Organoclays

Surface Structure of Organoclays**

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Mica with amphiphilic cations is of extensive technological interest. The mechanical stability of various plastics and rubbers, as well as barrier and optical properties in thin films, can be substantially improved by the addition of organically modified mica.[1] Besides, mica surfaces have proved to be an excellent model system for surface phenomena because the mineral can be cleaved into regular surfaces that extend over μm. The inorganic–organic interfaces have been the subject of numerous experimental studies[2–8] and theoretical investigations of related systems were performed at coarse-grained[9,10] and atomistic levels.[11–14] Accurate molecular dynamics simulation at the atomistic level supports the interpretation of experiments, for example, XRD and solid-state NMR data.[7,15] With our recent simulations,[13,14] the inclination angles of the alkyl chains and basal-plane spacings of the filler particles are reproduced in quantitative agreement with experiments, and predictions of the interface structure as well as conformational analyses of the hydrocarbon chains are possible. Herein, we report monolayer phases on mica platelets with alkali ions and surfactant ions of different length, at different temperatures, and we give insight into the occurring phase transitions.[6,7,13,14]

We consider that in dry mica surfaces in which 80% of the alkali ions, most commonly lithium in the reported experimental studies, are exchanged by organic ammonium ions of different length (Scheme 1) so that 20% of the alkali ions remain. This is a technologically realistic situation in view of the relatively difficult quantitative replacement of all interlayer cations (without intercalation). We investigate two borderline cases. The first simulated structure is a homogeneous mixture of surfactant ions and alkali ions on the mica surface. The second simulated structure refers to "phase-separation", that is, segregation of cations at the surface. In this case, we model the surfactant islands on mica in which the alkali exchange is quantitative. In both cases, we employ a mica model that contains the upper half of $5 \times 3 \times 1$ unit cells with realistic atomic charges.[13,16] For the homogeneous phase, twelve dialkyldimethylammonium ions (Scheme 1) and three potassium ions are attached, thus accounting for 80% cation exchange. For the simulation of "islands", 15

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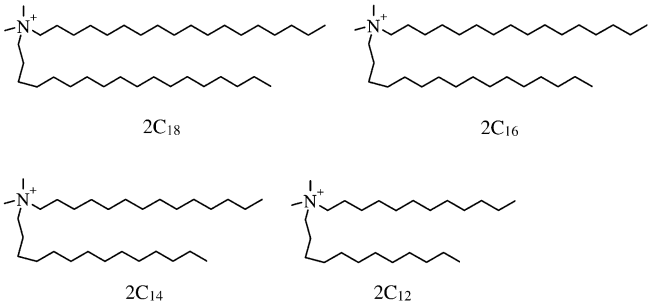

Scheme 1. The dialkyldimethylammonium ions used to modify the mica surface, and their abbreviations.

dialkyldimethylammonium ions are added to the surface, which corresponds to 100% ion exchange. All structures are periodic in the *xy* plane and open in the *z* direction.[17] At the outset, the plain, single-coated (mica-alkyl) structures are subjected to *NVT* dynamics (N = number of particles, V = volume, T = temperature; time step = 1 fs) at a given non-variable temperature and tilt angles of the alkyl chains were determined. Thereafter, duplicate assemblies (mica–alkyl–alkyl–mica) are constructed and equilibrated again (criterion: no more structural changes, > 400 ps). One hundred snapshots are subsequently taken at intervals of 1 ps to calculate the system's properties, such as basal-plane spacings and conformations of the alkyl chains. We conducted our calculations with the extended consistent force field 91, which is accurate in modeling organically modified silicates and was previously described together with other simulation details,[13,18,19] by using the Discover program from MSI.[20] We note that the *NPT* (P = pressure) ensemble is not required for the simulation (instead of *NVT*) because an added atmospheric pressure of ≈0.1 MPa does practically not affect the geometry of our condensed-matter system. The reasons are the elastic moduli of roughly 1 GPa in *z* direction and > 15 GPa in *x* and *y* direction.[21] Accordingly, differences in the ensembles are negligible (see also the analysis of the pressure and pressure profiles of our system in reference [14]).

