

Theoretical study of the anionic exchange thermodynamics of Zinc Hydroxide Chloride and Zinc Hydroxide Nitrate

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ABSTRACT: The hydrated structures of the Zinc Hydroxide Chloride (ZHC) and of the Zinc Hydroxide Nitrate (ZHN) were built and their electronic structure were calculated by ab initio density-functional theory methodology in order to study the anionic exchange with fluoride, bromide, iodide and, in the case of ZHN, chloride. It could be noticed that their lattice parameters differ from one another due to the electronegativity of the anions. The structure containing fluoride (ZHF) presented the lowest value of c parameter and volume, since the interactions inside the structure are very intensive because of the hydrogen bonds. The thermodynamical properties showed that the only spontaneous exchange for the ZHC structure is with iodide. However, those results showed that the ZHN structure exchanges its nitrates for all the studied anions, which is in agreement with the experimental values.

KEYWORDS: Density Functional Theory; Layered Hydroxide Salts; Anionic Exchange.

1. INTRODUCTION.

1.1. Structural description

Many layered compounds are studied due to their various applicabilities including selective removal of certain anions. The layered double hydroxides (LDH) and the layered hydroxide salts (LHS) are both examples of those compounds with a similar structure from the brucite, $Mg(OH)_2$ (Figure 1).

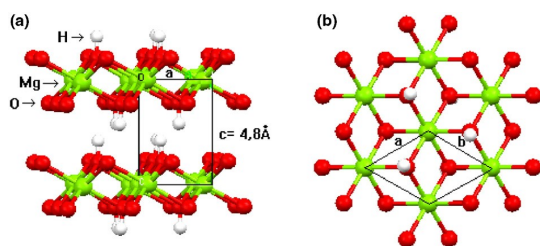


Figure 1: Brucite structure, $Mg(OH)_2$
(a) plane xz (b) plane xy (Arizaga, 2007)

The brucite structure is built with octahedron sheets, which are formed with Mg^{2+} as the central cation and the hydroxyls as the ligands. Due to the divalence from the Mg^{2+} cation, the resulting layers are neutral and the interlayer region is empty. One can construct the LDH structure from the brucite, if some of the divalent cations are exchanged for trivalent cations, therefore resulting in a positive charge that must be balanced with interlayer anions. In the case of the LHS, there are two possible structure modifications: exchange some cations for ones of the same valence and some hydroxyls for another anions (type I) or the removal of a octahedron in order to insert two tetrahedrons (type II) (Louër et al., 1973).

The type-I hydroxide salts do not have any interlayer content, because the layers are not positively charged. However, the type-II compounds can present interlayer anions, which can be grafted to the tetrahedron or free in the interlayer region. If the anions are not grafted to the tetrahedron, then it is very likely that those compounds have coordinated water molecules.

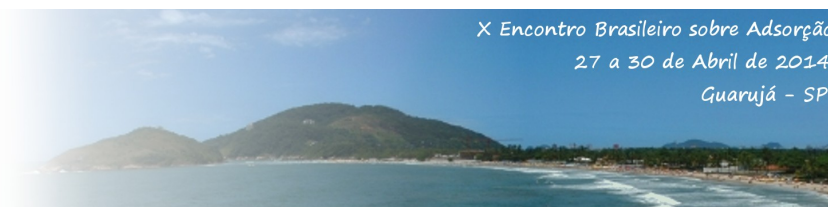


Figure 2 portrays the over view of the structures, which were studied in this work.

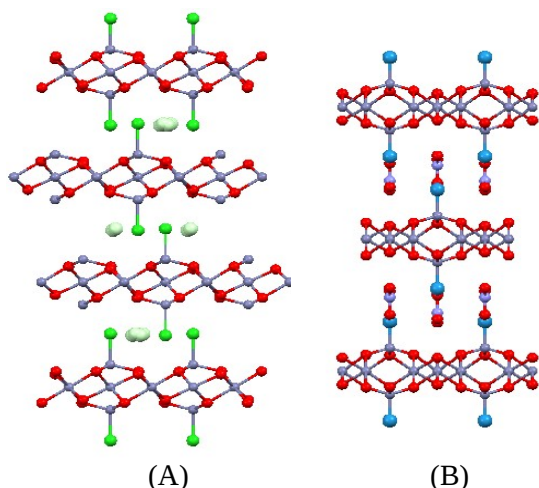


Figure 2: (A) $Zn_5(OH)_8Cl_2 \cdot H_2O$ structure (ZHC) and (B) $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$ structure (ZHN)

1.1. Anionic exchange

The increasing attention which has been given to the environment shows that the knowledge of less harmful industrial processes and new techniques related to pollutant removal are very important nowadays. The hydroxide salts can play an important role in this area, since many compounds present high selectivity for certain anions, which are able to be incorporated to the structure.

