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MOLECULAR VALIDATED MODEL FOR ADSORPTION OF PROTONATED DYE ON LDH

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Abstract - Hydrotalcite-like compounds are anionic clays of scientific and technological interest for their use as ion exchange materials, catalysts and modified electrodes. Surface phenomenon are important for all these applications. Although conventional analytical methods have enabled progress in understanding the behavior of anionic clays in solution, an evaluation at the atomic scale of the dynamics of their ionic interactions has never been performed. Molecular simulation has become an extremely useful tool to provide this perspective. Our purpose is to validate a simplified model for the adsorption of 5-benzoyl-4-hydroxy-2-methoxy-benzenesulfonic acid (MBSA), a prototype molecule of anionic dyes, onto a hydrotalcite surface. Monte Carlo simulations were performed in the canonical ensemble with MBSA ions and a pore model of hydrotalcite using UFF and ClayFF force fields. The proposed molecular model has allowed us to reproduce experimental data of atomic force microscopy. Influences of protonation during the adsorption process are also presented.
Keywords: Adsorption; Hydrotalcite; Dye; Molecular simulation.

INTRODUCTION

Layered double hydroxides (LDH) are an important class of natural compounds and also easily obtained by synthesis. They have a permanent positive charge on their surface. In addition, LDHs can exchange anions that lie between the layers. For these characteristics, these compounds are of great scientific and technological interest and are used as ion exchange materials (Dutta *et al*., 1991), catalysts (Reichle *et al*., 1986) and modified electrodes (Itaya *et al*., 1987). LDHs with magnesium and aluminum atoms on their layers are known as hydrotalcite and the framework of the layers are similar to brucite ($Mg(OH)_2$). We can imagine a starting structure, electrically neutral, being composed by one brucite layer (Figure 1a).

As magnesium is isomorphically replaced by Al^{3+}, a permanent positive charge is created that is balanced by intercalation species (Figure 1b). In hydrotalcite, CO_3^{2-} and water molecules are the intercalation species in the interlayer space.

The permanent positive charge is responsible for the extraordinary LDH performance in the adsorption of anionic dyes (Zhu *et al*., 2005; Abdelkader *et al*. 2011; Boudiaf *et al*. 2012; Aguiar *et al*., 2013). To be able to understand and predict the behavior of LDH's for anionic dyes adsorption, it is important to analyze on an atomic-scale, the surface phenomena that result in the macroscopic properties. Experimental techniques are limited for clarifying these phenomena.

Molecular simulation has been used successfully in the study of LDH. Wang *et al*. (2001) used molecular dynamics to establish the two most stable hydration states of hydrotalcite (Mg:Al = 2:1) with

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Cl^- ions and water intercalated. Kim *et al*. (2007) applied the Monte Carlo method using the canonical ensemble to measure diffusivity values and intercalation of CO_2 at high temperatures (> 200 °C) in hydrotalcite. The LDH/dye system is influenced predominantly by electrostatic interactions. This influence is revealed by changes in the amount adsorbed with variations in pH. MBSA (5-benzoyl-4-hydroxy-2-methoxy-benzenesulfonic acid) is an anionic dye model, ideal for studies of molecular simulation due its small size and well-known ionic behavior. In aqueous media the MBSA molecule has two ionic forms. At pH > 2, $MBSA^{1-}$ is the predominant species in solution. Increasing the pH (pH >8) produces a solution rich in the $MBSA^{2-}$ anion. We also know that changes in pH affect the surface of LDH where adsorption occurs. However, in this study, the effects of pH on the surface of LDH will not be considered.