Since we use a larger simulation box than in our previous study,[13,14] we consider the distribution of Al defects on the mica surface in a more elaborate way (Figure 1).[22–24] For a ratio Al/Si = 1:3 on the surface of natural mica, we see from Figure 1a that (1) 60% of the surface Si atoms are connected through O atoms to 1 Al atom and 2 Si atoms, (2) 20% of the Si atoms are connected through O atoms to 0 Al atoms and 3 Si atoms, and (3) 20% of the Si atoms are connected through O atoms to 2 Al atoms and 1 Si atom. Also, Al-O-Al contacts do not occur (Figure 1). With these statistical criteria, we obtain a more realistic distribution of Al-defect sites than in the regular arrangements.[13] As can be shown by molecular mechanics, the alkali ions and ammonium head groups preferably reside over cavities that contain two or three Al defects along their boundary (Figure 1b). This effect is a consequence of electrostatic forces, whereby precedence is given to the alkali ions, which have a greater charge density per volume relative to the more bulky tetraalkylammonium group. The distribution of the three Li^+ ions in the simulation

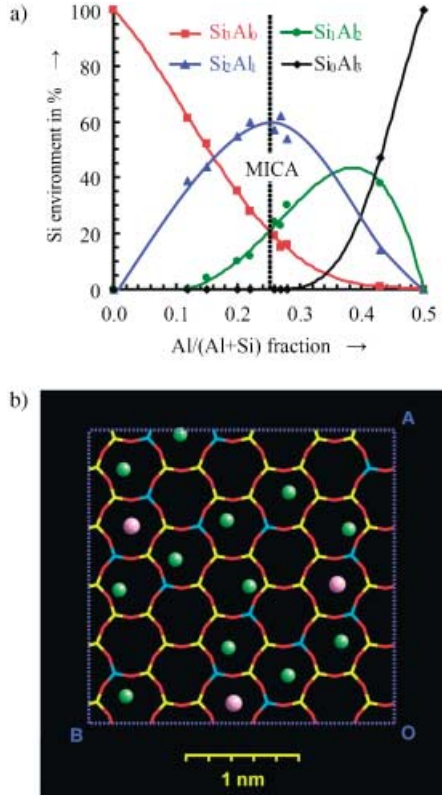

Figure 1. a) Si microenvironments on the surface of tetrahedral layers in phyllosilicates as a function of Al substitution, as observed by ^{29}Si NMR.[22–24] b) Application to our mica model. The proper statistical connectivity around Si (yellow) and Al (blue), locations of the alkali ions (pink pellets), and representative positions of the head-group N atoms (green pellets) of $2C_{18}$ ions on the mica surface are shown with 80% lithium exchange (oxygen red).

box for a homogeneous phase was chosen to be uniform (Figure 1b). Besides, we note that our simulation box with ≈10^1 alkyl chains is small compared to the 10^4 to 10^6 alkyl chains on a μm-sized mica flake.[5]

According to the simulation results after more than 400 ps, the positions of the ammonium head groups are relatively stable for all cations from $2C_{12}$ to $2C_{18}$, but rearrangements across surface cavities are, in principle, always possible and sometimes observed in the course of the simulations. At elevated temperatures, some ammonium ions relocate themselves into another cavity, especially in the homogeneous structures in which rearrangements are geometrically easier to achieve. A representative example of ammonium-head-group positions for $2C_{18}$ ions in the homogeneous phase is displayed in Figure 1b.

It is, however, not possible to decide from the simulations, which limiting structure (homogeneous or segregated phases) is preferred, because we cannot simulate a large system with two separate phases. Phase-separated and homogeneous structures can be distinguished by their different basal-plane spacings:[13] Phase-separated structures always have a higher basal-plane spacing than the corresponding homogeneous structure because the orientation of the surfactant chains is nearer to the surface normal. In Figure 2, the computed basal-plane spacings for one-phase and two-phase surfaces are

