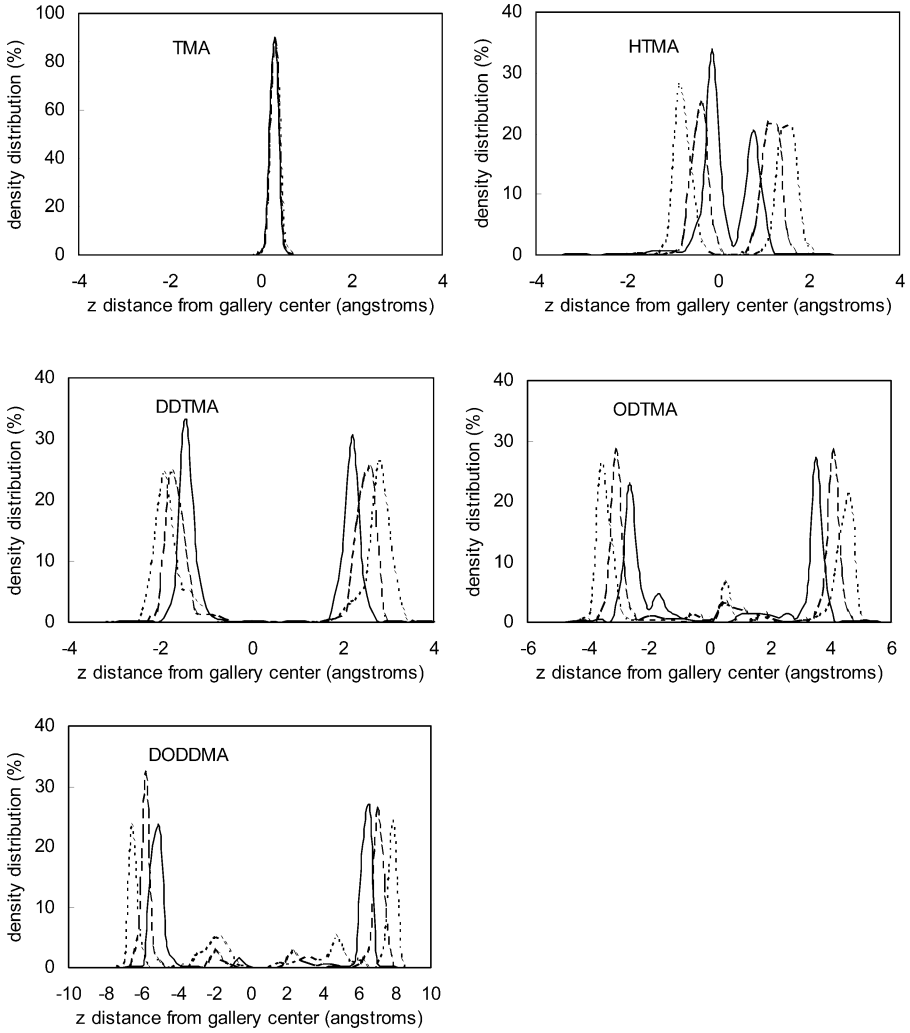

Figure 1. Headgroup density distribution of organoclays with different CEC and alkyl chain lengths as a function of z distance from gallery center: solid curve, CEC 85meq/100 g; dashed curve, CEC 102meq/100 g; dotted curve, CEC 119meq/100 g.

charge, the positions relative to the clay surface for both sharp peaks are conserved in all cases.

The density profiles of methyl groups strongly depend on the chain length as well as the layer charge as shown in Figure 2. The methyl groups in TMA−montmorillonites are close to a uniform distribution within the interlayer spaces although a number of peaks are present. This asymmetric distribution is probably due to the isotropic structure of TMA cations. In other organoclays, the methyl groups predominate within two layers close to the clay surface although they are present throughout the interlayer spaces. In the case of HTMA−montmorillonite, there is no middle peak with the low layer charge. But with the increase of layer charge, two small middle peaks appear in the density profile with medium layer charge, and one sharp peak appears with high layer charge. Comparison with the density distributions of headgroups clearly indicates that the middle methyl groups are attributed to the tail methyls of alkyl chains and they are pushed toward the middle plane. In addition, with the increase of alkyl chain length, the number of middle peaks increases from two for DDTMA−montmorillonites to three for ODTMA−montmorillonites, whereas the peaks and valleys are apparently smooth for DODDMA−montmorillonites.

