Ethylene glycol intercalation in smectites. Molecular dynamics simulation studies

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Abstract

Molecular dynamics simulations were performed in order to study the interactions of ethylene glycol (EG) with smectite. The simulations have also taken into account that EG-smectite complex contains, as a rule, some adsorbed water molecules. The simulations results show that in the two-layer glycolate the content of water is of about 1.0 H_2O per half of the smectite unit cell. For a typical smectite a clear thermodynamic preference for one- or two-layer structure of the complexes is observed. The calculated radial distribution functions and running coordination numbers indicate that the H_2O and EG molecules compete for the coordination sites near the calcium ions in the clay interlayers. The EG and H_2O packing in the interlayer space is controlled by the differences in the total smectite layer charge, charge distribution, and the type of the interlayer cation, strongly affecting the basal spacing and the structure of the complex. Varying amounts of EG and water and the ratio EG/H_2O are, however, the most important factors influencing the extent of the smectite expansion.

A comparison of the two-layer structure obtained from MD simulations with previous models leads to the conclusion that the arrangement of EG molecules in the interlayers, typically used in simulations of clay X-ray diffractograms, can be modified. In contrast to the earlier Reynolds model (1965), the main difference is that the interlayer ions tend to change their positions depending on the specific distribution of the clay charge. In the case of montmorillonite, Ca^{2+} ions are located in the middle of the interlayer space, while for beidellite they are located much closer to the clay surface. Water molecules in this structure do not form distinct layers but are instead spread out with a tendency to be concentrated closer to the interlayer ions and to the smectite surface. One-layer structure of EG/water-smectite complex, characteristic of vermiculite is also proposed.

1. Introduction

The intercalation of ethylene glycol (EG) in smectites (glycolation) is widely used to discriminate smectites and vermiculites from other clays and from each other. During this process, EG molecules penetrate into the interlayer spaces of the swelling clays, leading to the formation of a two-layer structure (~17 Å) in the case of smectites, or a one-layer structure (~14 Å) in the case of vermiculites. Although this technique has been known since the pioneering work of MacEvan (1946), the arrangement of glycol molecules between smectite layers is still not fully ascertained.

The X-ray work of Reynolds (1965) gave some insights, providing a simplified structure of two-layer EG/water-smectite complex. In this structure, the interlayer Ca^{2+} cations, solvated by water, are located in the middle of the interlayer space between two layers of 1.7 CH_2-OH on each sides of the mid-plane. This gives together 1.7 EG molecules on each side, ie. 3.4 EG puc or 1.7 EG phuc. This EG structure together with 0.8 $H_2O/O_{10}(OH)_2$ forms EG/water/smectite complex having basal spacing of 16.9-17.0 Å. Bradley et al. (1963) presented a structure of EG-vermiculite complex which contains a single layer of the alcohol surrounded by sodium cations in the middle of the interlayer.The ratio between EG and vermiculite is two molecules per unit cell, while no water in the structure was assumed.

Further studies were focused on the effects of the interlayer ions and localization of the layer charge on the *d*-spacing of EG/water-clay complexes. It was confirmed that the basal spacing is larger for clay minerals with lower layer charge, but it also depends on the source of the charge, the type of the exchangeable cations, the particle size and the relative humidity (Harward and Brindley, 1965; Brindley, 1966; Harward et al., 1969; Środoń, 1980; Sato et al., 1992). Variable basal spacing of two-layer glycol complex was taken into account in the

techniques of measuring the layer ratio in illite-smectites (Środoń, 1980, 1981, 1984). The charge location in the tetrahedral sheet leads to lower values of basal spacing and to a different behavior upon solvation, than those observed when the charge is located in the octahedral layer. Moreover, it was found that smectites may form a one-layer glycol complex instead of the two-layer complex at very low relative humidity (Eberl et al., 1987), or even at intermediate humidity values but with K^+ as the exchange cation (Eberl et al., 1986).

