Research paper

# Mechanism responsible for intercalation of dimethyl sulfoxide in kaolinite: Molecular dynamics simulations

Shuai Zhang[a], Qinfu Liu[a,*], Hongfei Cheng[a], Feng Gao[b], Cun Liu[c], Brian J. Teppen[b]

[a] School of Geosciences and Surveying Engineering, China University of Mining & Technology (Beijing), Beijing 100083, People's Republic of China
[b] Department of Plant, Soil, and Microbial Sciences, Michigan State University, East Lansing, MI 48824, United States
[c] Key Laboratory of Soil Environment and Pollution Remediation, Institute of Soil Science, Chinese Academy of Sciences, Nanjing 210008, People's Republic of China

## ARTICLE INFO

## ABSTRACT

Intercalation is the promising strategy to expand the interlayer region of kaolinite for their further applications. Herein, the adaptive biasing force (ABF) accelerated molecular dynamics simulations were performed to calculate the free energies involved in the kaolinite intercalation by dimethyl sulfoxide (DMSO). Additionally, the classical all atom molecular dynamics simulations were carried out to calculate the interfacial interactions between kaolinite interlayer surfaces and DMSO with the aim at exploring the underlying force that drives the DMSO to enter the interlayer space. The results showed that the favorable interaction of DMSO with both kaolinite interlayer octahedral surface and tetrahedral surface can help in introducing DMSO enter kaolinite interlayer. The hydroxyl groups on octahedral surface functioned as H-donors attracting the S=O groups of DMSO through hydrogen bonding interaction. The tetrahedral surface featuring hydrophobic property attracted the methyl groups of DMSO through hydrophobic interaction. The results provided a detailed picture of the energetics and interlayer structure of kaolinite-DMSO intercalate.

## 1. Introduction

Clay minerals are naturally occurring 2D materials abundant in worldwide, which have a long history of utilization in the industrial, engineering, and scientific fields (de Paiva et al., 2008; Murray, 1991). The demands for green ecological materials drive the continuous development of clay minerals-associated material chemistry. Clay minerals consist of stacked layers made of silica tetrahedral sheet and alumina octahedral sheet. Kaolinite, as one of the abundant and inexpensive clay minerals, is the excellent candidate of eco-environmental materials (Dedzo and Detellier, 2016). Kaolinite belongs to 1:1 type layered silicate with the structural formula of $Al_4Si_4O_{10}(OH)_8$. Each layer of kaolinite consists of an alumina octahedral sheet and a silica tetrahedral sheet connected by the shared plane of apical oxygens. Due to the 1:1 type structure, kaolinite exhibits two chemically different types of interlayer surfaces: silica tetrahedral surface covered by basal oxygens and alumina octahedral surface covered by hydroxyl groups. The adjacent kaolinite layers are held together by hydrogen bonds formed between the hydroxyl groups extending from the octahedral surface and the basal oxygens on the tetrahedral surface of the adjacent layer. Kaolinite is considered as non-expanding clay mineral owing to the strong cohesive force between the adjacent layers.