Thomas et al. studied the selectivity of the $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$ compound to retain fluoride, chloride, bromide and iodide. The results show that all the anions could be exchanged for the nitrates, but a selectivity degree could be noticed: $F^- > Cl^- > Br^- > I^-$ (Thomas et al., 2011). Thomas et al. also discussed about the processes kinetics due to the infrared absorption spectra. The spectra showed that not all the nitrates could be removed from the structure in some cases.

Anionic exchange tests were also conducted for the $Zn_5(OH)_8Cl_2 \cdot H_2O$ compound, but this time with carbonate and sulphate. A selectivity degree could also be observed for this compound (Ishikawa et al., 2007). It is widely known that the carbonate can be a contaminant in some LDH and LHS synthesis, because these anions seem to stabilize the structures. The following selectivity order could be observed: $CO_3^{2-} > SO_4^{2-} > Cl^-$ (Ishikawa et al., 2007).

In order to understand those experimental features, we computed the thermodynamics of the anionic exchange processes of ZHC and ZHN with fluoride, chloride, bromide and iodide.

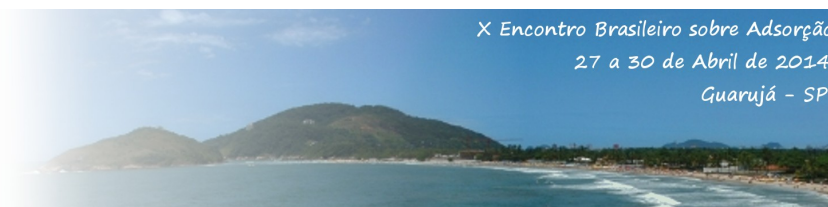
2. METHODOLOGY

All ab initio calculations were performed using the codes available in the Quantum Espresso package,¹² which implements the DFT (Hohenberg, 1964, Kohn et al., 1965) framework with periodic boundary conditions. We used the generalized gradient approximation (GGA/PBE) (Perdew et al., 1996) for the exchange-correlation functional, ion cores were described by Vanderbilt (Vanderbilt, 1990) ultrasoft pseudopotential, and the Kohn-Sham one-electron states were expanded in a plane wave basis set until the kinetic cutoff energy of 60 Ry (480 Ry for the density). Monkhorst-Pack (Monkhorst, 1976) meshes of $5 \times 5 \times 5$ k-point sampling in the first Brillouin zone were used for all cells. Equilibrium lattice parameters and atomic positions for all structures were found by minimizing the total energy gradient. For each set of lattice parameters, the relative ion positions were relaxed until all force components were smaller than 0.001 Ry/Bohr. All the molecular graphics were generated by XCRYSDEN (Kokalj, 1999, 2003) graphical package, and the simulated X-ray powder diffractograms were obtained by Mercury software.

We carried out vibrational calculations to characterize optimized structures as either minimal or maximal. In order to analyze the thermodynamics, we computed the variation of entropy, enthalpy and Gibbs free energy related to the dehydration exchange reactions, which were obtained from the calculated thermodynamic property of each solid or isolated ionic species.

The ions in gas state were treated according to the formalism described in our previous work (Costa et al., 2010, 2011). We have still considered an additional contribution to the electronic energy in order to remove the long-ranged Coulomb interaction between the periodic images of charged molecules. This effect was compensated with the Makov-Payne correction.

In order to obtain the contributions of H, S and G of the anions in the aqueous solution (H_A , S_A , G_A , respectively), we considered the formation



of a hydrated ion from gas state, as it is shown in the following equation:

$$\Delta H_A^{aq} = (H_A + \Delta H_A^{aq'}) \quad (01)$$

$$\Delta S_A^{aq} = (S_A + \Delta S_A^{aq'}) \quad (02)$$

$$\Delta G_A^{aq} = (G_A + \Delta G_A^{aq'}) \quad (03)$$

3. RESULTS

Firstly, the simulated main cell parameters of ZHC and ZHN were compared with the experimental ones. Table 1 shows the comparison between the simulated and experimental cell parameters.

Table 1: Main geometric parameters of ZHC and ZHN. S, Ex, Er stand for simulated, experimental parameters and relative error, respectively. Cell parameters in angstrom and degrees.

	ZHC			ZHN		
	S	Ex	Er	S	Ex	Er
a	6.45	6.34	1.76	19.82	19.48	1.73
b	6.44	6.34	1.61	5.60	5.52	1.45
c	23.67	23.65	0.07	6.37	6.24	2.08
α	90.09	90.00	0.10	90.01	90.00	0.01
β	89.90	90.00	0.22	93.78	93.28	0.54
γ	120.03	120.00	0.02	89.62	90.00	0.42
Volume	852.0	823.4	3.47	704.8	669.2	5.32

*Experimental values taken from Hawthorne, 2002; Stählin, 1970

It could be seen that a good agreement between the simulation and the experimental data was achieved.