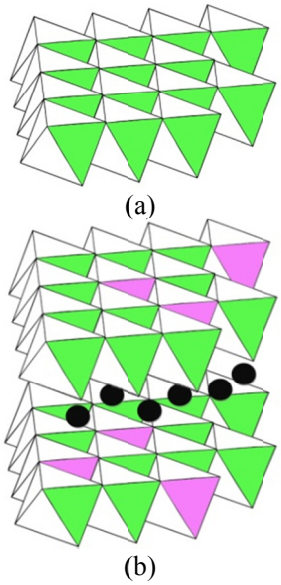

Figure 1: Brucite layer (a) and hydrotalcite structures (b). Green - Mg; Pink - Al and Black - CO_3^{2-}(adapted from Serwicka *et al*., 2004).
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Thus, our main goal is to validate a molecular simulation model of the system LDH/Dye, which can adequately describe the adsorption of the anionic dye model MBSA in LDH surface, to get first insight and experience in describing these systems. For this purpose, Monte Carlo simulations in canonical ensemble were performed with MBSA ions in a proposed model of hydrotalcite pore. The simulated data were validated with experimental data from atomic force microscopy (Cai *et al*., 1994). Special attention is given to the aspects related to the impact of protonation on the adsorption. To the best of our knowledge, no such previous theoretical study had been performed.

METHODOLOGY

LDH Model

The model was based on a crystal structure obtained by refinement of powder X-ray diffraction (Bellotto *et al*., 1996). The hydrotalcite unit cell crystallizes in space group R3m (a= b= 3.04 Å, b = 22.77 Å). The unit cell containing only magnesium atoms was multiplied by ten in a and b directions, resulting in a supercell contained a total of 100 crystallographic unit cells (10 x 10 x1). The magnesium was replaced by aluminum following a 3:1 ratio of Mg:Al. The interlayer space was designed introducing enough CO_3^{2-} ions to neutralize the overcharged layers. For each two aluminum atoms in the layer there should be one CO_3^{2-} in the interlayer space. Along with CO_3^{2-} ions, water molecules were introduced in the proportion of four water molecules per CO_3^{2-} (Wang *et al.,* 2001). The energy of the interlayer space was minimized while maintaining the positioning of the layer fixed. The whole supercell is showed in Figure 2.

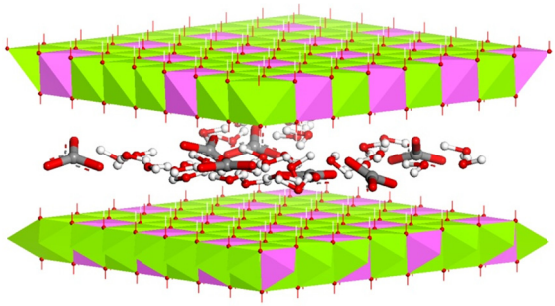

Figure 2: Model of the stacked LDH unit. White – H; Red – O; Pink – Al; Green – Mg; Gray and Red cylinders – CO_3^{2-}.
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After that, the c direction was multiplied by two and the inner space between the two layers was extended to simulate a LDH average size pore of 72 Å between inner layers. The results of these last steps are showed in Figure 3.

The pore size of 72 Å was based in the study of Reichle *et al*. (1986). They estimate that most of the LDH pore volume was concentrated between 50 and 100 Å. The hydrotalcite with carbonate ions is one of the most stable structures of LDH, not allowing new species to intercalating in the interlayer space through ion-exchange. In this case, adsorption on hydrotalcite takes place exclusively by surface interaction.

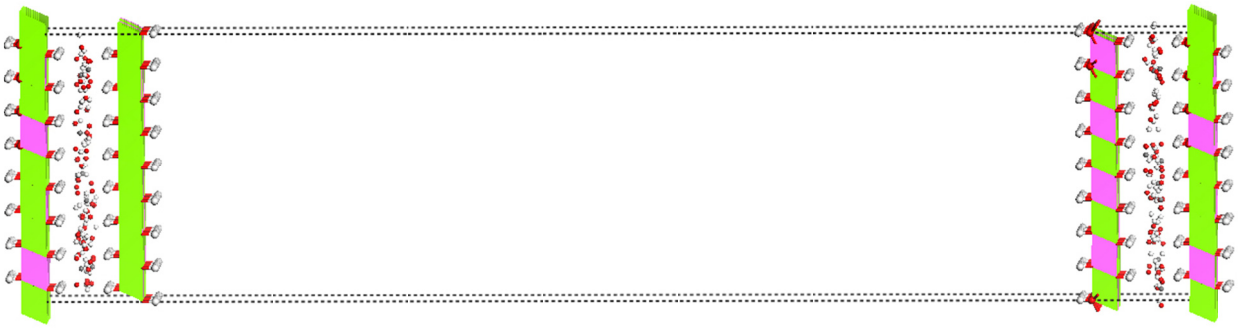

Figure 3: Simulation cell with 72 Å between layers to represent the hydrotalcite pore. White – H; Red – O; Pink – Al; Green – Mg.
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MBSA Model

