



## Research Paper

## 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 simulation results show that in the two-layer glycolate the content of water is about 1.0 H<sub>2</sub>O per half of the smectite unit cell. For a typical smectite a clear thermodynamic preference for one- or two-layer structure of the complexes was observed. The calculated radial distribution functions and running coordination numbers indicate that the H<sub>2</sub>O and EG molecules compete for the coordination sites near the calcium ions in the clay interlayer spaces. The EG and H<sub>2</sub>O 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<sub>2</sub>O 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 interlayer spaces, typically used in simulations of clay mineral 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 mineral charge. In the case of montmorillonite, Ca<sup>2+</sup> ions are located in the middle of the interlayer space, while for beidellite they are located much closer to the clay mineral 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.

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## 1. Introduction

The intercalation of ethylene glycol (EG) in smectites (glycolation) is widely used to discriminate smectites and vermiculites from other clay minerals and from each other. During this process, EG molecules penetrate into the interlayer spaces of the swelling clay minerals, 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 MacEwan (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<sup>2+</sup> cations, solvated by water, are located in the middle of the interlayer space between two layers of 1.7 CH<sub>2</sub>–OH on each side of the mid-plane. This gives together 1.7 EG molecules on

each side, i.e. 3.4 EG per unit cell. This EG structure together with 0.8 H<sub>2</sub>O/O<sub>10</sub>(OH)<sub>2</sub> 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 space. 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*-value of EG/water–clay mineral 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 (Brindley, 1966; Harward and Brindley, 1965; Harward et al., 1969; Sato et al., 1992; Środoń, 1980). 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.

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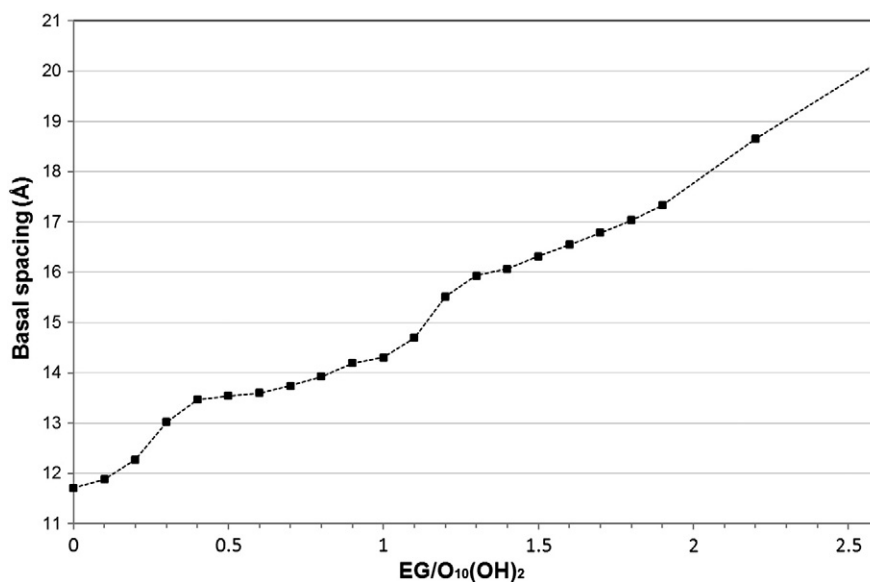


Fig. 1. Simulated basal spacing variability with increasing content of EG in EG/water–smectite complex containing 0.8 H<sub>2</sub>O/O<sub>10</sub>(OH)<sub>2</sub>.

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<sup>+</sup> 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<sub>2</sub>O 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–clay minerals 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–clay minerals 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

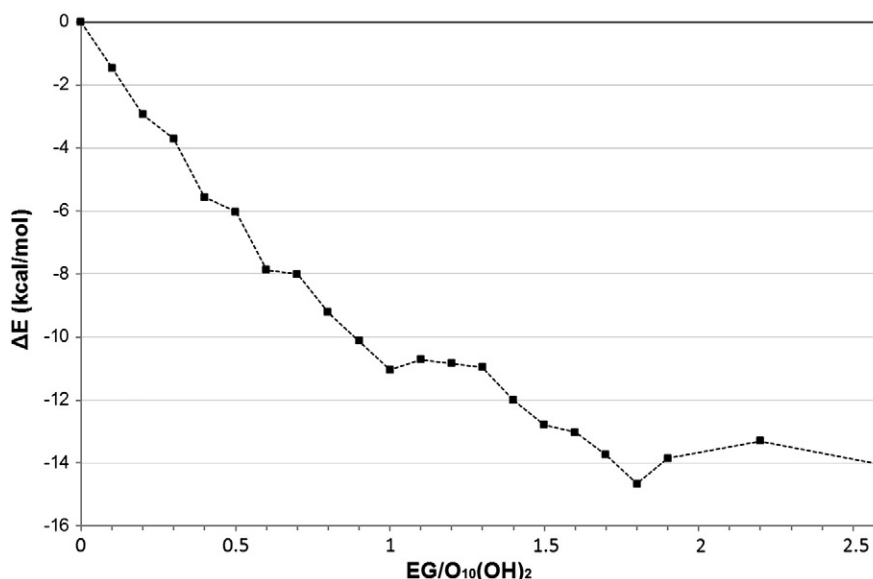


Fig. 2.  $\Delta E$  of the glycolation reaction calculated for the water–smectite complex containing 0.8 H<sub>2</sub>O/O<sub>10</sub>(OH)<sub>2</sub>.

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