The interlayer structures of organoclays can be further demonstrated from the density profiles of methylene groups in the alkyl chains. A distinct increase in the number of middle peaks with chain length is shown in Figure 3, which is in good agreement with the structural models based on measured basal spacings and the simulated results on primary alkylammonium modified clays.[9,32] In addition to the structure of monolayer in HTMA−montmorillonite with low clay layer charge, bilayer in DDTMA− and other HTMA− montmorillonites, and pseudo-trilayer in ODTMA−montmorillonites, an apparent pseudo-quadrilayer structure is also present in our simulations in the cases of double long alkyl, DODDMA−montmorillonites. In HTMA−montmorillonites, the two large peaks indicate that their alkyl chains lie flat on the clay surface in bilayer structure. In DDTMA−montmorillonites, each methylene peak gradually splits into a doublet with the increase in clay layer charge. In ODTMA− and DODDMA−montmorillonites, the peaks and valleys are remarkably smoothed, which means the existence of a paraffin-type structure. Thus, a mixture of paraffin-type and multilayer is more reasonable to explain their structures, in which the alkyl chains do not stay flat within a single layer but interlace. Moreover, in ODTMA−montmorillonites the methylene groups with pseudo-trilayer structure are likely to jump to the middle layer because the two valleys in the density profiles are not close to zero. In DODDMA−montmo-

