

## ADSORPTION AND INTERCALATION OF SMALL MOLECULES ON KAOLINITE FROM MOLECULAR MODELLING STUDIES

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Kaolinite is an abundant natural material with considerable industrial potential. Despite its simple composition ( $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$  and layered structure being a phyllosilicate), it is notable that only little known about the interaction of kaolinite sheets with small organic reagents at the molecular level. These assumed to govern intercalation, delamination, and then the complete exfoliation processes. A common methodology to model the molecular structure of kaolinite is the employment of periodic boundary conditions. The application of molecular cluster models gained importance nowadays by capitalizing on the availability of wide range of theoretical tools for describing structural features and reaction mechanisms. In this study, we present our results using theoretical methodologies and modelling strategies from literature that are applied for adsorption and intercalation of urea, ethylene glycol, and potassium acetate.

**Keywords:** kaolinite, intercalation, adsorption, hydrogen bonding, molecular cluster model

### Introduction

A significant hindrance in the design, optimization, and execution of experimental research involving clay minerals is the lack of our understanding of molecular level processes occurring at the outer (adsorption) or at the inner surface (intercalation) of layers of clay. Molecular modelling approaches have the potential to aid experimental design, mitigating cost of chemicals used, rationalizing unsuccessful trial-and-error experiments, and thus contributing to tailored utilization of clay minerals as industrial raw materials.

Given the periodic nature of the crystalline clay minerals, a common approach in modelling is the use of periodic boundary conditions [1–4]. A competitive approach is based on molecular cluster models [5–9]. An advantage of using the latter is the availability of a broad range of quantum chemical tools for studying the local chemical environment of the site(s) of adsorption and/or intercalation.

In the given study, we have utilized kaolinite, which is a member of the 1:1 class of clay minerals. This implies that the layers of this simplest phyllosilicate are composed of octahedral (O) and tetrahedral (T) sheets. The O-sheet contains hexacoordinate  $\text{Al}^{3+}$  ions, while the T-sheet has tetracoordinate  $\text{Si}^{4+}$  ions. The O- and T-sheets are connected *via* tricoordinate oxide anions, while the separate OT or 1:1 layers are connected through hydrogen bonds (H-bonds) (Fig. 1).

### Computational Methods

The computational models were created from the unit cell of the experimental X-ray diffraction structure of crystalline kaolinite [10]. We will discuss results here for models for separate O- and T-sheets with

