

# Investigation of effects of cations on adsorption of decanoic acid by montmorillonite clay

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## Abstract

This report investigates the role of charge-balancing cations in the adsorption of oil molecules onto smectite clay minerals. Using molecular dynamics simulations, the study examines the adsorption mechanisms of deprotonated decanoic acid on clay surfaces in the presence of sodium ( $\text{Na}^+$ ) and calcium ( $\text{Ca}^{2+}$ ) ions. The results indicate that divalent ions enhance adsorption, compared to monovalent ions. This is attributed to the ability of divalent cations to form cationic bridges between the negatively charged carboxylate group of decanoic acid and the negatively charged montmorillonite clay surface, leading to stronger adsorption interactions.

## Introduction

The adsorption of organic molecules onto soil-forming mineral surfaces plays a crucial role in various natural and industrial processes, including oil recovery, soil chemistry, and environmental pollution remediation. Understanding how charge-balancing cations present in the soils influence adsorption mechanisms is essential for predicting molecular behaviour in complex environmental systems. This study focuses on the adsorption of decanoic acid onto smectite clay in the presence of monovalent sodium ( $\text{Na}^+$ ) and divalent calcium ( $\text{Ca}^{2+}$ ) ions. By using molecular dynamics simulations, we aim to get atomistic level insights of clay-oil interactions, obtaining mechanistic and quantitative information on the underlying processes.

## Methodology

### System Setup

The clay used in this study is representative of montmorillonite (MMT), with unit cell stoichiometry of  $[\text{Al}_3\text{Mg}][\text{Si}_8\text{O}_{20}](\text{OH})_4$ . The substitution of octahedral  $\text{Al}^{3+}$  for  $\text{Mg}^{2+}$  gives rise to the negative layer charge, which is charge-balanced by positive cations  $\text{Na}^+$  or  $\text{Ca}^{2+}$ . These cation-clay systems are named Na-MMT and Ca-MMT, respectively. The pKa of decanoic acid is 4.9, i.e., at  $\text{pH} > 4.5$  decanoic acid is deprotonated to form carboxylate anions,  $\text{CH}_3(\text{CH}_2)_8\text{COO}^-$ .

The clay unit cell with the size of  $0.5160 \text{ nm} \times 0.8966 \text{ nm} \times 0.9347 \text{ nm}$  in  $x$ ,  $y$ ,  $z$  directions was replicated  $7 \times 6 \times 1$  times, to form a layer in  $xy$ -plane of  $3.62523 \text{ nm} \times 5.39930 \text{ nm}$ . The simulation box was then expanded in the  $z$ -direction to be approximately  $10 \text{ nm}$ , where the clay layer occupied the region of  $0 < z < 1 \text{ nm}$ . Subsequently, 11 deprotonated decanoic acid molecules were inserted into the

system, corresponding to 0.1 M concentration. The system was solvated, by the random insertion of water molecules into the space of the box. Any water molecules that were inserted into the clay layer were then manually removed. The ions were added to the system, ensuring the system is neutral and ionic concentration of 0.1 M. Na-MMT system was set up with addition of NaCl ions and Ca-MMT system with  $\text{CaCl}_2$ .

MMT clay and ions were assigned the ClayFF force field,<sup>1</sup> decanoic acid was assigned the CHARMM36 force field,<sup>2</sup> water was assigned the SPC model with force field parameters part of ClayFF force field distribution.

## Simulation Protocol

All simulations were carried out with GROMACS 2024.4,<sup>3</sup> with electrostatic and van der Waals cut-off distances set to 1.2 nm. Every simulation was first energy minimised with convergence achieved once the maximum force acting on any one atom is under  $500 \text{ kJ mol}^{-1} \text{ atom}^{-1}$ . Subsequently, the system was equilibrated for 100 ps with a step-size of 1 fs in isothermal-isobaric (*NPT*) ensemble using a V-rescale thermostat at 300 K and a semi-isotropic C-rescale barostat at 1 bar. The use of semi-isotropic barostat allows to independently rescale simulation box in *xy*-plane and in *z*-direction, allowing for the layer to compress at a different rate to the hydrated interlayer space while achieving the set pressure. The equilibration was followed by a 100 ns *NPT* production run with the timestep of 2 fs and H-bond constraints. All other parameters are kept the same as for equilibration.

