Molecular Dynamics Simulation of the Energetics and Structure of Layered Double Hydroxides Intercalated with Carboxylic Acids

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Introduction

Incorporation of bio- and organic species into the interlayers of layered double hydroxide compounds (LDHs) is gaining increasing attention due to many potential applications such as controlled release drug delivery and environmental remediation. Intercalation of large organic molecules into LDH interlayers can be difficult, but recent studies have shown that enhanced swelling leading to exfoliation (delamination) of the LDH layers can be achieved in contact with a solution if the LDH is loaded with suitable organic intercalates[1-6]. Such exfoliation offers a gentle way of opening the interlayer space to allow insertion of large bio- or organic-molecules.

We present results from our molecular dynamics (MD) simulation of the Mg/Al (3:1) layered double hydroxide (LDH) containing the mono-carboxylic acids, formate, acetate, and propanoate, as the charge balancing anions. The study provides new molecular scale insight into the energetics of hydration and consequent swelling of these compounds when intercalated with organic- and bio-molecules with carboxylate functional groups. The results are compared to the tri-carboxylate citrate intercalated LDH[4].

Method

The basic structural model[7] consists of 6×6×1 rhombohedral ($R\bar{3}m$) unit cells of Mg/Al (3:1) LDH, hydrotalcite (HT), of formula unit: $\mathbf{Mg_3Al(OH)_8A^{-}\cdot \mathit{n}H_2O}$, where A^- is the charge balancing cation: formate, acetate or propanoate in the present case. Each supercell contained three metal-hydroxide layers, 27 carboxylic acid anions (9 per interlayer), and a variable number of water molecules, $27 \times n$, where $0 \leq n \leq 18$.

NPT-ensemble MD simulations of 50 ps duration were carried out at 300 K and 1 bar pressure to compute the *average lattice parameters* and *hydration energies* at different hydration levels, *n*.

NVE-ensemble MD simulations of 200 ps duration were carried out at 300 K to investigate the detailed *interlayer structure, hydrogen bonding* and other important structural and dynamical properties.

Force fields: LDH layers are modeled using CLAYFF force field[8], organic molecules by the CVFF[9], and water through the SPC model[10].

Results

The Gross Interlayer Structure And Lattice Expansion With Hydration

- ☐ The organic anions orient parallel to the layers in the dry, $n = 0$, system (Fig. 1) in order to maximize the number of hydrogen bonds accepted by the carboxylate groups.
- ☐ Under progressive hydration the organic anions change their orientation in favor of perpendicular to the layers (Fig. 1).
- ☐ Despite the comparable lateral dimension of the mono-carboxylates, propanoate exhibit larger d-spacing (Fig. 2) in the dry system owing to its stronger (unfavorable) hydrophobic interaction with the layers.
- ☐ The slow lattice expansion for $n < 3$ clearly suggest water filling the vacant interlayer space between the anions (Fig. 2).
- ☐ Mono-carboxylic acid intercalated hydrotalcite (HT) exhibit nearly parallel expansion with hydration for $n > 3$ (Fig. 2).
- ☐ In contrast, citrate-HT exhibit slower expansion with hydration suggesting that the tricarboxylate-citrate forms compact hydration structures (Fig. 2).