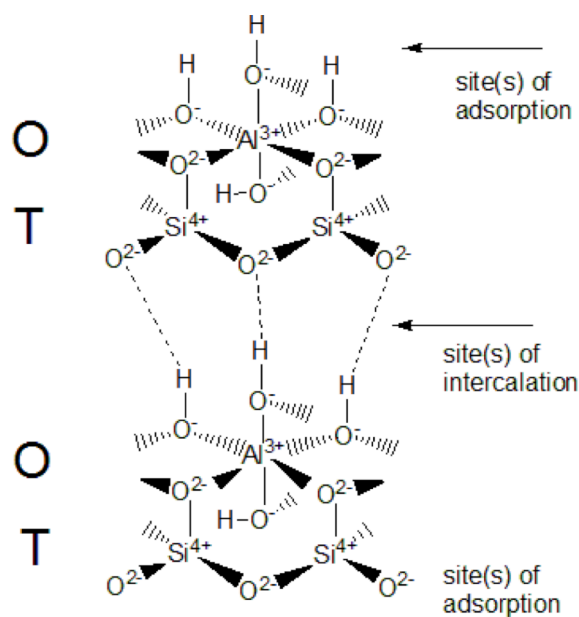


Figure 1: Schematic presentation of adjacent OT layers of delaminated kaolinite

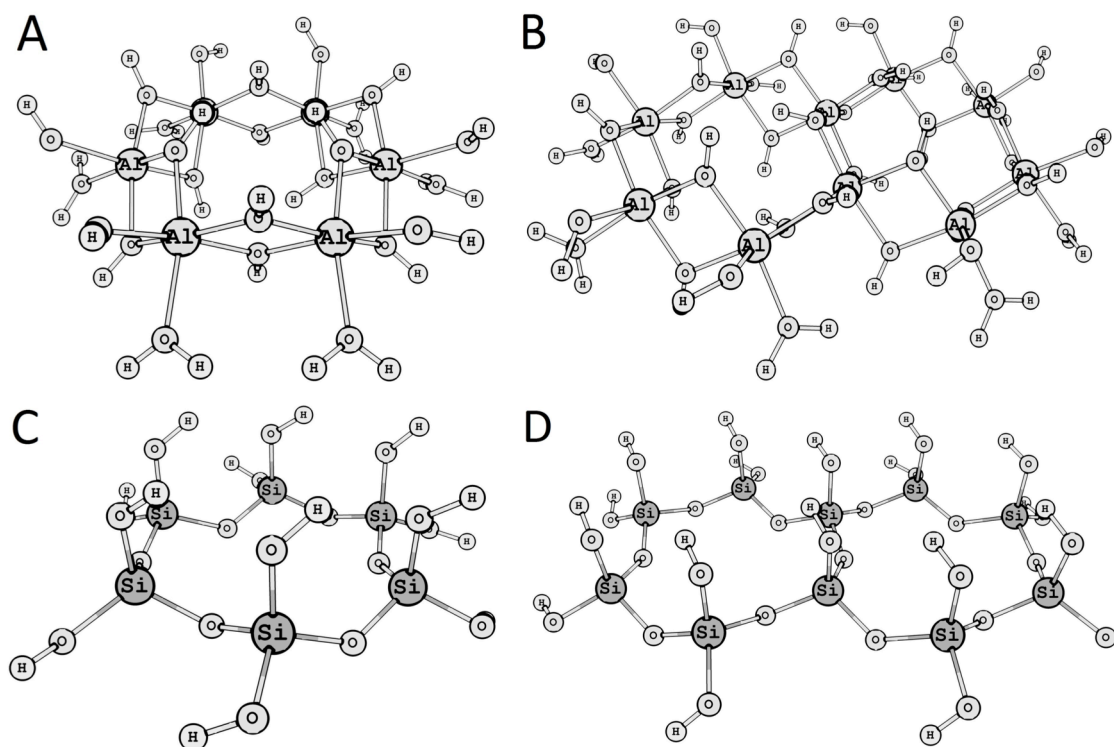


Figure 2: Computational models for the hexagonal honeycomb-like units of [6Al] (A) and [10Al] (B) octahedral, [6Si] (C) and [10Si] (D) tetrahedral cluster models for O- and T-sheets of kaolinite, respectively

stoichiometry of  $\text{Al}_6\text{O}_{24}\text{H}_{30}$  and  $\text{Si}_6\text{O}_{18}\text{H}_{12}$ , respectively (Figs. 2A and C). These are the smallest possible cluster models for the hexagonal, honeycomb like units of the O- and T-sheets. In addition, two larger models of  $\text{Al}_{10}\text{O}_{38}\text{H}_{46}$  and  $\text{Si}_{10}\text{O}_{29}\text{H}_{18}$  were also considered (Figs. 2B and D) for the larger intercalating agents (ethylene glycol, potassium acetate). The unit cell of kaolinite was multiplied in all crystal dimensions to create a super-cell. This was then truncated to the cluster models presented above. The charge neutrality was achieved by terminating dangling bonds with protons at the periphery of the models. The initial positions of the adsorbent reagents were set at the centre of the hexagonal honeycomb-like unit of both O- and T-sheets and it was allowed to fully relax during optimizations.

Given that the computational models shown in Fig. 2 are simplifications of the experimental crystal structure environment, structural constraints were applied during geometry optimizations. In all calculations, the atoms of the organic reagents, the surface hydroxide groups ( $s\text{-HO}^-$ ) of the O-sheet, and the bridging oxide groups ( $b\text{-O}^{2-}$ ) of the T-sheets were allowed to move, while the positions of the rest of the atoms were kept fixed. After structural optimizations, the positions and relative arrangements of the organic reagents with respect of the outer and inner surfaces, the shortest distances of possible ion/dipole interactions or H-bonds were noted. For computational models of T...reagent...O intercalation, the basal spacing was set at the beginning of calculations to the experimental values of 10.7, 9.5, 11.5 Å, and 14.2 Å for urea [11], ethylene glycol [12], and potassium acetate in the absence or in the presence of water [13], respectively.