MBSA molecules were represented by an atom–atom model. To represent the different states of ionization, the hydrogen atom attached to the sulfonic group was removed to give the anion $MBSA^{1-}$; after that, removing the hydrogen attached to the oxygen atom of the benzene ring gives the anion $MBSA^{2-}$. Hydronium ions were represented by a spherical model of hydrogen atoms with a positive charge (+1). The MBSA anion energies are minimized using the Steepest Descent algorithm with the generic force field COMPASS (Sun, 1998). The COMPASS potential function is given as:

$$E_t = \sum_{i=2}^{4} k_i^b (b-b_0)^i + \sum_{i=2}^{4} k_i^a (\theta-\theta_0)^i + \sum_{i=2}^{4} k_i^t (1-\cos i\varnothing)^i + k^0(\chi-\chi_0)^2 + \sum E^{cross-terms} + \sum E^{elec} + \sum E^{VDW} \quad (1)$$

The total energy consist of a sum of functions for bond lengths (b), angles (a), torsion angles (t) and out-of-plane bending angles (o) and cross terms (as for example: between two bonds with one common atom, two angles with a common bond and so on). The nonbonded energies were represented by electrostatic (elec) and van der Waals (VDW) interactions. All constant values can be found in the original COMPASS validation paper (Sun, 1998). Those steps are crucial for obtaining reliable results, since unoptimized molecules frequently did not reach adsorption equilibrium.

The partial charges used was obtained based on the Charge Equilibration methodology (Rappe and Goddard, 1991) and are shown in Table 1 and Figure 4. Both the energy minimization and charge distribution were implemented in the commercial packages Cerius2 from Accelrys.

Table 1: Charges of the MBSA ions (see Figure 4 for atom reference).

Atom	Charges (e)		Atom	Charges (e)	
	$MBSA^{1-}$	$MBSA^{2-}$		$MBSA^{1-}$	$MBSA^{2-}$
C1	-0.198	-0.221	H1	0.127	0.104
C2	0.042	0.019	H2	0.127	0.104
C3	-0.127	-0.15	H3	0.127	0.104
C4	0.042	-0.023	H4	0.127	0.104
C5	0.052	0.029	H5	0.127	0.104
C6	-0.127	-0.15	H6	0.127	0.104
C7	0.315	0.292	H7	0.41	-
C8	0.052	0.029	H8	0.127	0.104
C9	-0.127	-0.15	H9	0.053	0.03
C10	-0.127	-0.15	H10	0.053	0.03
C11	-0.127	-0.15	H11	0.053	0.03
C12	-0.127	-0.15			
C13	-0.127	-0.15			
C14	0.001	-0.022	S	1.318	1.295
O1	-0.706	-0.729	O4	-0.419	-0.442
O2	-0.706	-0.729	O5	-0.452	-0.305
O3	-0.706	-0.729	O6	-0.202	-0.225

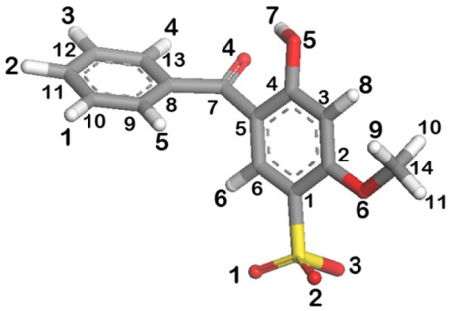

Figure 4: Model of$MBSA^{1-}$molecule with atom types. White – H; Red – O; Gray – C; Yellow – S.
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Forcefield

The system LDH/dye was described using the LJ potential for repulsion-dispersion forces plus Coulombic contributions between point charges:

$$U\left(r_{ij}\right) = 4.\varepsilon_{ij}.\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] + \frac{q_i q_j}{r_{ij}} \qquad (2)$$

where ε_{ij} (kcal/mol) represents the depth of the potential well, σ_{ij} (Å) is the finite distance at which the energy of interaction is zero and r_{ij} (Å) is the distance between the molecular centers i and j. In the second term, q_i and q_j are point charges separated by the distance r_{ij}. The cross LJ terms were obtained using the usual arithmetic and geometric combination rules (Lorentz-Berthelot).