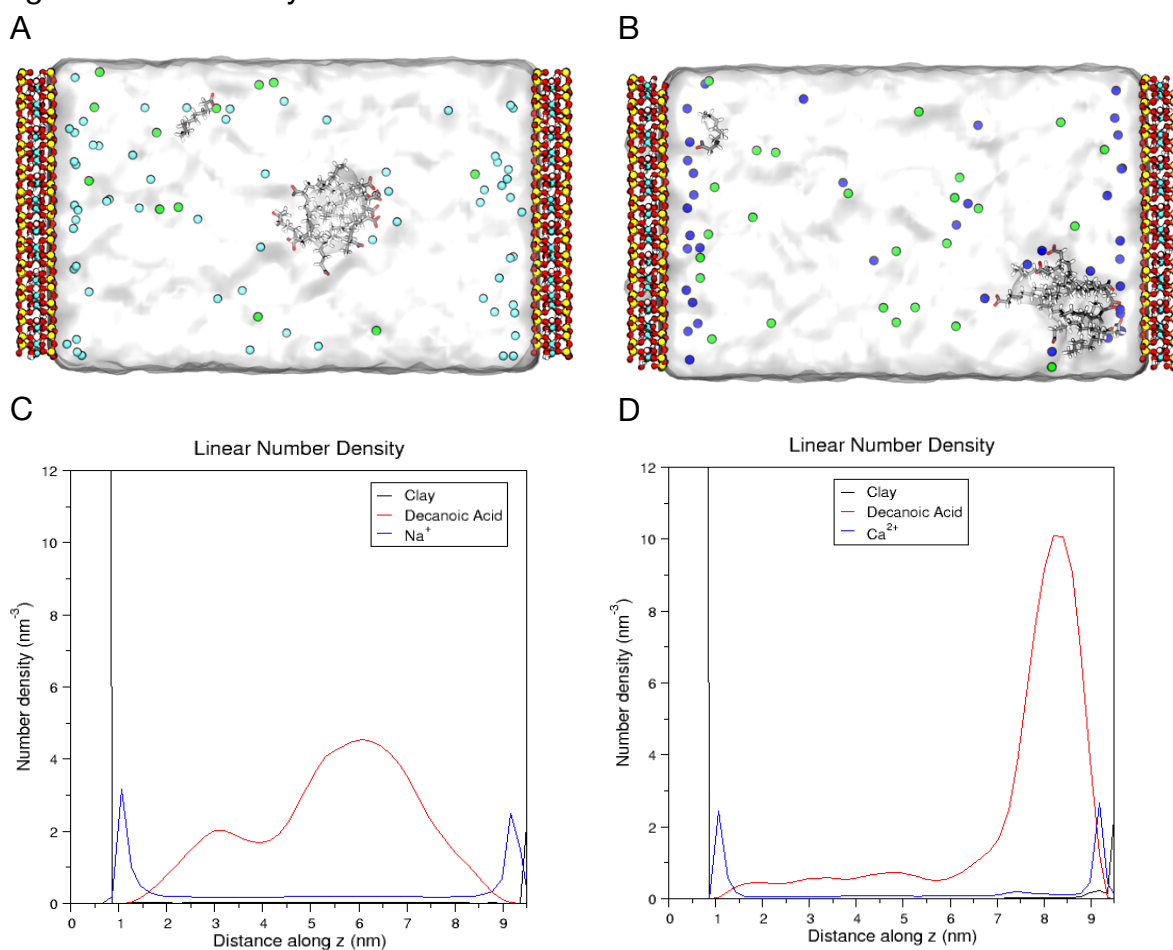
## Analysis

System equilibration was confirmed by monitoring the potential energy, pressure and temperature stability over time, ensuring no significant drifts. For further trajectory-based analysis, the simulation was deemed converged when root-mean-square-deviation (RMSD) of individual components (i.e., clay, water, decanoic acid and ions) plateaued, indicating that each of the components has explored the available phase-space. For both simulations, RMSD of decanoic acid was the slowest to level, which happened after approx. 15 ns of simulation. Therefore, first 20 ns of production simulation were discarded from the further analysis.

Linear number densities were calculated along the *z*-axis, i.e. perpendicular to clay layer, allowing to access the average positions of each component in the system. Radial distribution functions (RDF) were calculated for water and carboxylate group oxygens around each of cations. RDF provides information on coordination geometries and binding probabilities of species. Plots are produced with XmGrace, and renderings of the structures are made with VMD (Visual Molecular Dynamics) software.<sup>4</sup> In the renderings colours are as follows: C - grey, H - white, O - red, Si - yellow, Al - cyan, Mg - pink,  $\text{Na}^+$  - cyan spheres,  $\text{Ca}^{2+}$  - blue spheres,  $\text{Cl}^-$  - green spheres, for clarity water may be shown as a transparent surface.