The calculations were carried out using the B3LYP hybrid density functional [14,15] with LANL2DZ basis set [16] as implemented in Gaussian09 [17]. The interaction energies were not considered in this work due to the modest level of theory and lack of consideration of explicit or implicit solvation shell. The main focus of the given work is to establish initial structural models for rationalizing experimental observations and prepare for more advanced computational modeling. The optimized structures presented in this work were made available at [computational.chemistry.montana.edu/SI](http://computational.chemistry.montana.edu/SI).

## Results and Discussions

### Kaolinite-Urea Interactions

The lowest energy, optimized structure for the adsorbed urea on O-sheet can be characterized by two short O(urea)... $s\text{-HO}^-$  distances of 1.92 and 1.95 Å, while one of the amide groups approaches the opposite  $s\text{-HO}^-$  group within 1.73 Å as shown in Fig. 3A. The presence of both donor and acceptor interactions for the same reagent molecule result in a tilted orientation of the urea. An alternative orientation in which only the carbonyl group is interacting with three  $s\text{-HO}^-$  groups (see below for intercalation model) was not found to be a stationary structure at this level of theory. Figs. 3B and C illustrate the two different orientations of the urea at the T-sheet, where the amide groups are H-bonded to the  $b\text{-O}^{2-}$  groups of the same  $\text{Si}^{4+}$  ion (*geminal*) with  $\text{NH}\dots b\text{-O}^{2-}$  distances of 2.03 and 2.12 Å or two different  $\text{Si}^{4+}$  ions (*vicinal*) with 2.02 and 2.08 Å

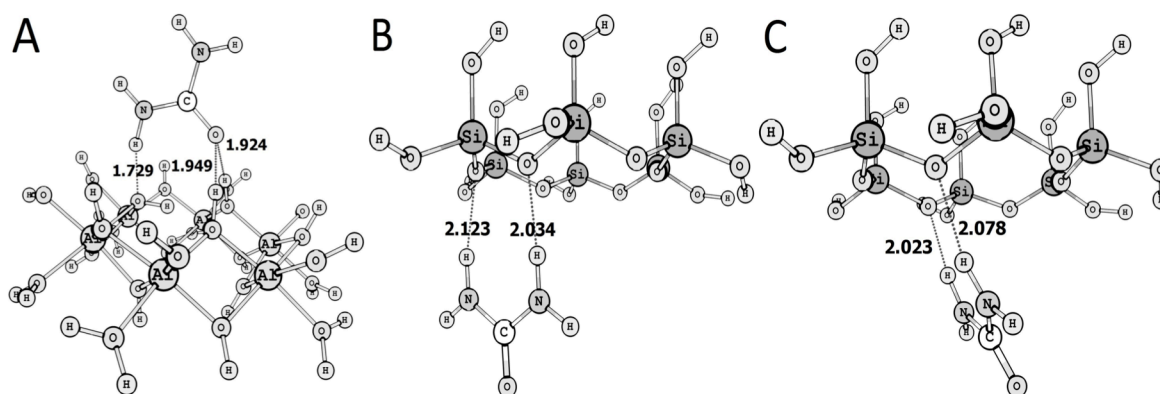


Figure 3: Computational models for urea adsorption at O- (A) and T-layers in *geminal* (B) and *vicinal* (C) arrangements

