

# **Supporting Information for Thermodynamic Mechanism and Interfacial Structure of Kaolinite Intercalation and Surface Modification by Alkane Surfactants with Neutral and Ionic Head Groups**

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## Simulation Protocol

A 10000 step energy minimization was performed using the conjugate gradient technique to remove the high energy contact of the systems before switching to MD simulation runs. After that the MD simulations were carried out in the NPT ensemble with a constant temperature of 300 K and a constant pressure of 0.1 MPa for 10 ns to equilibrate the systems. In order to compute the potential of mean force (PMF) of surfactants transferring between methanol preintercalated clay interlayer and the surrounding solution phase using the adaptive biasing force method (ABF), a steered molecular dynamics simulation (SMD) was performed to generate a series of initial configurations along the reaction coordinate. The SMD was performed in the NVT ensemble after the 10 ns of equilibrium runs in the NPT ensemble. The SMD involved pulling the center of mass of surfactants from the kaolinite interlayer to solution phase along the  $z$ -axis (Figure S2) with a constant pulling velocity of 1 Å/ns. The series of generated configurations with surfactants located in 30 evenly distributed windows along the reaction coordinate were used in the following ABF simulations. The production runs of ABF simulations were parallelly performed in each window with 0.2 Å overlap. The bin size of width in the ABF simulations was 0.05 Å. The biasing force was applied after 5000 samples were collected in each bin. The ABF production runs were carried out in the NVT ensemble with the constant temperature of 300 K for each window. The free energy profiles of transfer process of surfactants were generated by linking the PMF produced in all adjacent windows.

To evaluate the interaction energies of surfactants with kaolinite interlayer surfaces and interlayer methanol in the interlayer environment of methanol preintercalated kaolinite.

Additional 1 ns of production runs were performed in the NPT ensemble with the constant temperature of 300 K and constant pressure of 0.1 MPa after the initial 10 ns of equilibrium runs. During the production runs, the trajectories were collected every 2000 steps for the following interfacial structure analyses and interaction energies calculation.

The temperature and pressure for the NPT and NVT simulations were controlled using the Nose-Hoover thermostat and barostat. Periodic boundary condition was applied in three dimensions. The step size of simulation runs was 1 fs. The short range van der Waals interaction was truncated at 10 Å with an analytical tail correction. The Ewald method with a cutoff of 10 Å and accuracy of 0.0001 was used to compute the long range electrostatic interactions. During the simulations, all the atoms in clay structure including the surface hydroxyl groups were kept flexible, while the edges of clay layers were attached to fixed springs with the force constant of 20 kcal/mol to prevent the clay layers from rotating across the periodic boundary.

### **Interaction Energy Calculation**

The interaction energies of interlayer environment (alumina surface, siloxane surface, and interlayer methanol) of methanol preintercalated kaolinite with surfactants were calculated based on the trajectories of systems (total 500 frames) collected in the 1 ns of production runs after the 10 ns of equilibrium runs as stated in the Simulation Protocol section using eq 1:

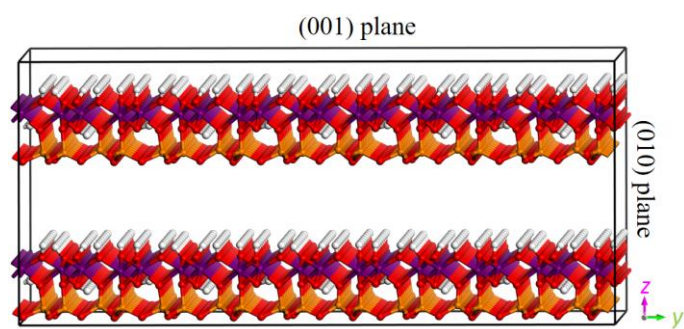
$$E_{interaction} = E_{total} - (E_{surface\ or\ in-met} + E_{surfactant}) \quad (1)$$

Where the  $E_{total}$  refers to the total energies of the kaolinite alumina surface–surfactants, siloxane surface–surfactants, and interlayer methanol–surfactants systems;  $E_{surface\ or\ in-met}$  represents the energies of isolated kaolinite alumina surface, siloxane surface, and interlayer