## Results and Discussion

Upon visual examination of the systems (Figures 1A and 1B) it became apparent that in both systems, decanoic acid forms a cluster with its hydrophobic chains pointing towards the centre and carboxylate groups exposed to water. Cations surround the deprotonated groups. Furthermore, both  $\text{Na}^+$  (cyan spheres, Figure 1A) and  $\text{Ca}^{2+}$  (blue spheres, Figure 1B) form a layer above the negatively charged surface of the clay. Occasional single molecule of decanoic acid is dispersed away from the cluster (as seen in Figure 1A) but will rapidly return to organic cluster. The biggest difference between two systems is that when a monovalent cation is present the organic cluster remains in the middle of the clay nanopore, not interacting with clay surfaces. In the Ca-MMT system, the divalent cation facilitates interaction between the organics and clay surface. This observation is also confirmed by linear number density profiles (Figures 1C and 1D), that provide a probabilistic representation of the location of each component during whole simulation. In the case of Na-MMT, decanoic acid (red line, Figure 1C) remains in the centre of the simulation box and, therefore, not in contact with the clay surface. In the case of Ca-MMT, decanoic acid peak (red line, Figure 1D) is located next to the clay surface. The cations (blue line, Figures 1C and 1D) are positioned next to the clay surface and, in the case of Ca-MMT, also lay between the organics and the clay.



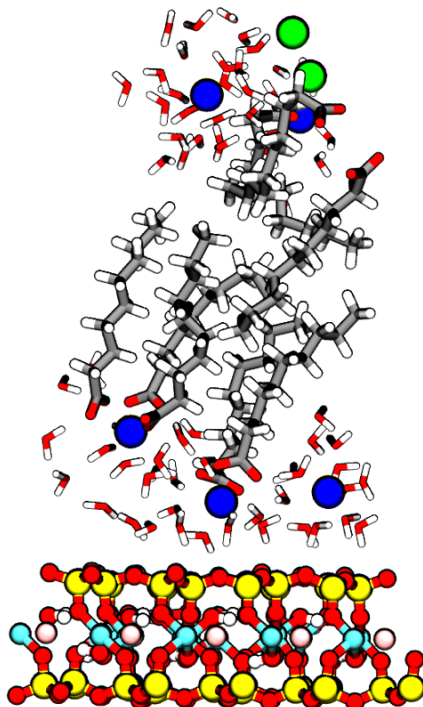
**Figure 1:** Visualisation of representative configurations of (A) Na-MMT and (B) Ca-MMT systems with deprotonated dodecanoic acid. Their corresponding linear number densities are given in (C) and (D) respectively.

The analysis of RDF provides information on the distance between cation and oxygens of water and carboxylic acid, reported in Table 1. The calculated distances between ions and water oxygen are in-line with literature values,<sup>5,6</sup> confirming reliability of the force fields and simulations. The distances between ions and oxygens of deprotonated carboxylic acid are slightly shorter than those of water, highlighting strong interactions between deprotonated group and cations.

**Table 1:** Distances between cation and oxygen of water and carboxylic group, coordination numbers of waters around each cation. Reference values taken from literature refs. 5 and 6.

Cation	Distance to O (water), nm		Coordination number of water		Distance to O (decanoic acid), nm
	calculated	Ref.	calculated	Ref.	calculated
<b>Na<sup>+</sup></b>	0.238	0.243	5.75	6	0.224
<b>Ca<sup>2+</sup></b>	0.245	0.246	7	7.2	0.233

Overall, deprotonated decanoic acid is adsorbed onto MMT clay in the presence of divalent cations only. The adsorption is enabled by bridging of divalent cation between negative clay surface and deprotonated carboxylic groups. This mechanism is not possible for monovalent ions. Figure 2 shows the bridging mechanism enabled by Ca<sup>2+</sup> (blue) cations. We also note that cations are not directly positioned on the clay surface but interact with it through a water layer. This observation is consistent with previous literature studies.<sup>7</sup>



**Figure 2:** Visualisation of representative configurations of decanoic acid bridged by Ca<sup>2+</sup> cations to the surface of MMT.

## Conclusions

This study details the effect of cations on the adsorption of organic species by clay minerals. In the case of a deprotonated organic species, the presence of divalent ions will enable their adsorption onto the clay surface via a bridging mechanism. This is not possible when charge-balancing ions are monovalent. This work gives insights into the intricate interactions between organic and mineral species in the soil and have implications for the fields of environmental science and engineering.

## References

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