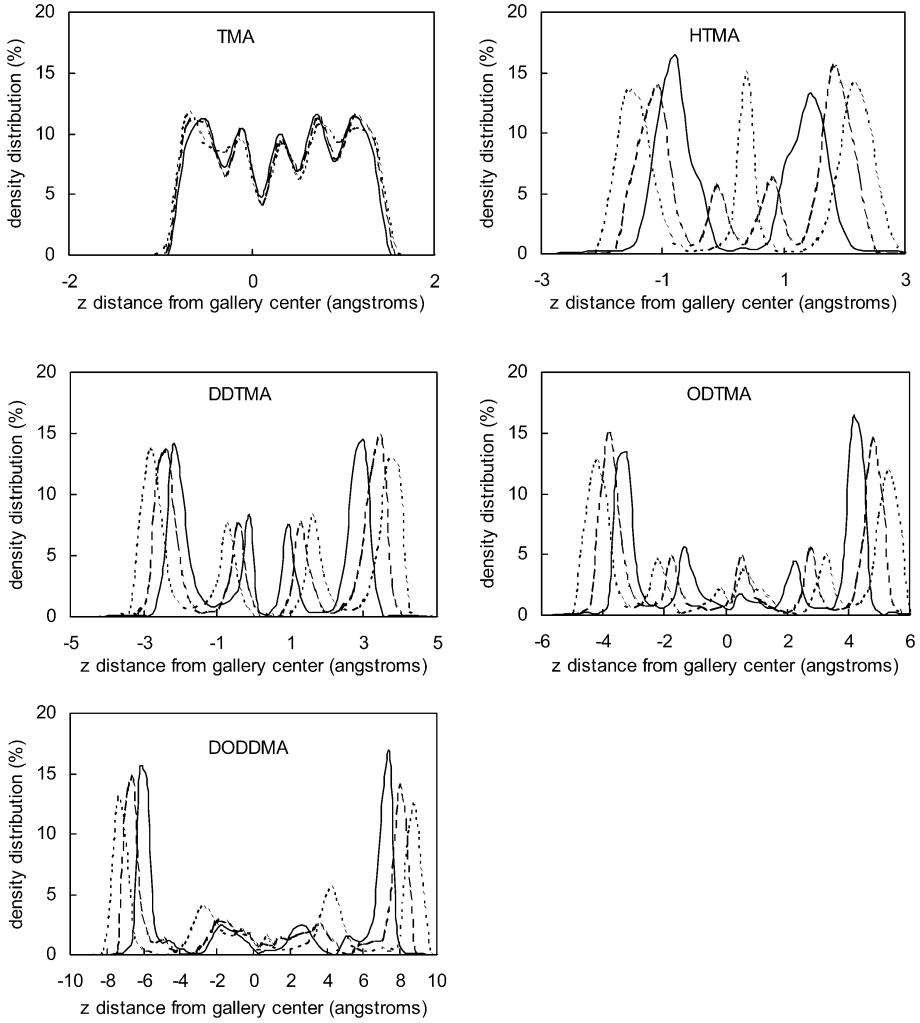

Figure 2. Methyl group density distribution of organoclays with different CEC and alkyl chain lengths as a function of z distance from gallery center: solid curve, CEC 85 meq/100 g; dashed curve, CEC 102 meq/100 g; dotted curve, CEC 119 meq/100 g.

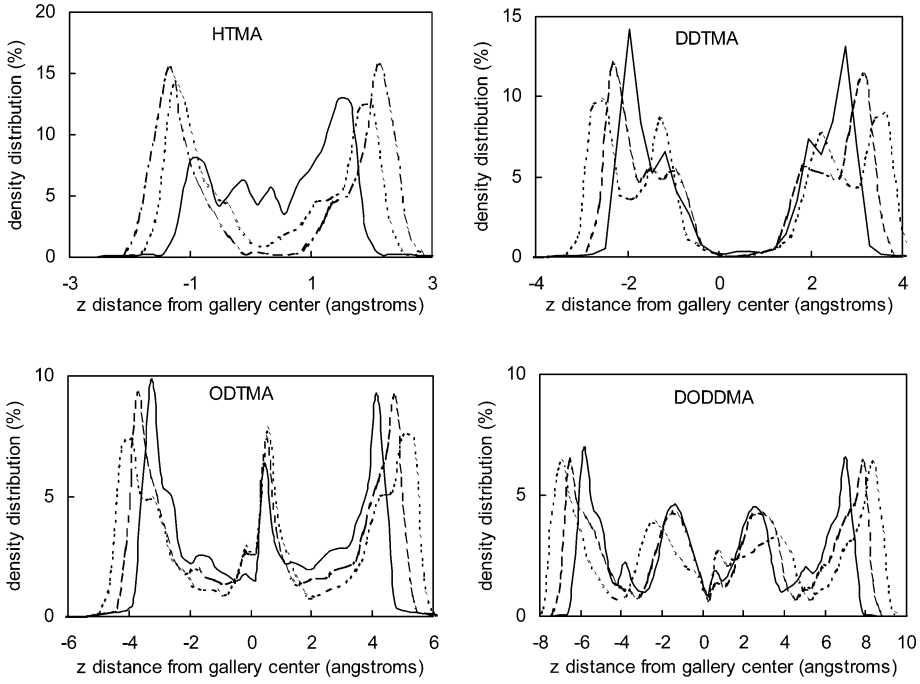

Figure 3. Methylene group density distribution of organoclays with different alkyl chain lengths and CEC as a function of z distance from gallery center: solid curve, CEC 85 meq/100 g; dashed curve, CEC 102 meq/100 g; dotted curve, CEC 119 meq/100 g.