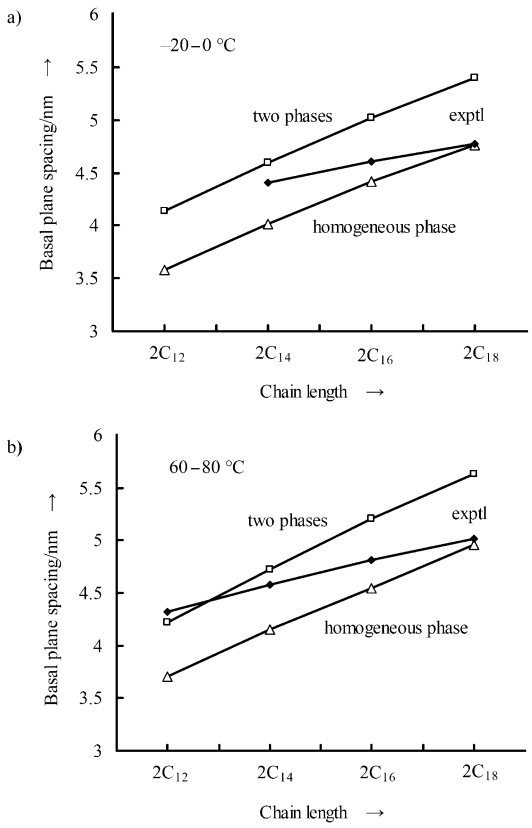

Figure 2. Computed basal-plane spacings for the two limiting cases of one homogeneous phase and two phases of dialkylammonium ions (80%) and alkali ions (20%) on mica. The experimental values are also shown and indicate the real structure. The overall structure is not dependent on the temperature.

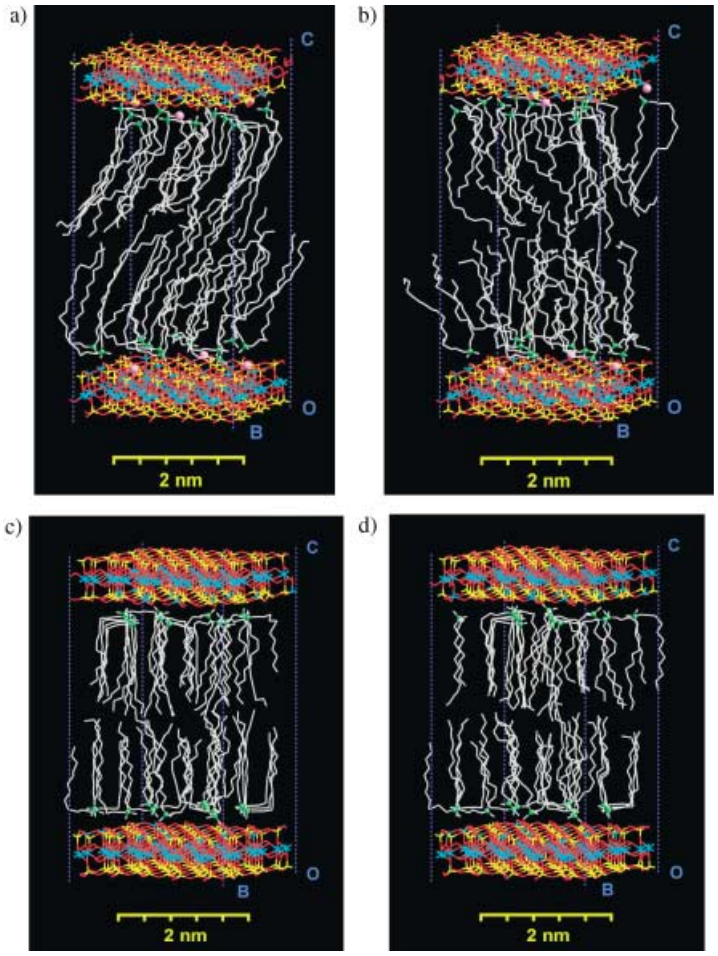

Figure 3. Snapshots of the homogeneous $2C_{18}$–K^+ phase (80% alkylammonium, 20% alkali ions) on mica after 400 ps of molecular dynamics a) at 0 °C and b) at 80 °C. A partial "melting" of the tethered chains is visible. Snapshots of C_{12} ions (as found in the islands) on mica c) at −20 °C and d) at 60 °C. The absence of a significant change and the almost perpendicular orientation of the alkyl chains are apparent.

compared with the experimental values[7] at low and high temperatures. Both graphs indicate that the $2C_{18}$ chains are homogeneously mixed with the alkali ions on the surface. With decreasing chain length, a trend towards phase segregation between organic chains and alkali ions is apparent. The $2C_{12}$ ions are fully organized into islands. The result is supported by the close match between experimental and computed basal-plane spacings for $2C_{18}$-mica and $2C_{12}$-mica (Table 1).