More recently, Mosser-Ruck et al. (2005) have demonstrated several differences and inconsistencies between the methods of saturation with EG, suggesting that this procedure should be somehow standardized. The dynamics of glycolation for smectites saturated with different cations and equilibrated from various hydrates was studied by Svensson and Hansen (2010). It was found that during the reaction, a redistribution of H_2O molecules in the sample took place and higher hydrates were formed, proceeding to the formation of a two-layer structure of EG. This effect depends on the partial pressure of water and on the nature of the exchangeable interlayer cation. It can be attributed to the higher concentration of water in the interlayer space due to its substitution by EG.

In spite of the relatively abundant literature on the understanding and characterization of the EG/water-clays complex, in the contemporary computer programs which simulate the structures of smectite and illite-smectite from X-ray diffraction (XRD) data, the simplified structure of this complex developed by Reynolds (1965) is still widely used. The one-layer structure is only approximated, e.g. assuming interlayer cation and EG lying in the middle of interlayer spaces.

The present study was undertaken in order to investigate the structure of EG/water-clays complex in more detail using molecular dynamics (MD) simulations. It is focused on such important questions as: (i) does the structure proposed by Reynolds (1965) finds a confirmation in MD simulations; (ii) how much water is co-adsorbed with EG; (iii) how this

water is distributed in the clay interlayers; (iv) should the magnitude of clay basal spacing be attributable purely to the varying amounts of EG and water in the interlayer, or the varying thickness of the EG/water complex should also play a role?

2. Methods

The structural models of smectites were built on the basis of pyrophyllite crystal structure (Lee and Guggenheim, 1981), where several isomorphic substitutions were introduces at particular atomic sites. In most simulations, the structural model assumed the following composition, considered as the most common in the mixed layer clays (Środoń et al. 2009):

$$EXCH_{0.4}(Si_{3.96}Al_{0.04})(Al_{1.46}Fe_{0.17}Mg_{0.37})O_{10}(OH)_2 \quad (1)$$

Additional simulations were also performed for pure montmorillonite and beidellite with particular charges of 0.3 and 0.5 per half of the smectite unit cell (thereafter phuc). All these structures were built by substituting the relevant number of Al atoms with Mg and Si with Al. For all the models, the Mg/Fe/Al ordering in the octahedral sheets was set following the work of Ortega-Castro et al. (2010). The Al for Si substitutions in tetrahedral sheet were randomly distributed following the Löwenstein rule, which states that Al-O-Al linkages are excluded. The simulation supercell was built as 8×4×2 unit cells in the *a*, *b*, and *c* crystallographic directions, respectively. This resulted on the simulated system size of ca 41.6Å×36.1Å×*X*Å. The value of *X* varied depending on the amount of EG and water in the interlayer spaces.

The partial atom charges and other parameters of interatomic interactions of the smectite layers were described using the CLAYFF force field (Cygan et al., 2004), which has already proven itself quite successful in describing many clay-related systems in good

agreement with available diverse experimental data (e.g., Cygan et al., 2009; Suter and Coveney, 2009; Striolo, 2011; Michot et al., 2012; Marry et al., 2013). For the H_2O and EG molecules the flexible SPC model (Berendsen et al., 1981, Teleman, et al., 1987) and the AMBER (Hornak et al., 2006) force field were used, respectively. Ewald summation was applied to calculate the long range corrections to the Coulombic interactions (e.g., Frenkel and Smit, 2002) and the cutoff distance was set to 8.5 Å.

The structural models of EG/water-smectite complexes were constructed using the Monte Carlo approach with the help of the Towhee computer program (http://towhee.sourceforge.net). For these initial structures, energy minimizations were performed first, followed by *NPT*-ensemble MD simulations at 1 bar in temperature cycles using Langevin dynamics to control the temperature and Langevin piston to control the pressure. The time step to integrate the equations of atomic motion was set at 0.001 ps and the dynamic trajectories of all atoms and system properties were recorded every 1 ps. During the first period of every cycle, the temperature was set at 700 K and the simulation was run for 150 ps. Then the temperature was dropping in steps of 50 K, with short 10 ps equilibration MD runs at each step until the temperature reached 300 K. After that, each simulation continued at 300 K for 250 ps for which the equilibrium system properties were recorded for further analysis. Each cycle was repeated from two time origins (?), depending on the type of calculation. In the calculations of *z*-density profiles, one atom of the octahedral sheet was fixed at its initial position. However, its interactions with neighboring atoms were fully calculated during the simulation. All MD simulations were performed using the LAMMPS computer program (Plimpton, 1995).