Intercalation is the promising strategy to expand the interlayer region of clay minerals for their further applications (Cheng et al., 2017; Chiu et al., 2014; Liu et al., 2016). The intercalation of kaolinite can weaken the cohesive force between kaolinite layers and facilitate the delamination of kaolinite stacks to increase the specific surface area, optical and other physical properties (Tsunematsu and Tateyama, 1999). However, due to the hydrogen bonds in the kaolinite interlayer, the direct intercalation of kaolinite is limited to a few molecules such as urea, DMSO, hydrazine, and potassium acetate, etc. that have strong ability to form hydrogen bonds (Cheng et al., 2012; Dedzo and Detellier, 2016; Frost et al., 1997; Ledoux and White, 1966). The DMSO is one of the most commonly used compounds to intercalate kaolinite, which has been experimentally investigated using X-ray diffraction (XRD), infrared and Raman spectroscopy, and nuclear magnetic resonance (NMR) so far (Frost et al., 1998; Hayashi, 1997; Johnston et al., 1984; Ledoux and White, 1966). The structure of intercalated DMSO in kaolinite interlayer and their interactions with kaolinite interlayer surfaces were deduced based on the experimental results. Thompson and Cuff (Thompson and Cuff, 1985) analyzed the kaolinite-DMSO intercalation complex using X-ray and neutron power diffraction and proposed that the S=O group of DMSO hydrogen bonded with the hydroxyl groups of kaolinite inner surface, one methyl group was keyed
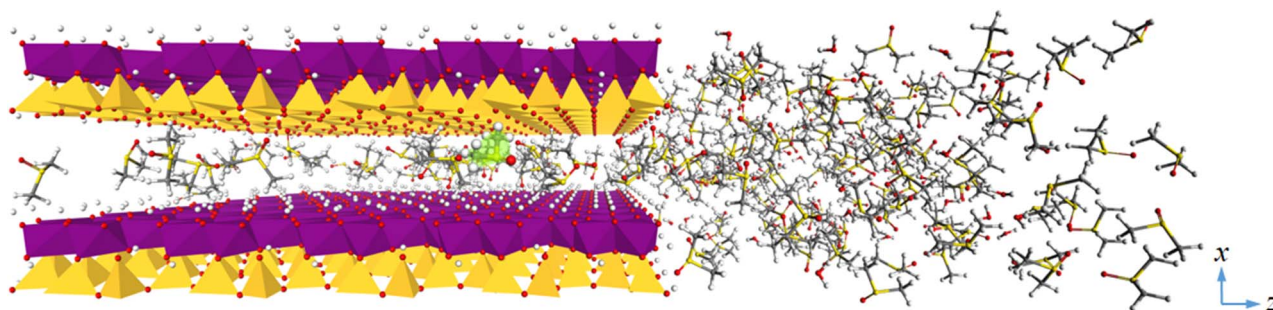
**Fig. 1.** The initial configuration of kaolinite interlayer-DMSO solution two phase model. The kaolinite layer is shown in polyhedron style; the DMSO solution is shown in ball and stick style, where the ball color scheme is O (red), C (gray), S (yellow), and H (white). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

into the ditrigonal cavity on the tetrahedral surface, and the other was parallel to the interlayer surfaces. Duer et al. (Duer and Rocha, 1992; Duer et al., 1992) studied the molecular motions of DMSO in kaolinite-deuterated DMSO by $^2$H NMR and found another structure model of DMSO whose two methyl groups were approximately parallel to the interlayer surfaces with the S=O group forming hydrogen bonds with inner surface hydroxyl groups. It was agreed that the inner surface hydroxyl groups were hydrogen bonded with S=O groups of DMSO, while the interaction between methyl groups of DMSO and kaolinite interlayer surfaces was debatable (Frost et al., 1998; Johnston et al., 1984; Olejnik et al., 1968; Zhang et al., 2015). Experimental results, however, remained speculative regarding the precise arrangement of the DMSO in kaolinite interlayer and its interaction with kaolinite interlayer surfaces. In the past two decades, the molecular simulations have evolved as a powerful tool for probing the interfacial structure and interactions of clay minerals-organics and clay minerals-solution phase at atomic scale (Deng and Szczerba, 2011; Greathouse et al., 2015; Heinz and Ramezani-Dakhel, 2016; Liu et al., 2009; Szczerba et al., 2014; Zhao and Burns, 2012; Zhou et al., 2015; Zhou et al., 2014; Zhu et al., 2012). The previous studies on kaolinite intercalation with small organic molecules (DMSO, urea, methanol) using molecular simulations mainly emphasized the structure of intercalated molecules in kaolinite interlayer (Cheng et al., 2015; Fang et al., 2005; Rutkai and Kristóf, 2008; Rutkai et al., 2009). The molecular dynamics simulations of DMSO in kaolinite interlayer by Fang et al. (Fang et al., 2005) found the DMSO structure model was in line with that proposed by Thompson and Cuff using the X-ray and neutron power diffraction (Thompson and Cuff, 1985). Rutkai and Kristóf (Rutkai and Kristóf, 2008) found that more than one DMSO structure models coexisted in the kaolinite interlayer based on Monte Carlo simulations of DMSO in kaolinite. The adsorption energies of DMSO and acetic acid with two types of kaolinite surfaces were calculated using the quantum chemical method with relatively simple models (Michalková and Tunega, 2007; Tunega et al., 2002). The results showed that the octahedral surface exhibited stronger affinity to DMSO and acetic acid compared with the tetrahedral surface. In spite of extensive experimental and theoretical studies of kaolinite intercalation by DMSO, the understanding of the interactions of DMSO with kaolinite interlayer surfaces and the underlying driving force responsible for the kaolinite intercalation by DMSO are still disputable.