Also, the thermal behavior previously reported[7] for mica covered with $2C_{18}$, $2C_{16}$, $2C_{14}$, and, $2C_{12}$ chains can be explained:

1) For $2C_{18}$ chains, only one sharp phase transition is observed with DSC (differential scanning calorimetry) on heating, which is reversible upon subsequent cooling and reheating.[7] It is in accordance with a homogeneously mixed surface structure where the tethered alkyl chains undergo a reversible partial melting without significant rearrangements (see Figure 3 a/b). We count the number of *gauche* arrangements from the end of one C_n chain through the nitrogen atom to the end of the second C_n chain. The $2C_{18}$ chains, which have generically ≈ 4 *gauche*-torsions near the ammonium head group, have then roughly 3.3 *gauche* arrangements per C_{18} backbone and a significant tilt angle of 29° (Table 1) below the order-disorder transition at 55 °C.[7] In the partially molten state, no tilt angle can be specified.
2) For $2C_{14}$ chains, one sharp DSC signal of relatively small

Table 1: Computed characteristics:[a]

		Basal plane spacing		No. of *gauche* arrangements			Tilt angle
		Exptl[b]	MD-simulation	Total	Backbones	Max. poss.	
$2C_{18}$	0 °C	4.7–4.8	4.76	9.6	≈5.6	34	29 ± 5[c]
	80 °C	5.02	4.96	11.5	≈7.5	34	–[d]
$2C_{12}$	−20 °C	–	4.14	5.9	≈1.9	22	5 ± 4
	60 °C	4.33	4.22	6.7	≈2.7	22	5 ± 4

[a] For $2C_{18}$ on mica in which 20% of the alkali ions remain and for $2C_{12}$ ions on mica at 100% ion exchange (corresponding to "islands" in the 80% coverage systems): basal-plane spacings (in nm), average number of *gauche* incidences in the alkyl chains, and their tilt angles (in degrees) [b] Reference [7]. [c] The orientation in the layer with interspersed alkali ions is not very strict. [d] Too disordered.

enthalpy at $\approx 35\,^{\circ}C$ is observed upon heating, which produces a metastable phase.[7] This phase exhibits subsequent transitions on cooling and reheating at the same temperature, but they are weaker and indistinct.[7] These facts are in agreement with substantial accumulation of the C_{14} ions into islandlike structures and some mixed domains on the mica surface as can be concluded from Figure 2. There is a reduced possibility for conformational disorder (significantly smaller area of the DSC peak and less pronounced changes in the IR spectrum compared to $2\,C_{18}$ chains during the transition[7]). In the sharp transition, the chain backbones "partially melt" with some rearrangements of the ammonium head groups occurring simultaneously. Subsequent cooling and reheating reveals the instantaneous freezing and remelting of the obtained metastable phase with rearranged head group positions (less well-defined transition). The original structure is formed after several hours at room temperature because reverse rearrangements to reorganize the displaced head groups are slow at ambient temperature.[6,13]

3) For $2\,C_{12}$ chains, neither a phase transition in the IR spectrum nor a pronounced change in ^{13}C NMR signals at higher temperature is found (DSC results not available),[7] and the basal-plane spacing is also not significantly changing from 60 °C to 20 °C (not shown at −20 °C).[7] The chains seem to be tightly packed in the islands and too short for extensive conformational disorder (Figure 3c,d). The number of *gauche* incidences is only 1.0 to 1.3 per C_{12} backbone (Table 1). Therefore, no order–disorder transition is possible (Figure 3c,d) in contrast to the higher homologues.