3. Results and discussion

3.1. EG/water-smectite complex with variable content of EG

Experimental data show substantial preference for the formation of the EG/water-smectite complex as a two-layer structure, especially when solvated with liquid EG (e.g. Mosser-Ruck et al., 2005). It is therefore interesting to investigate the mechanism of this process, the thermodynamics of reaction, variation of the basal spacing and the structure of the complex.

In the present study, MD simulations with constant number of water molecules and varying number of EG molecules were performed for a smectite with the composition according to Środoń et al. (2009). The number of interlayer water molecules was set, according to Reynolds (1965), at 0.8 H_2O phuc.

The calculated evolution of the basal spacing (Fig. 1) confirms the formation of two possible structures: one- and two-layer complexes. The one-layer structure is well defined, marked with a plateau of the basal spacing at ca. 14 Å. This value corresponds to the composition of 0.8 EG/$O_{10}(OH)_2$, while for 1.0 EG/$O_{10}(OH)_2$ the basal spacing is even slightly above 14 Å. The two-layer structure is less defined and its basal spacing is in the range between 16.8 Å and 17.3 Å for the compositions of 1.7 EG/$O_{10}(OH)_2$ and 1.9 EG/$O_{10}(OH)_2$, respectively. These values explain the relatively large variability of the basal spacing, which depends on the mode of the complex preparation. The resulting basal spacing values also correspond very well with the values obtained by Reynolds (1965) who found them in the range of 16.9-17.0 Å for 0.8 H_2O/$O_{10}(OH)_2$ and 1.7 EG/$O_{10}(OH)_2$.

In order to study the thermodynamics of the glycolation process, the following reaction was considered:

water-smectite + EG → EG/water-smectite (2)

The calculation of ΔE for this reaction required computation of the potential energy of pure EG. For this purpose, a EG simulation box consisting of 330 molecules was built and equilibrated. Its potential energy was calculated with the same approach as used for the simulations of the complexes. The resulting value equals to 11.672 ± 0.006 kcal/mol.

The plot of ΔE for the reaction (2) (Fig. 2) shows two minima: a local one at ~1.0 EG/$O_{10}(OH)_2$ (corresponding to the one-layer structure) and a second global one at ~1.8 EG/$O_{10}(OH)_2$ (corresponding to the two-layer structure). The respective values of the basal spacing are equal to ~14.3 Å and ~17.0 Å, which agrees well with experimental data. The reaction of formation of the two-layer structure has much lower value of ΔE, indicating a strong preference for the formation of the two-layer structure for typical smectite. It should be noted, however, that ΔE is just the internal energy, not the Gibbs free energy of reaction. Therefore, the results cannot be directly applied for the prediction of chemical equilibria, because they do not take entropic factors into account.

To quantitatively assess the molecular mechanism of the EG/water-smectite complex formation, the atom-atom radial distribution functions (RDF) and the corresponding running coordination numbers (RCN) were calculated. The shape of the RCN obtained for the interlayer Ca^{2+} ion and the oxygen atom of EG (O_{EG}) (Fig. 3a) shows that with increasing number of EG molecules in the interlayer space, the number of O_{EG} atoms coordinated to Ca^{2+} ions atoms also increases. This effect can be attributed mainly to the gradual filling of the interlayer space around these ions, with simultaneous expulsion of water molecules from the neighborhood of Ca^{2+} ions and thus from the interlayer spaces. This is confirmed by the shape of the RCN calculated for Ca^{2+} ions and oxygen atoms of water (O_W) (Fig. 3b). The increasing number of EG molecules leads to the decrease in the number of water molecules in