For the interactions between MBSA molecules and the LDH framework, we used the ClayFF force field (Cygan *et al*., 2004). This force field has been developed especially for clay minerals.

The interaction between MBSA molecules are computed based in the UFF force field (Rappe *et al*., 1992). Table 2 presents the parameter's values for each atomic species ($r_0 = \sigma$ / 1.1224).

Table 2: Forcefield parameters.

Atom	r_0 (Å)	ε_{ij} (kcal/mol)	Charges (C)
Magnesium[a]	5.909	$1.3298.10^{-6}$	1.36
Aluminium[a]	4.7943	$9.0298.10^{-7}$	1.575
Hydrogen[a]	-	-	0.425
Oxygen[a]	3.5532	0.1554	-0.95
Nitrogen[b]	3.660	0.069	[c]
Carbon[b]	3.851	0.105	[c]
Oxygen[b]	3.500	0.060	[c]
Sulfur[b]	4.035	0.274	[c]
Hydrogen[b]	2.886	0.044	[c]

[a]Cygan *et al*., 2004 (LDH); [b]UFF-Rappe *et al*., 1992 (MBSA); [c]See Table 1 and Figure 4

Computational Details

The electrostatic potential was calculated by Ewald method. The Ewald method accuracy was set for an energy tolerance of 0.001 kcal/mol within a cut-off of 15.2 Å. This means that larger cut-offs will give energy variation in the third decimal place as done in a similar study (Lima *et al*, 2015). All LJ potential had also a 15.2 Å truncation. We also did tests with increasing LJ cut-offs and obtained similar results. After 1.5 x 10^6 equilibration steps, more 1.0 x 10^6 steps were used to obtain the average values of the thermodynamic properties and the most stable configuration.

The simulations in the canonical ensemble (NVT) were performed with a variable number of MBSA anions until the surface was saturated. The number of molecules at saturation will be compared with that obtained experimentally by Cai *et al*. (1994) for $MBSA^{1-}$. The molecular simulation algorithm of Cerius2 (Accelrys) was used to obtain the NVT equilibrium configurations. During the Monte Carlo simulations, the MBSA molecules and LDH framework were considered rigid. While this approach is acceptable for LDH, it is not suitable for dye molecules. However, MBSA is a special case because its structure consists basically of two aromatic rings with reduced mobility. Furthermore, the molecule has previously been minimized and we did not expect significant conformation changes.

RESULTS AND DISCUSSION

Model Validation

In order to compare simulated and experimental data (Cai *et al*., 1994), an increased number of MBSA molecules were introduced in the simulation cell until saturation. During simulation, $MBSA^{1-}$ molecules are translated and rotated inside the simulation cell until equilibrium is reached (Figure 5).

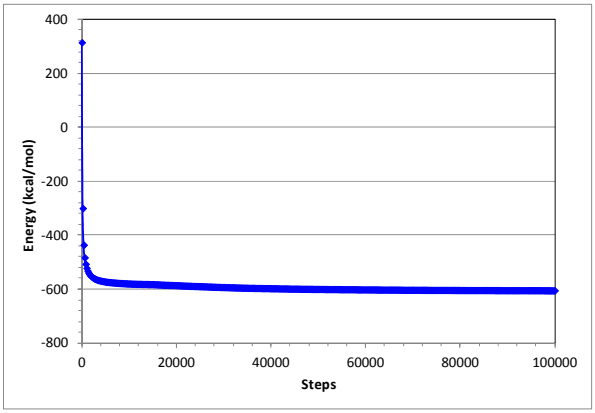

Figure 5: The evolution of the energy in the system LDH/$MBSA^{-1}$ at 298 K. The most stable configuration occurred after about 30,000 steps.