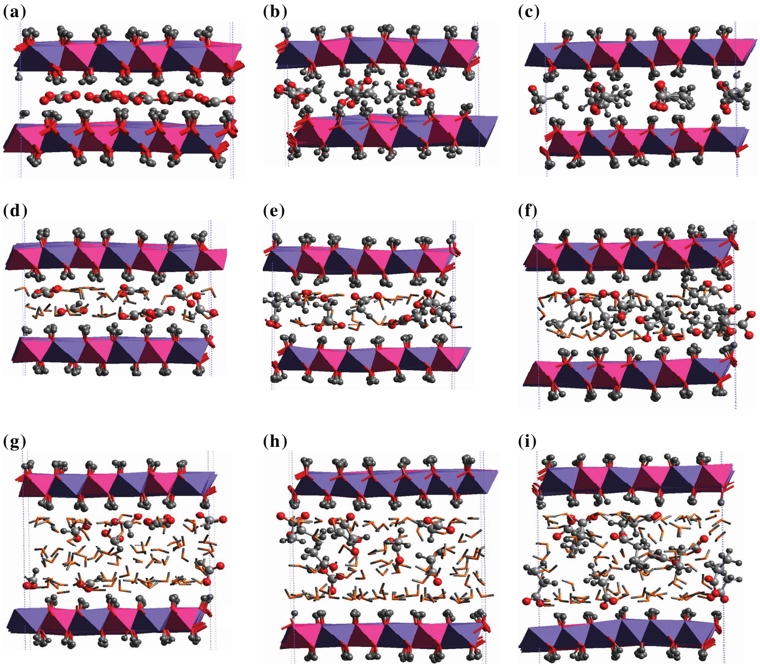


Figure 1. Representative snapshots from MD simulations of hydrotalcite intercalated with formate (left column), acetate (middle column), and propanoate (right column) with progressive hydration. Top row, $n = 0$; middle row, $n = 4$; bottom row, $n = 10$

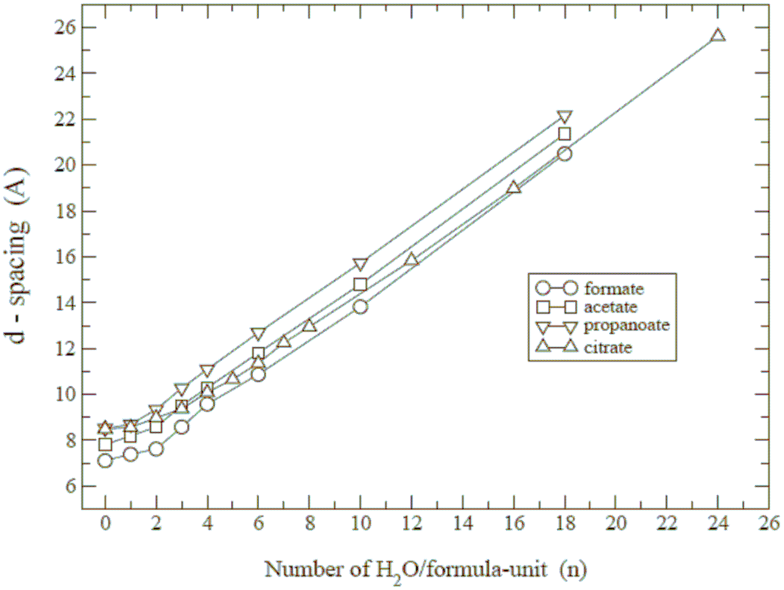


Figure 2. Variation of interlayer spacing as a function of the number of water molecules per formula-unit, *n*, from *NPT*-MD simulations at 300 K and 1 bar pressure of formate-, acetate-, propanoate- and citrate-HT.

Energetics Of Hydration

- The hydration energies (HE) of the carboxylate-HT are most negative at low water contents suggesting its high water affinity (Fig. 3).
- The high water affinity of these systems is due to the presence of a large number of under-saturated hydrogen bonds (H-bonds) of the anions and the metal hydroxides (M-OHs) of the layers (see also Fig. 4).
- Unlike most HTs intercalated with inorganic species[11,12] such as, Cl^-, CO_3^{2-} etc., the HE of organic-HTs do not exhibit well defined hydration states.
- The slow approach of the HE towards the bulk value (as indicated in Fig. 3) is a clear signature of the enhanced swelling behavior of the organic-LDHs under water rich environment. This again contrasts the behavior of HTs intercalated with inorganic species.
- The tri-carboxylate citrate intercalated HT, however, shows superior swelling behavior (Fig. 3) owing largely to (i) smaller hydrophobic chain size per carboxylate group, and (ii) structural in-commensurability with the layers that prompts it accept more H-bonds from water than from the layer.

Hydration Energy,

$$\Delta U_H(N_w) = \frac{\langle U(N_w)\rangle - \langle U(0)\rangle}{N_w}$$

$U(N_w)$ – total Potential Energy of the system having a N_w water molecules.

The difference between the hydration energy and the potential energy per molecule of bulk water measures essentially the affinity of the system to absorb water.