196 the ion coordination spheres. This effect finds its confirmation in the study of Svensson and
197 Hansen (2010).
198 One important result visible in the RDF plots is that the dominating distance between
199 calcium ions and oxygen atoms of EG ($Ca\text{-}O_{EG}$) is 2.45 Å, which is almost identical to the
200 typical distances between calcium ions and oxygens of water ($Ca\text{-}O_W$). These values are
201 almost the same in spite of the structural differences between the complexes formed by both
202 of these molecules with calcium ions (Fig. 4), and do not depend on the number of EG
203 molecules in the interlayer space. Some differences are only visible at very low EG content in
204 the complex in the form of slight shift of both $Ca\text{-}O_{EG}$ and $Ca\text{-}O_W$ dominating distances by
205 about 0.025 Å. In the case of EG, the cis conformation generally dominates, with two oxygen
206 atoms coordinated to the calcium ion. Thus a chelate complex is formed. In contrast, water
207 molecule contains only one negative oxygen atom and therefore the structure of hydrated Ca^{2+}
208 is simpler.
209
210 **3.2. Two-layer EG/water-smectite complex with varying water content**
211
212 The original Reynolds (1965) study and further experimental evidences, like, e.g.,
213 variability of basal spacing of two-layer EG-smectite complex depending on relative humidity
214 (Hsieh, 1989), indicate that the complex EG-smectite contains water. In order to study this
215 effect, the EG-smectite complex containing a constant number of EG molecules:
216 1.7 $EG/O_{10}(OH)_2$ (after Reynolds, 1965) was simulated with variable amounts of water.
217 The plot of clay basal spacing versus variable water content (Fig. 5) indicates that,
218 with increasing number of water molecules, the basal spacing increases more or less linearly.
219 However, for the structures with very low water content the value of basal spacing does not
220 change. This plateau corresponds to ~16.5 Å. These results confirm the data of Hsieh (1989),

who observed a relatively linear relationship between relative humidity and the basal spacing, and indicate that the amount of water in EG/water-smectite complex may vary.

In order to calculate the thermodynamics of the hydration reaction of EG-smectite complex, the value of ΔE of the following reaction was calculated:

$$\text{EG-smectite} + \text{water} \rightarrow \text{EG/water-smectite} \quad (3)$$

The potential energy of water was taken into account by a separate MD simulation for a water box consisting of 508 molecules. The resulting value is - 9.83 ± 0.08 kcal/mol. Within the statistical accuracy, this value is identical to the value of - 9.8823 kcal/mol calculated for the SPC water model by Mark and Nilsson (2001). The values of ΔE for the reaction (3) for different water contents in the EG-smectite complex (Fig. 6) indicate that the most probable content of H_2O in this complex with EG is 1.0 phuc. This value corresponds quite well to the value of 0.8 calculated by Reynolds (1965). It should be noted, however, that the hydration levels of the complex can vary in a relatively broad range, so it should be taken into account both in the standardization of the preparation procedure of EG/water-smectite complex and in the modeling and refinement of the XRD data. It should be also noted that the obtained estimates are only semi-quantitative because, as it was mentioned above, the entropic factors were not taken into account.

Radial distribution functions and running coordination numbers provide further insights into the mechanism of EG and water co-adsorbtion in smectite. From the RDF obtained for the pair of Ca^{2+} ion and O_{EG} (Fig. 7a) it is visible that the oxygen atoms are located at the distance of ~2.45 Å from the calcium ions. The second maximum at ~4.6 Å, which corresponds to the second coordination sphere, is of very small height. The increasing water content in the structure leads to the lowering of the coordination number of O_{EG} around

calcium ions, which is visible in the RCN plots (Fig. 7a). This indicates that water partially expels EG molecules from the close neighborhood of the calcium ions in the interlayer space. This finds further confirmation in the shape of the RCN calculated for Ca^{2+} ion and the oxygen of water (O_W) (Fig. 7b). The more water in the structure, the higher the running coordination number for the Ca^{2+}-O_W pair is. Independent on the water content in the structure, RDF plots show that the O_W and O_{EG} are located in the first coordination sphere of Ca^{2+} at the distance of ~2.45 Å. A comparison of these results with Fig. 3 indicates that EG and water molecules compete for the coordination of calcium ions in the smectite interlayers.