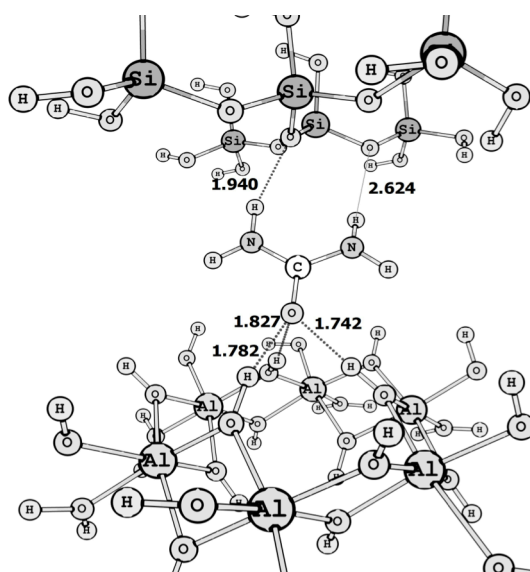


Figure 4: Computational model for intercalation of urea in kaolinite

distances. The energetic difference between the geminal and vicinal coordination is not significant (less than 10 kJ mol<sup>-1</sup>) at this level of theory.

When the adsorption of urea is considered simultaneously at both the O- and T-sheets, a model can be obtained for a plausible structure of the urea intercalated between two OT-layers (Fig.4). In this computational model, the carbonyl group of urea forms three H-bonds at 1.74, 1.78, and 1.83 Å distances with three *s*-HO<sup>-</sup> groups of the hexagonal O-sheet cross from each other. At the same time, the intercalated urea forms two H-bonds with the *geminal* *b*-O<sup>2-</sup> groups at 1.94 and 2.62 Å distances. The tilted orientation of the urea is the consequence of the experimental basal spacing of 10.7 Å, which was kept fixed during the structural optimizations. It is important to recognize that according to our computational model, there is not enough room between the expanded layers of kaolinite to accommodate urea perpendicular to the basal planes or with parallel carbonyl groups to the crystallographic 'c' axis.

#### Kaolinite-Ethylene Glycol Interactions

Ethylene glycol is generally used in exchange-intercalation as a step followed by initial dimethyl

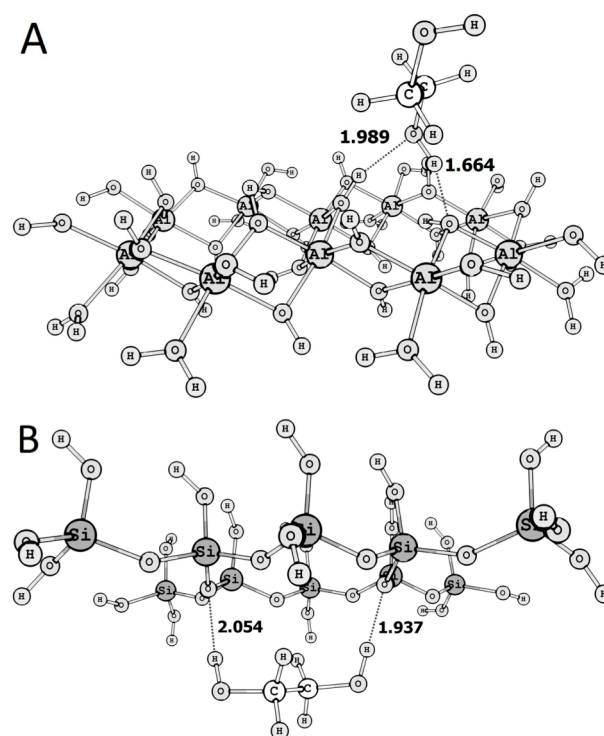


Figure 5: Computational models for the adsorption of ethylene glycol at the (A) O- and (B) T-sheets

sulfoxide or potassium acetate intercalation. As shown in Fig.5A, the donor interaction between the reagent hydroxyl group and the Al<sup>3+</sup> bound *s*-HO<sup>-</sup> is much shorter (1.66 Å) than those seen for urea adsorption (1.73 Å), while the acceptor interaction is slightly longer (1.99 Å). Given that the *b*-O<sup>2-</sup> groups of the T-sheet can only act as H-bond acceptors with ethylene glycol, the reagent spans the entire hexagonal honeycomb-like unit of the T-sheet by forming longer (2.05 and 1.94 Å), thus weaker H-bond interactions than with the O-sheet.