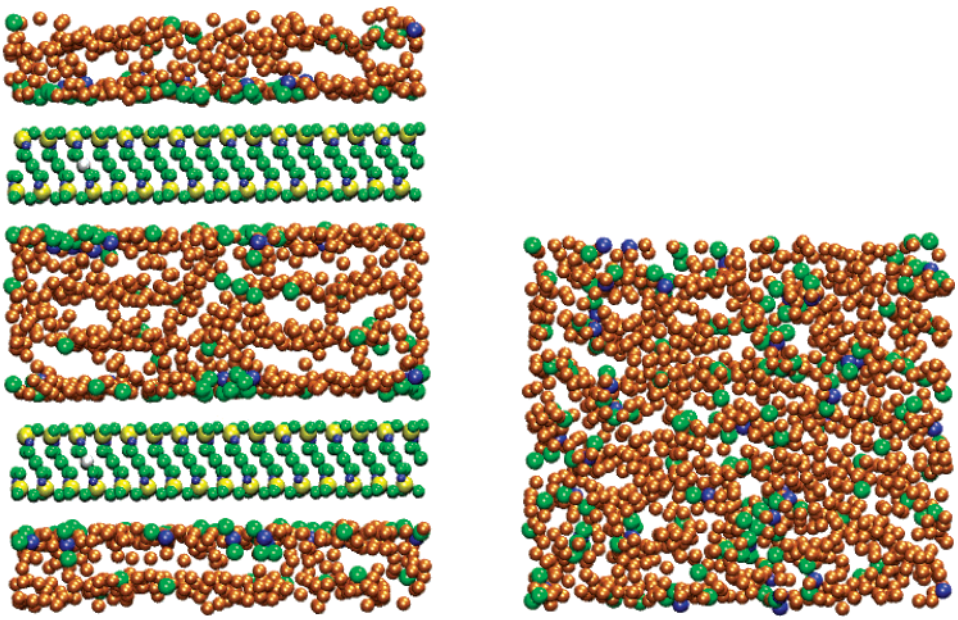

Figure 4. Snapshot at 800 ps for a system at 300 K consisting of two montmorillonite layers and forty dioctadecyldimethylammonium chains viewed from side (left) and normal to the layer surface (right): blue ball (N), green ball (methyl C), orange ball (methylene C).

rillonites, the methylene groups with pseudo-quadrilayer structure not only jump to the next layer but also extend to the next nearest layer.

Interlayer Conformation. Figure 4 shows a snapshot of the simulation cell of a model DODDMA-modified montmorillonite with CEC of 85 meq/100 g following 800 ps of NPT simulation at 300 K. Twenty DODDMA chains are included in each interlayer space (total of 40 in the simulation cell). The average cell parameters over the last 400 ps of the simulation are $a = 35.41$ Å, $b = 30.69$ Å. Compared with the initial cell parameters, a contraction of about 14% of the MD cell size is observed during the equilibration stage, whereas, however, the contraction or expansion is less than 1% during the data collection stage. This result indicates that the modified Dreiding force field is a reasonable choice for modeling the organoclay systems. The side view in Figure 4 clearly demonstrates the layering behavior of dioctadecyldimethylammonium chains within the interlayer space of montmorillonite. Pseudo-quadrilayer structure is observed and the alkyl chains in each layer adopt an orientation with their longest axis approximately parallel to the clay surface. The positively charged headgroups (nitrogen atoms) of quaternary alkyl chains are found close to the clay surface, which is expected due to the negative charge on the clay layers. The methyl carbon atoms observed in the middle layers are mainly attributed to the tail methyls in the long alkyl chains. It can be seen that all-trans conformation is hard to be identified from our simulated results. Thus, the idealized structural models, such as pseudo-trilayers and paraffin-type monolayers and bilayers, do not directly reveal the significant structural characteristics of alkyl chains. This finding is consistent with the experimental observations by the use of advanced techniques. For example, FTIR results show the substantial existence of the disordered, gauche conformation of alkyl chains even though the ordered, trans conformation is still predominant in most conditions.[10] In addition, an NMR study reported by Wang et al.[11] indicated the coexistence of ordered trans and disordered gauche conformations.

Conclusions

We have reported a molecular simulation investigation of the layering behavior and interlayer structure of quaternary alkylammonium modified clay minerals. The effects of alkyl chain length and layer charge on the basal spacings and interlayer structures have been studied in some detail. The simulated results agree well with the experimental results reported in the literature. The basal spacings increase with the increase of alkyl chain length and layer charge. In addition to the monolayer, bilayer, and pseudo-trilayer structures proposed from the structural models, a pseudo-quadrilayer structure has been observed in the organoclays modified by double alkyl chains. The alkyl chains in two HTMA− and three DDTMA−montmorillonites lie flat on the clay surface in bilayers. A mixture structure of paraffin-type and trilayer or quadrilayer is demonstrated in ODTMA− and DODTMA−montmorillonites, respectively. In these structures the alkyl chains do not lie flat within a single layer but interlace. Further studies are under way to investigate the effects of charge origin and their distributions within octahedral and tetrahedral sheets on the structure of interlayer molecular configuration, and to quantify the structure of the interlayer arrangement including alkyl alignment, order parameters, chain configuration, and trans and gauche conformation ratio.

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