3.3. Two-layer EG/water-smectite complex with different smectites

Many previous studies have shown that the basal spacing of the EG/water-smectite complex varies depending on the layer charge and its source/location (e.g., Sato et al., 1992). Therefore, it is interesting to check if the basal spacing will differ for different smectites in the case of the same/fixed amounts of EG and water in the interlayer. These values were set after Reynolds (1965) at 0.8 H_2O and 1.7 EG phuc. Beidellite and montmorillonite with the layer charge of 0.3 and 0.5 phuc were chosen.

The results show that the basal spacing varies in a very broad range – visibly higher values are reached for smectites with lower charges (Table 1). Taking into account the uncertainty of the basal spacing calculation, the obtained values do not depend much on the location of the charge. Therefore, the experimentally found differences in the basal spacing between beidellite and montmorillonite (e.g., Sato et al., 1992) should be attributed to the differences in the amounts of adsorbed EG and water.

Although the location of the charge does not have substantial influence on the basal spacing, its impact on the structure of the EG/water-smectite complex is very important (Fig.

8). In the case of beidellite, which has layer charge located entirely in the tetrahedral sheet, Ca^{2+} ions tend to be adsorbed close to the surface (Fig. 8a, b). For low charge montmorillonite, Ca^{2+} ions are located generally in the middle of the interlayer (Fig. 8c). In the case of montmorillonite with higher charge, the tendency of ions to be adsorbed closer to the surface is visible. However, a lot of ions are still located in the middle of the interlayer space (Fig. 8d).

3.4. Two-layer EG/water-smectite complex with different interlayer ions

The nature of the interlayer cation was found to affect the structure of the EG/water-smectite complexes (e.g. Sato et al., 1992). Potassium-saturated and ammonium-saturated smectites with low layer charge show the highest basal spacing after glycolation, much higher than, e.g., their sodium- or calcium- saturated analogues (Środoń, 1980). For high-charge K-smectites the one-layer structure is observed (Eberl et al., 1986). The transition from the two-layer to one-layer structure clearly reflects the variable amounts of EG and water in the interlayer. The variation in the basal spacing of the two-layer complex may be due to different factors. To investigate this effect, smectites with the same contents of EG and water and with different interlayer cations were simulated (Table 2).

The results confirm the experimental data (Środoń, 1980) that the basal spacing is higher for monovalent cations, which seems to be generally intuitive because of the two reasons:

- larger ion radius of these ions,
- two times higher content of the monovalent cations that balances the same negative charge of smectite.

However, there is also a distinct variability of the basal spacing in the case of monovalent cations. For potassium this value is very high: 17.08 Å, in contrast to 16.859 Å for sodium. This effect can be explained partially by the larger ion radius of potassium, but it also reflects a different interlayer structure, namely the fact that potassium ions tend to concentrate closer to the clay surface, because of their lower hydration energy than that of the sodium ions, which tend to concentrate in the middle of interlayers (Fig. 9). Additionally, Na^+ ions, due to their relatively small size, can deeper penetrate the pseudohexagonal gaps in the tetrahedral sheets, which can also affect the basal spacing.