At equilibrium, the molecules of $MBSA^{1-}$ assumed a perpendicular position with the LDH surface. This same orientation of the anions with respect to the hydrotalcite surface was verified experimentally by Cai *et al*. (1994) for $MBSA^{1-}$ adsorption onto

hydrotalcite. The authors used atomic force microscopy to generate impressive nanoscale images of the MBSA anions. This specific position is associated to the sulfonic acid group of the $MBSA^{1-}$ molecule which has a superior concentration of negative charges. The sulfonic acid group moves towards the surface that is positively charged (Figure 6).

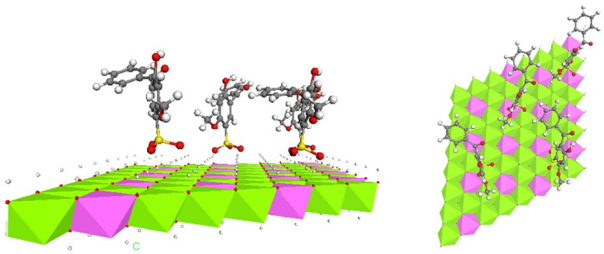

Figure 6: Side and top view of the equilibrium position of $MBSA^{1-}$ at the end of the simulation.
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In the simulation, the $MBSA^{1-}$ anions exhibit a packing of 1 molecule/59.5 $Å^2$, resulting in approximately 12.2 molecules when the simulation cell surface was fully saturated. The experimental adsorption capacity was 2.41 x 10^{-10} mol/cm^2 (Cai *et al*., 1994) that results in 1 molecule/69.1 $Å^2$ (equivalent to 10.5 molecules at our simulation cell surface). Thus, in the experiment, the LDH adsorbs 13% less molecules. Considering that we are using a prefect surface in the simulation, some discrepancy from the experimental data was expected. Having validated the models for the system LDH/$MBSA^{1-}$, we moved towards the protonation study.

Impact of Protonation

The interaction energy of an increasing number of MBSA anions and each LDH pore surface are shown in Table 3. Analyzing from an electrostatic point of view, the charge increase on $MBSA^{2-}$ until 8 molecules should increase adsorption.

Table 3: Interaction energy between MBSA anions and LDH.

Number of MBSA anions	$MBSA^{-1}$ Interaction Energy (kcal/mol)	$MBSA^{-2}$ Interaction Energy (kcal/mol)
1	-585.77	-1026.77
2	-595.22	-1121.70
4	-597.25	-981.47
6	-505.95	-784.59
8	-465.74	-582.83
10	-416.43	-399.20

Experimentally, the extra protonation results in a 56% decrease in adsorption (Cai *et al*. 1994). We want verify if our model could also predict adsorption reduction. The species introduced in the simulation cell to study MBSA's protonation consist of anions and protons. In aqueous solution, as the pH increases, the deprotonation of MBSA is initially partial (-1), and finally complete (-2). Assuming that all protonated hydrogen came from $MBSA^{1-}$ and $MBSA^{2-}$, we obtain H_{cation}: $MBSA_{anion}$ ratios of 1:1 and 2:1 for $MBSA^{1-}$ and $MBSA^{2-}$ respectively. The interaction energy (= E_{total} - $\sum E_{each\ component\ alone}$) computed between an increasing number of H+ cations and one MBSA anion molecule showed interesting results (Table 4).

Table 4: Interaction energy between MBSA anion and H^+ cations.

Number of H^+ cations	$MBSA^{1-}$ Interaction Energy (kcal/mol)	Number of H+ cations	$MBSA^{2-}$ Interaction Energy (kcal/mol)
1	-78.77	2	-177.69
2	-129.76	4	-268.99
4	-161.63	8	-365.88
6	-204.07	12	-505.68
8	-261.61	16	-661.85
10	-324.66	20	-849.54

To $MBSA^{1-}$, the energy of interaction between the molecule and ionized cations are always lower than the energy of interaction with the surface (Table 3), therefore, in the equilibrium, the molecules are adsorbed on the surface. For $MBSA^{-2}$, when the interaction involves 12 or more cations, the energy of interaction between the molecule and ionized cations becomes equivalent to the surface energy.