We rationalize the phase behavior of the alkyl chains on mica under two aspects: We found previously[13] a gradual transition from separated phases towards a homogeneous phase upon increasing the saturation of the mica surface with alkyl chains. Herein, we illustrate that for a given degree of alkali exchange the length of the alkyl chains is also an important factor: long chains prefer a homogeneous phase, chains of a medium length lead to island formation, and very short chains might prefer a single-phase system again, as we surmise from the alkali-like nature of the head groups.

The arrangement on the mica surface, provided the exchange reaction is driven to equilibrium, is determined by thermodynamics. Between the two borderline cases, the structure with the lowest free energy is predominantly formed, depending on their difference in free energy, $\Delta A_{1\rightarrow 2}$ (see reference [25] for a different example). The difference in free energy between a one-phase system and a two-phase system, while the stoichiometry remains constant, $\Delta A_{1\rightarrow 2}$, is given at a certain temperature as

$$\Delta A_{1\rightarrow 2} = \Delta E_{1\rightarrow 2} - T\Delta S_{1\rightarrow 2}. \quad (1)$$

With respect to our system, we can interpret the quantities in Equation (1) as follows: $\Delta E_{1\rightarrow 2}$ is equal to the difference in average van der Waals energy between the chain backbones. For very low surface coverage, when the chains could not at all or scarcely interact in a one-phase system, $\Delta E_{1\rightarrow 2}$ is negative and proportional to the chain length. For higher surface coverage, the chains optimize their dispersive interactions by an appropriate inclination angle in both the one-phase and the two-phase system and $\Delta E_{1\rightarrow 2}$ approaches zero, independent of chain length. However, a small negative value remains because the dispersion interactions near the ammonium head groups in the islands of the two-phase structure are better. The entropy term $\Delta S_{1\rightarrow 2}$ accounts for changes in the configurational space of our system. As indicated by the phase transitions with changing temperature, the configurational space encompasses primarily order versus disorder in the chain backbones and, secondarily, order versus disorder in the head-group arrangement on the surface. In a two-phase system, chain disorder is substantially reduced because there is less conformational freedom in the islands than in the corresponding homogeneous structure. Accordingly, $\Delta S_{1\rightarrow 2}$ has a negative value. The difference in conformational freedom is more pronounced, the longer the chains are so that $\Delta S_{1\rightarrow 2}$ increases substantially its negative value with chain length. Another effect that makes always a small negative contribution to $\Delta S_{1\rightarrow 2}$ is the reduction of head-group disorder relative to the alkali ions in a two-phase system. This value is estimated to be $\Delta S_{head} = -0.5\,R$ for 80 % alkali exchange,[26] although it cannot be decoupled from the conformational entropy for longer chains. We may, however, approximately write

$$\Delta A_{1\rightarrow 2} = \Delta E_{vdW} - T(\Delta S_{head} + \Delta S_{chain}). \quad (2)$$

In consequence: (1) If the degree of ion exchange is so low that the chains cannot feel dispersive interactions with each other in a one-phase system even with extreme tilt, ΔE_{vdW} is strongly negative and overpowers the other contributions; thus, a two-phase system is formed. (2) If the chain length in such a system is increased such that ΔS_{chain} becomes highly negative, $\Delta A_{1\rightarrow 2}$ will be positive and a one-phase system is preferred. (3) If the chain length is reduced towards zero, ΔE_{vdW} will be very small, ΔS_{chain} disappears, and the negative term ΔS_{head} will lead to a slightly positive $\Delta A_{1\rightarrow 2}$ of $+0.5\,RT$. This difference in free energy is small so that intermediate arrangements are possible, however, with the tendency towards a one-phase system. These considerations lead to a kind of "phase diagram" of surface saturation versus chain length for alkylammonium-modified clay surfaces (Figure 4).

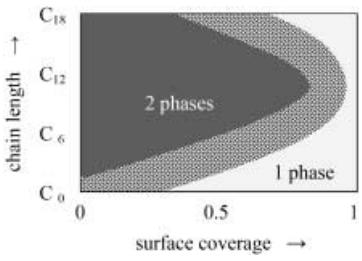

Figure 4. Approximate sketch of a "phase diagram" for alkylammonium-micas, which indicates the type of system found for various degrees of surface coverage (see reference [13]) and chain length.

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