3.5. Comparison of MD-simulated structures with previous experimental data

One of the most important objectives of this work was to check if the structure of the EG-smectite complex obtained from the Fourier analysis of the experimental X-ray data (Reynolds, 1965) agrees with the results of molecular dynamics simulations. The experimental structure was obtained for low charge montmorillonite (ca. 0.33 phuc), therefore the results calculated for montmorillonite with the layer charge of 0.3 were taken for comparison. Due to the fact that from XRD analysis of oriented specimens it is very difficult to discriminate the type of atoms contributing to the electronic density, the MD profile was transformed into electronic density profiles. The interlayer configurations of Reynolds (1965) were transformed taking into account temperature factors *B*. The relation between the *B* factor and the full-width at half maximum intensity of the Gaussian distribution was calculated from equation (e.g. Dazas et al., 2013):

$$FWHM = \frac{\sqrt{B}\sqrt{\ln(2)}}{\pi} \quad (4)$$

The electronic density profiles resulting from the MD simulation show some discrepancies in comparison to the suggested electronic distribution of Reynolds (1965)

structure (Fig. 10). The position of EG from Reynolds (1965) agrees quite well with that of MD simulations (EG is considered as a sum of contributions from its carbon and oxygen atoms). According to the MD simulations, calcium ions are mostly located close to the middle of the interlayer (two maxima of the thick solid line near ~-0.7 Å and +0.7 Å), which is in agreement with the Reynolds model. The largest difference between the results of MD simulations and those obtained from the Fourier analysis of experimental XRD data is the position of water molecules, which tend to concentrate closer to the smectite surface and not in the middle of the interlayer space. Generally, comparisons of the total electronic density profiles (thick lines in Fig. 10) show very small difference in the contributions of EG but much larger differences in the middle of the interlayer occupied by cations and water. This indicates that, although the structure of Reynolds (1965) has been successfully used to model EG/water/smectite complexes, some improvement of this structure is possibly necessary.

In the case of smectites with different values and localizations of the charge, the discrepancy between the MD results and experimental data (Reynolds, 1965) are much more apparent (Fig. 8). This indicates that the experimental EG/water-smectite structure can be applicable only to some specific types of smectites (i.e., montmorillonite with low charge). In other cases, different atomic distributions should be used in the modeling of XRD data.

It was found experimentally that EG can form one-layer structure and also mixed layered structures, composed of one- and two-layered ones. Because of the absence of a good model for the EG one-layer complex, it was important to study this structure and propose such a model.

To build this structure, the composition of 1.0 $EG/O_{10}(OH)_2$ and 0.8 $H_2O/O_{10}(OH)_2$ (corresponding to local minimum in Fig. 2) in the interlayer space were assumed. The typical smectite structure of Środoń et al. (2009) was taken into account. For the EG atoms (Fig. 11) two maxima are visible on both sides from the middle of the interlayer: one is due to the

carbon atoms, while the second one - due to the oxygen atoms located closer to the surface and to the calcium ions. Ca^{2+} ions are mainly located in the middle of the interlayer space. Water molecules tend to coordinate the calcium ions and basal oxygens of the clay surface.

A comparison of total electronic density profile with the density profile of Bradley et al. (1961) shows substantial differences (Fig. 12). These are related to the fact that Bradley et al. (1961) obtained their structure for vermiculite, which has on average two times larger layer charge than a typical smectite, and also for dry EG. Water molecules should, however, be assumed to be present in the structure, as can be found in the data of Hsieh (1989). Important difference lies also in the basal spacing of these two structures: 12.9 Å for Bradley et al. (1961) and 14.3 Å for studied structure. It should therefore be noted that the obtained structure does not correspond to the structure of complex in vermiculite but can rather be related to the one-layer contribution in mixed one- and two- layered EG smectite complexes.

4. Summary and Conclusions

The results of molecular dynamics simulations of EG/water-smectite complexes were compared to the earlier experimental data. The thermodynamic preference of two-layer structures was confirmed by the simulations. The water content in the EG/water-smectite complexes is estimated to be close to 1.0 H_2O phuc. Generally, H_2O and EG molecules compete for the coordination sites around Ca^{2+} ions in the interlayers.

The simulation results allow us to conclude that the model structure used for over 40 years in the interpretation of XRD measurements of smectites and illite-smectites (Reynolds, 1965) should be revised. EG forms two distinct layers between the silicate sheets, but the interlayer ions can form both inner- and outer-sphere complexes with water, not only the outer-sphere ones as it was previously assumed. Water molecules in this structure are found

not only to concentrate close to the calcium ions in the middle of the interlayer, but also to adsorb closer to the clay surface, like the EG. An atomistically detailed model of the one-layer complex is also proposed based on the MD simulations.