When the complete system with 10 MBSA anions/pore surface and the corresponding quantity of cations (10 or 20) is simulated in the LDH pore, we observed that, while all $MBSA^{1-}$molecules were on the surface, 38% of the $MBSA^{2-}$ molecules remained in the interlayer space of the pore as shown in Figure 7. Our simulations always showed a smaller amount of $MBSA^{2-}$ adsorbed, even when the number of molecules at experimental saturation (approximately 10 molecules) was changed.

When MBSA is first protonated, one H^+ cation surrounds the $MBSA^{1-}$ anion to stabilize it. For the $MBSA^{2-}$ anion there are two H^+ cations. The positively charged LDH surface attracts anionic molecules that adsorb on the surface, making the whole system more energetically stable. Thus, once $MBSA^{1-}$ is adsorbed by the surface it will attract more weakly the H^+ from the first protonation. Because each

$MBSA^{2-}$ anion produces a second H^+, it suffers strong competition from H^+ cations, so the amount of $MBSA^{2-}$ that remains on the surface decreases.

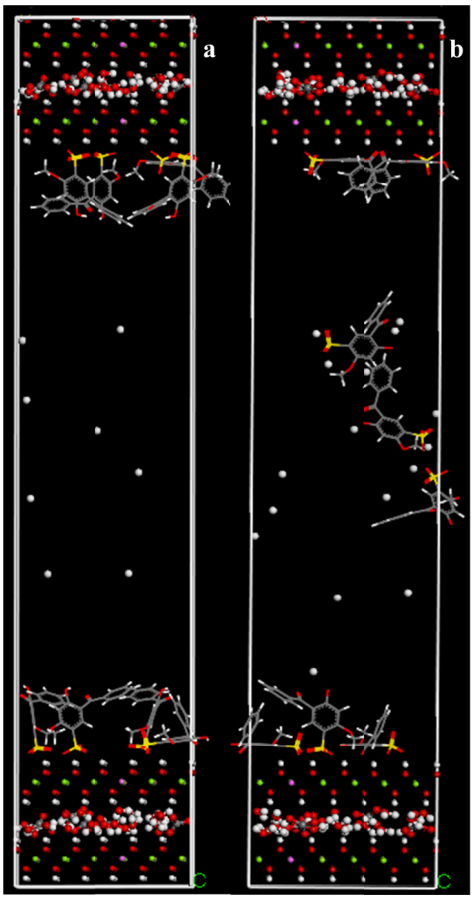

Figure 7: Equilibrium position of (a) $MBSA^{1-}$ and (b) $MBSA^{2-}$.
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Evidences of a similar anion-cation stabilization phenomena could be found in the study of Bhargava *et al*. (2007). The authors deduced from quantum methods a function showing the spatial distribution of the anions around 1-n-butyl-1,3-methylimidazolium hexafluorophosphate cations.

The $MBSA^{2-}$ theoretical adsorption decrease of 38% is less than the experimental decrease of 56%. However, these are very promising results and represents a first attempt to quantify the impact of protonation in adsorption of this class of systems. Changes in the LDH surface when the pH increases to 10.5 may also contributed to the $MBSA^{2-}$ adsorption reduction. Xu *et al*. (2008), for example, have found a variation of LDH zeta potential from 45 to 30 mV when the pH changes from 6.5 to 10, respectively.

CONCLUSIONS

Through simulations on the NVT ensemble, we have validated an adsorption model for $MBSA^{1-}$ on LDH through its position on the surface of hydrotalcite and the amount adsorbed at saturation. We have obtained evidence that the model is also able to evaluate the impact of increasing protonation that occurs in real systems as the pH varies. The decrease in the amount adsorbed of the more deprotonated species $MBSA^{2-}$ is related to the strong interaction of hydrogen cations with MBSA molecules, competing with the surface for global minimum energy.

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