The complementarity of the O- and T-sheets with respect of being H-bond donor and acceptor, respectively, allows for an ideal orientation of the functional groups of ethylene glycol for maximizing the strength of H-bond interactions. The O-sheet forms a short (1.61 and 1.79 Å) interaction between the O(glycol)...*s*-HO<sup>-</sup> groups. The T-sheet accepts the HO groups of the ethylene glycol at 1.73 and 1.88 Å distances. Comparison of the urea (Fig.5) and ethylene

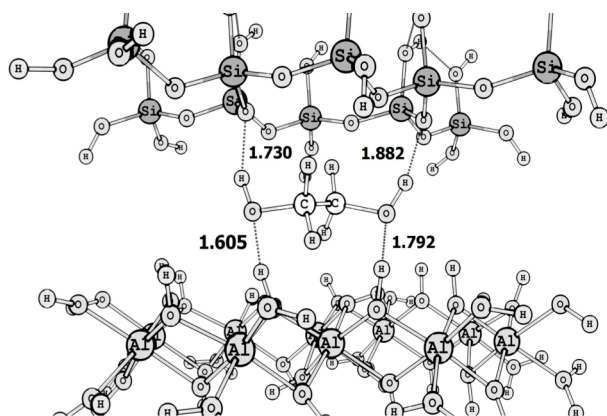


Figure 6: Computational model for ethylene glycol intercalation in kaolinite

glycol (Fig.6) intercalated models, the network of interactions between the layers and reagents parallel well the different experimental basal spacing (10.7 vs. 9.5 Å, respectively). While the urea opens the interlayer space more; however, it anchors the two layers with a stronger set of interactions than ethylene glycol. This can be correlated with the limited reactivity of urea/kaolinite complex in exchange intercalation; while ethylene glycol often provides the last step before complete delamination and exfoliation of clays.

#### Kaolinite-Potassium Acetate Interactions

A limitation of the *in vacuo* models used in this study greatly hinders the dissociation of the potassium ion from acetate and thus in both adsorption models the cation remained at the centre of the hexagonal honeycomb-like model for the O- and the T-sheets in the vicinity of the anion acetate. In addition, the ionized carboxylic group of the reagent form two short and thus strong H-bonding interactions at 1.65 and 1.89 Å distances with two germinal *s*-HO<sup>-</sup> groups of the O-sheet. The shortest acetate C-H...*b*-O<sup>2-</sup> distance in Fig.7B is 2.95 Å, which indicates the presence of weak

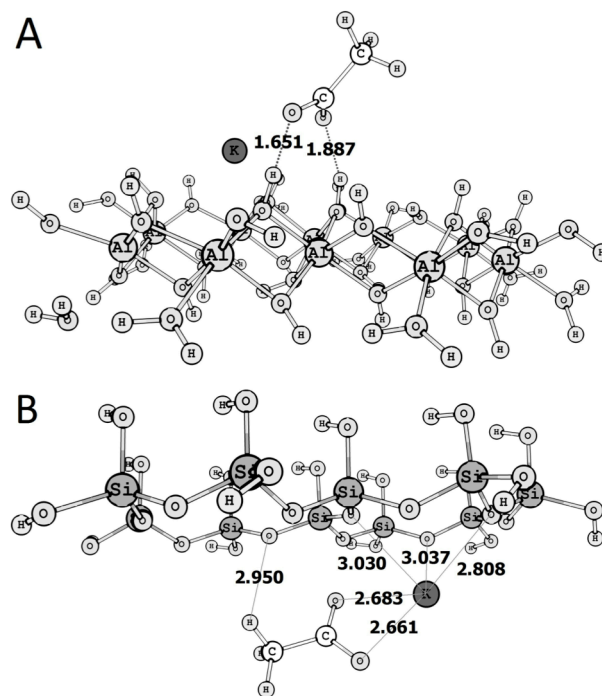


Figure 7: Computational models for the adsorption of potassium acetate on (A) O- and (B) T-sheets

interactions between the methyl group and the *b*-O<sup>2-</sup> groups. In the adsorption model for the T-sheet, the acetate appears to be held in place by the cation at about 2.66 and 2.68 Å.