It was confirmed that the thickness of the glycol complex strongly depends both on the nature of the interlayer cation and on the total layer charge, but to a lesser extent also on the charge location. Therefore, this variable thickness of the complex has to be taken into account in the XRD pattern modeling.

One has to bear in mind, however, that any results of molecular simulations are, to some extent, force field dependent. The CLAYFF (Cygan et al., 2004) used in our present work has already proven itself among the best performing force field parameterizations for many clay-related simulations (e.g., Heinz et al., 2005; Striolo, 2011; Michot et al., 2012; Marry et al., 2013). Nevertheless, new improvements are continued to be made. In particular, a new INTERFACE force field, specifically designed to model organo-inorganic clay-related nanostructures has been published when this paper was already under revision (Heinz et al., 2013). Its application in our future studies of the smectite-EG systems should be expected to further improve the currently presented results and make them more quantitatively accurate.

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Figure captions

Figure 1. Simulated basal spacing variability with increasing content of EG in EG/water-smectite complex containing 0.8 $H_2O/O_{10}(OH)_2$.

Figure 2. ΔE of the glycolation reaction calculated for the water-smectite complex containing 0.8 $H_2O/O_{10}(OH)_2$.

Figure 3. Radial distribution functions (RDF, left scale) and running coordination numbers (RCN, right scale) calculated for: a) calcium atom – oxygen of EG ($Ca\text{-}O_{EG}$); b) calcium atom – oxygen of water ($Ca\text{-}O_W$), in the structures of EG/water-smectite complex containing 0.8 $H_2O/O_{10}(OH)_2$ with varying EG content.

Figure 4. Ca^{2+} coordination with (a) EG and (b) water in the interlayer space of smectite.

Figure 5. Simulated basal spacing variability with increasing water content in EG/water-smectite complex containing 1.7 $EG/O_{10}(OH)_2$. Line is provided to guide the eye only.

Figure 6. ΔE (kcal/mol) calculated for the reaction of hydration of the EG-smectite complex. Line is provided to guide the eye only.

Figure 7. Radial distribution functions (RDF, left scale) and running coordination numbers (RCN, right scale) calculated for: a) calcium atom – oxygen of EG ($Ca\text{-}O_{EG}$); b)

520 calcium atom – oxygen of water ($Ca\text{-}O_W$), in the structure of EG/water-smectite
521 complex containing 1.7 EG/$O_{10}(OH)_2$ with varying water content.
522
523 **Figure 8.** Atomic density profiles (arbitrary units) of calcium, carbon, oxygens of EG and
524 water obtained from MD simulations for bilayer EG/water-smectite complex with
525 different smectites: a) beidellite, charge = 0.3; b) beidellite, charge = 0.5; c)
526 montmorillonite, charge = 0.3; d) montmorillonite, charge = 0.5.
527
528 **Figure 9.** Atomic density profiles (arbitrary units) of calcium, sodium, potassium, carbon,
529 oxygens of EG and water obtained from MD simulations for bilayer EG/water-
530 smectite complex for a typical smectite substituted with different cations: a)
531 calcium; b) potassium; c) sodium.
532
533 **Figure 10.** Atomic density profiles (arbitrary units) of calcium, carbon, oxygen of EG and
534 water obtained from MD simulations for two-layer EG/water-smectite complex.
535 The distribution of EG and water atoms according to Reynolds (1965) is shown
536 for comparison as white/grey and black bars. The location of the smectite surface
537 is indicated by vertical dashed lines.
538
539 **Figure 11.** Atomic density profiles (arbitrary units) of calcium, carbon, oxygen of EG and
540 water obtained from MD simulations for one-layer EG/water-smectite complex.
541 The location of the smectite surface is indicated by vertical dashed lines.
542