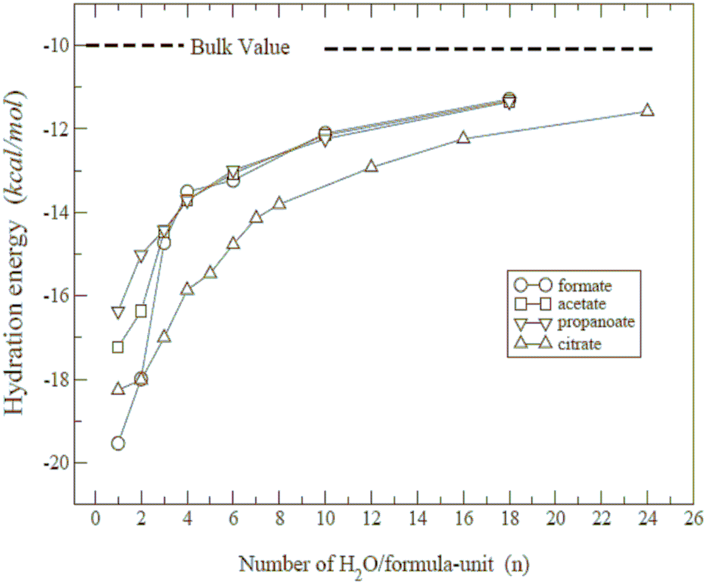
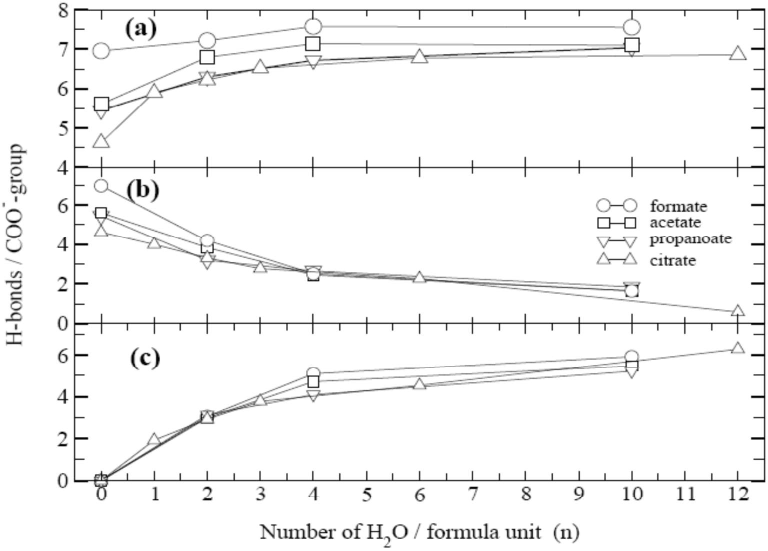


Figure 3. Variation of the system hydration energy as a function of the number of water molecules per formula-unit, *n*, from *NPT*-MD simulations at 300 K and 1 bar pressure of formate-, acetate-, propanoate- and citrate-HT.

H-bonding And The Origin Of Swelling

- ☐ The H-bonding patterns shown in Fig. 4 clearly suggest that organic anions prefer accepting H-bonds from water than from the M-OH groups of the HT. This is attributed to the small size of the water molecules as well as their ability to form flexible H-bond network.
- ☐ In the low hydration states ($0 < n < 4$) as the added water molecules, (i) cater to the basic requirements of the different H-bonding species (M-OH and the anions), and (ii) replacing some of the H-bonds accepted by the anions from the M-OH by those from water (Fig. 4). In this range the energy of hydration increases sharply indicating decrease in the water affinity of the HT (Fig. 3).
- ☐ In the intermediate hydration levels ($4 < n < 10$) water molecules bring in the following structural changes: (i) solvating the hydrophobic tails (unfavorable) as the anions themselves start reorganizing perpendicular to the layers, (ii) solvating the M-OH groups previously “masked” by the long hydrophobic tails (favorable), (iii) replacement of H-bonds between the M-OH and anions at a slower rate (favorable). The competing processes (i) and (ii) results in the relatively smaller changes in the HE.
- ☐ The relatively slow variation of the hydration energy beyond $n = 10$ is due to the “improvements” to the integrated H-bond network between the different species at the interlayer towards a more bulk water like and less strained network, that bring relatively low energy gains.



- **Figure 4.** Hydrogen bond statistics for different anionic species as a function of the number of water molecules per HT formula-unit: (a) the average number of H-bonds accepted by anions from LDH and water; (b) the average number of H-bonds donated by the LDH hydroxyls to the anions; (c) the average number of H-bonds donated by water molecules to the anions.