Some of the plausible structures for the intercalation of potassium acetate were obtained from simulations in the absence (Fig.8A) and presence (Fig.8B) of solvent water. Similarly to the other models the values of basal spacing were set to their corresponding experimental values of 11.5 and 14.2 Å, respectively. The 2.7 Å difference allows for the accommodation of a water molecule as shown in Fig.8B. In agreement with the absorption models in Fig.7, we found short H-bond distances between the carboxylate group and the *s*-HO<sup>-</sup> of the O-sheet at 1.59 and 1.83 Å distances. When water

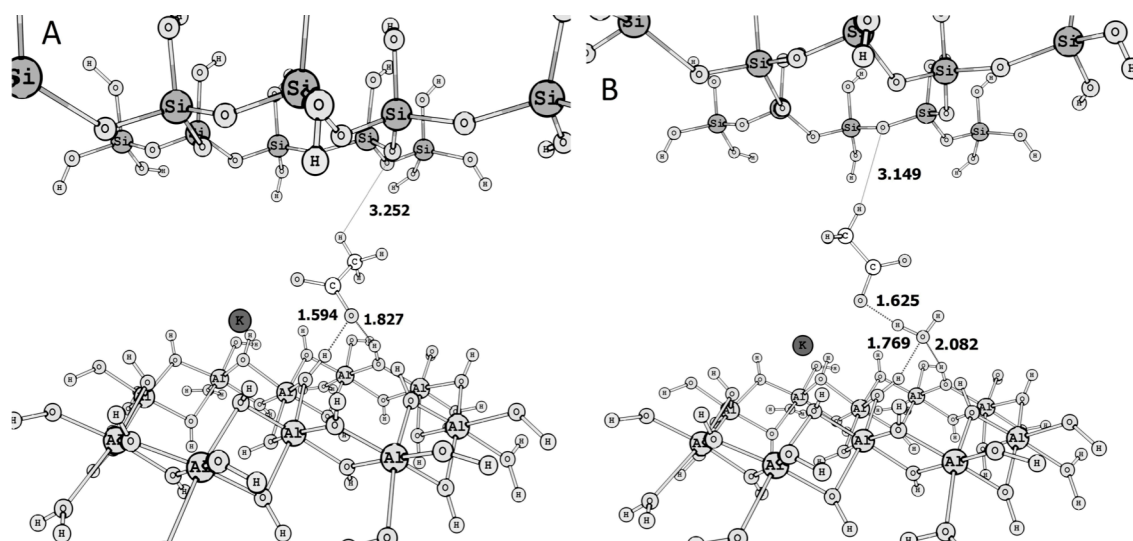


Figure 8: Computational models for potassium acetate intercalation in the (A) absence and (B) presence of solvent water



is present, it is likely to solvate the negatively charged end of the acetate ion with a characteristic  $\text{-COO}^- \dots \text{H-OH}$  distance of 1.63 Å. The interaction of the water and the O-sheet is asymmetrical with 1.77 and 2.08 Å  $\text{O(water)} \dots \text{s-HO}^-$  distances.

Given the energetic preference of the  $\text{O-H} \dots \text{OH}^-$  H-bonding interaction, the methyl group of the acetate will only interact with anionic groups of the T-sheet with representation  $\text{C-H} \dots \text{b-O}^{2-}$  distances of 3.15 and 3.25 Å. The lack of a representative solvent environment is of less importance for the position of the potassium ion in the intercalation models, since the inner environment of this model will likely be only exposed to bulk solvent only to a limited extent.

### Conclusions

We have started with a few notable preliminary results the establishment of a structural database for reference models related to the adsorption and intercalation of small molecules and kaolinite. We found that even a modest level of theory with respect of the basis set can provide reasonable structures. These results allow us for visualizing molecular structures in order to rationalize experimental observables and generate new ideas for research directions. Furthermore, these models can be considered as initial structures for higher-level calculations that are currently in progress in our laboratory.

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