In present study, the adaptive biasing force (ABF) accelerated MD simulations were performed to calculate the free energies involved in the transfer of DMSO molecule in kaolinite interlayer and the surrounding DMSO solution phase. This method has been successfully employed to calculate the free energies of intercalation of alkyl surfactants in kaolinite and the sorption process of organic contaminants from bulk water by clay minerals (Liu et al., 2015; Zhang et al., 2017a). In addition, all atom molecular dynamics simulations were performed to calculate the interaction energies of DMSO with two types of kaolinite interlayer surfaces and the structural arrangement of DMSO in

kaolinite interlayer with the aim at elucidating the underlying driving force responsible for the intercalation of kaolinite by DMSO.

## 2. Models and simulation method

In present work, the kaolinite unit cell was built based on our previous study (Zhang et al., 2014). The kaolinite supercell was created with 8 × 5 × 1 unit cells. The basal surface area is 41.19 Å × 44.67 Å in $x$, $y$ plane. In order to calculate the potential of mean force (PMF), that is the free energy, of transfer of DMSO molecule in kaolinite interlayer and the bulk DMSO solution, the two phase model, kaolinite interlayer-DMSO solution, was constructed. For constructing such model, two kaolinite supercells were firstly stacked along $z$-axis with periodic boundaries in three dimensions. The interlayer space placed at the center of the stacked two supercells was expanded with DMSO molecules to form the kaolinite-DMSO interlayer nanopore. The other two interlayers through which the $z$ periodic boundary passed were kept undisturbed. Analogous clay mineral models have been adopted in previous studies (Greathouse et al., 2015). Then the model (010) edge was created by cleaving along the required Miller plane, where the dangling bonds were saturated with hydroxyl groups. A 30 Å of vacuum slab with packed DMSO solution was added above the kaolinite (010) edge to create the kaolinite interlayer-DMSO solution two phase model whose initial configuration is shown in Fig. 1. In this model, the orientations of $x$-, $y$-, and $z$-axis were reset, and the $z$-axis was set perpendicular to the (010) edge surface as shown in Fig. 1.

The free energies involved in transferring DMSO molecule in kaolinite interlayer and the DMSO solution were calculated using the adaptive biasing force (ABF) method. In order to evaluate the enthalpic energy gain through the interactions of guest molecules with kaolinite interlayer surfaces that induces the penetration of guest molecules into kaolinite interlayer (Zhang et al., 2017b), the models of kaolinite interlayer surfaces-DMSO molecules including silica tetrahedral surface-DMSO and alumina octahedral surface-DMSO models were also constructed. For constructing such models, an amorphous slab containing DMSO molecules with the same size of kaolinite supercell in $x$- and $y$-axis was created. The kaolinite supercell was cleaved along its (001) and (00$\bar{1}$) Miller plane to produce the alumina octahedral surface terminated with a plane of surface hydroxyl groups and the silica tetrahedral surface terminated with a plane of basal oxygens, respectively. Then the amorphous DMSO slab was brought in contacting with the two types of surfaces to construct the initial octahedral surface-DMSO and tetrahedral surface-DMSO models whose initial configurations are shown in Fig. 2a and b. The mole ratio of kaolinite to DMSO was adopted according to the formula of $Al_2Si_2O_5(OH)_4(DMSO)_{0.7}$ derived from the thermal analysis of kaolinite-DMSO intercalation complex in our previous study (Zhang et al., 2015), which falls into the mole ratio range of kaolinite to DMSO (0.19–0.8) calculated based on MD simulations, which can reproduce the experimental $d$-spacing of the intercalation complex (Fang et al., 2005). The interaction energies were