Nature Of The Anion – M-OH Interaction

- ☐ In the dry system, formate ions have the plane of their -COO^- groups oriented parallel to the layers, while that of the propanoate ions orient perpendicular. The acetates are more disordered and show dynamical switching between these two orientations. The orientational preference of the different species need be understood as an effort of the carboxylate groups to maximize the H-bonding under the increasing lattice spacing.
- ☐ The atomic density profiles suggest a highly ordered arrangement of the propanoate at the interlayer that is necessary to accommodate these large species. This size effect predicts larger anions to orient at larger angles to the interlayer.
- ☐ The orientation of the carboxylate groups also change with hydration.
- ☐ The atomic density profiles suggest increased dynamics of the species and diminished preference of the carboxylate groups for specific M-OH sites under progressive hydration.
- ☐ Water molecules exhibit strong site preferences and prefer hexagonal arrangement, that is on top of the M-OH groups.
- ☐ Under hydration the anions progressively loose contact with the M-OH layers but stays near the surface largely as outer sphere species.

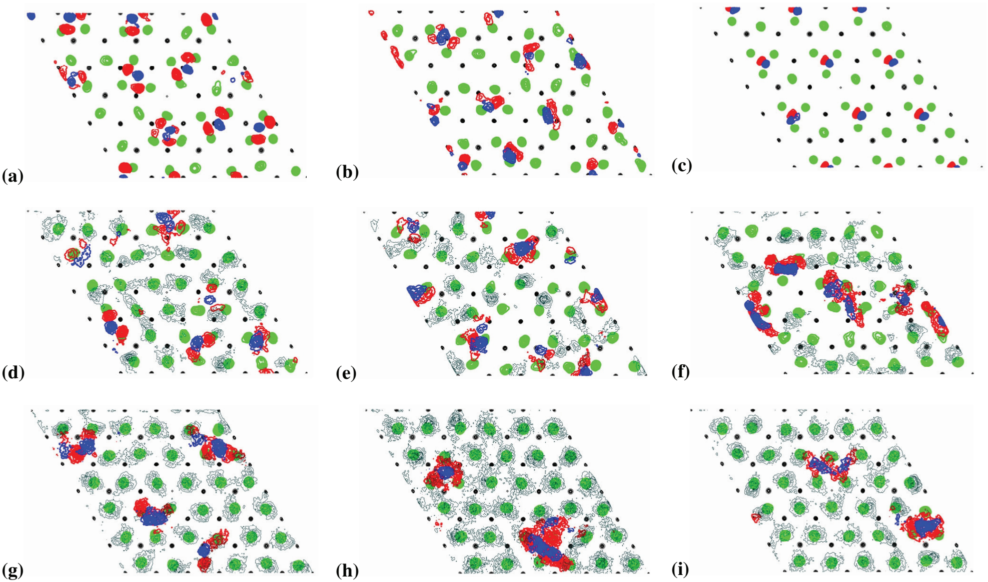


Figure 5. MD-simulated atomic probability density maps of hydrotalcite intercalated with formate (left column), acetate (middle column), and propanoate (right column) with progressive hydration. Top row, *n* = 0; middle row, *n* = 4; bottom row, *n* = 10. Green contours: hydrogens of M–OH groups; red: oxygens of carboxyl groups; blue: carbons of carboxyl groups; thin light blue: oxygens of H_2O molecules.

Findings

- ☐ The molecular dynamics study of the hydration energetics of layered double hydroxides intercalated with carboxylic acids suggest absence of structurally well defined hydration states.
- ☐ The study predict that these solids would continually absorb water in water rich environment and plausibly delaminate.
- ☐ This conclusion is consistent with the recent experimental observation of the delamination of lactate- and citrate-HT [2,5].
- ☐ The origin of the enhanced swelling of organo-LDHs are proposed to be due to the high water affinity of the intercalate-anions.
- ☐ As evidenced in our studies the citrate-HT exhibit superior swelling behavior than mono-carboxylate anions.
- ☐ The superior swelling behavior of of citrate-HT is due to a combination of factors such as the higher incommensurability of the citrate with the M-OH layers and its ability to form compact hydration structures.
- ☐ It is proposed that the swelling behavior and delamination of layered double hydroxides can be improved by starting with larger interlayer species with multiple carboxylic sites.

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