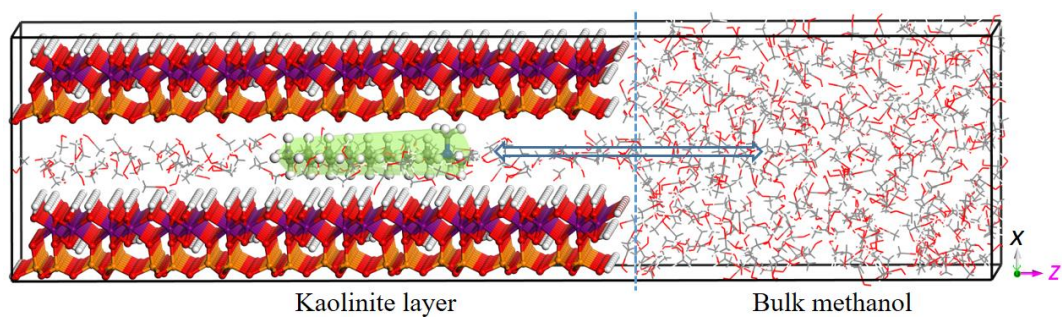
methanol.  $E_{surfactant}$  represents the energies of isolated surfactants. When the interaction energy of surfactants with one of the components of interlayer environment was calculated, the other components were removed to avoid their effects on the target energy calculations. For example, when the interaction energies of surfactants with the alumina surface exposing on the lower kaolinite layer of the system (Figure S2) was calculated, the upper kaolinite layer exposing the siloxane surface, interlayer methanol, as well as the bulk methanol/water in solution phase in the systems were all removed to avoid their effect on the target energy computation. The scheme of interaction energies calculation in the case of dodecylamine with interlayer environment (alumina surface, siloxane surface, and interlayer methanol) of methanol preintercalated kaolinite using the equation 1 was given in Figure S3. Additionally, a vacuum slab with a width of 40 Å was added along the direction perpendicular to the kaolinite basal surface for each frame prior to the single point energy calculation to avoid the influence of periodic boundary condition.

For the calculation of interaction energy, the single point energies ( $E_{total}$ ,  $E_{surface\ or\ in-met}$ , and  $E_{surfactant}$ ) of each frame collected in the production runs were first computed. Then the interaction energy of each frame was computed using equation 1 and averaged over the 500 frames of trajectories. The interaction energy is composed of electrostatic and van der Waals energies. In order to clarify the proportions of electrostatic and van der Waals energies accounting for the interaction energy, each component (electrostatic and van der Waals energies) was also computed separately.<sup>1,2</sup> For splitting the van der Waals energy contribution of head groups of surfactants, the van der Waals force field parameters assigned to the atoms of alky chains were set zero in the van der Waals energy component calculation. Accordingly,

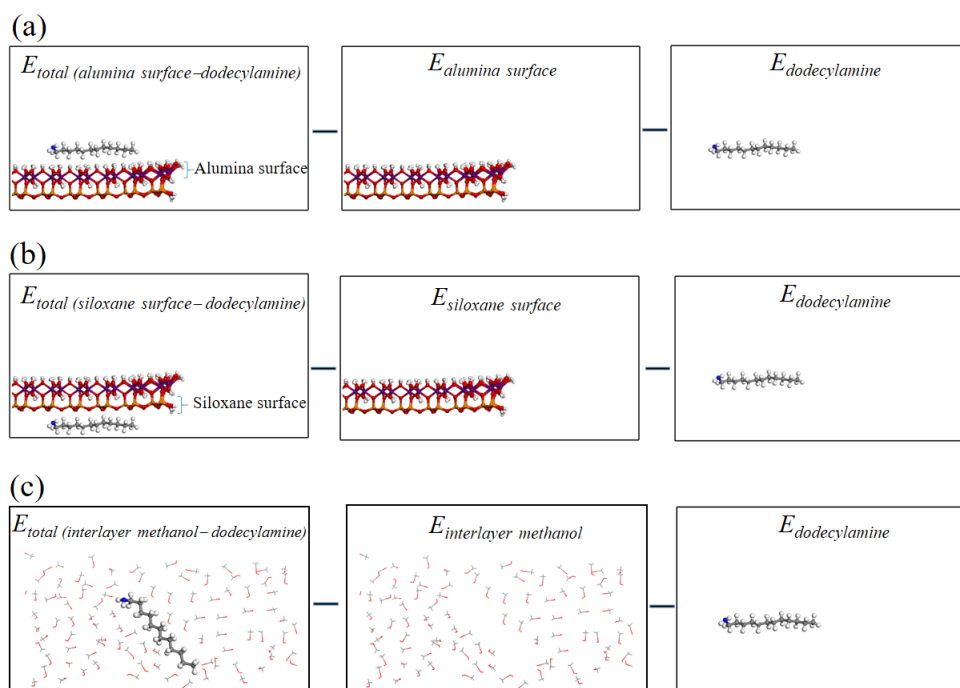
the van der Waals energy contribution of alky chains was specified by setting zero for the van der Waals force field parameters assigned to the atoms of head groups when calculated the van der Waals energies. The split of electrostatic energy contributions of head groups and alky chains of surfactants employed the same method by setting zero of the charges for the alkyl chains and head groups, respectively, during the electrostatic energy calculation.<sup>3</sup>



**Figure S1** The initial crystalline kaolinite structure. The ball color scheme is O, red; H, white; Si, orange; and Al, purple.



**Figure S2.** The initial configuration of methanol preintercalated kaolinite interlayer–bulk methanol two phase model with intercalated CATC. The methanol molecules are displayed in line style for the sake of visual clarity.



**Figure S3.** Scheme of interaction energies calculation in the case of dodecylamine with interlayer environment (a) alumina surface, (b) siloxane surface, and (c) interlayer methanol of methanol preintercalated kaolinite using the equation 1. (a) and (b) are the side view of kaolinite interlayer–solution phase model; (c) is the top view of interlayer region of kaolinite interlayer–solution phase model. The methanol molecules are shown in line style for the sake of visual clarity.

## References

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