As it was mentioned above, the vibrational modes were computed in order to study the thermodynamical features of the anionic exchange

where, H_A , S_A , G_A are the calculated enthalpy, entropy and the Gibbs free energy of the anions in the gas phase and ΔH_A^{aq} , ΔS_A^{aq} , ΔG_A^{aq} are the values concerning the standard enthalpy, entropy and the Gibbs free energy of formation of the hydrated ion A^{n-} from its gaseous state, respectively, which have been taken from experimental measurements reported by Lide.

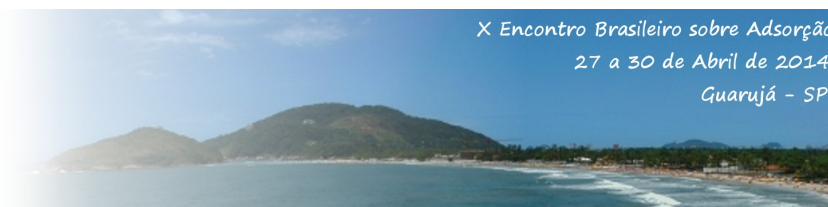
processes. The vibrational frequencies also showed a good agreement the experimental values obtained from infrared absorption spectra (Srivastava, 1967, Stählin, 1971).

For the sake of simplicity, the exchanged compounds will be abbreviated as ZHF, ZHB e ZHI for fluoride, bromide and iodide, respectively. The table 2 shows all the cell parameters for those compounds. Those values show that the basal spacing increases with the diminishing of the anion electronegativity. The same thing can be observed for the unit cell volume, since the interactions increases with the electronegativity. No drastical changes were noticed regarding the structure of the exchanged compounds, which makes them isostructural with each other.

Table 2: Main geometric parameters of ZHF, ZHB and ZHI. Cell parameters in angstrom and degrees.

	ZHF	ZHB	ZHI
a	6.40	6.48	6.54
b	6.40	6.48	6.49
c	21.55	24.45	25.52
α	89.72	89.97	89.72
β	90.12	89.86	89.99
γ	120.27	120.02	119.77
Volume	762.8	704.8	932.8

The Table 3 presents the values of the Gibbs free energy variation, the enthalpy variation and the entropic contribution ($T\Delta S$) for the anionic exchange with ZHC. All the values were



normalized by the number of zinc cations in the unit cell.

$$\Delta G = \frac{(G_{ZHA} + 2G_{Cl}) - (G_{ZHC} + 2G_A)}{N_{Zn}} \quad (04)$$

Where the values G_{ZHA} and G_{ZHC} are the Gibbs free energy of the exchanged compound and the ZHC, respectively. The values G_{Cl} and G_A are the Gibbs free energy of the chloride and the exchange anion, respectively. N_{Zn} represents the amount of zinc cations in the studied unit cells.

The negative values of the Gibbs free energy indicate that a certain process is spontaneous. So one can conclude that the only spontaneous process for the ZHC is with iodide anions.

Table 3: Thermodynamical study of the anionic exchange for the ZHC compound at 298,15 K and at 1 atm. Thermodynamical properties in kcal mol⁻¹

Anionic Exchange	ΔG	ΔH	TAS
ZHC → ZHF	1.91	3.35	1.44
ZHC → ZHB	1.99	-0.27	-2.26
ZHC → ZHI	-1.62	-4.61	-2.99

The Table 4 shows the thermodynamical properties of the anionic exchanges with the ZHN. Those values were also normalized by the same equation mentioned above (Equation 4). As it can be seen in Table 4, all processes are spontaneous, which agrees with the anionic exchange experiments (Thomas et al., 2011). However, another calculation regarding the kinetics of the processes would be necessary in order to predict the experimental selectivity order. As it was mentioned in the introduction, Thomas et al. discussed the kinetic aspects of these processes and proposed that the difficulty of the anions incorporation into the ZHC structure is due to level of hydration of the anions. The more hydrated an anion is, the harder it is for them to enter the interlayer region. Unfortunately, this kind of energy barrier calculation would be very difficult to achieve, because the construction of a huge

structure would be necessary in order to simulate it. Furthermore, this calculation would demand the involvement of a solid and liquid phase, making the calculations to be even harder.

Table 4: Thermodynamical study of the anionic exchange for the ZHN compound at 298,15 K and at 1 atm. Thermodynamical properties in kcal mol⁻¹

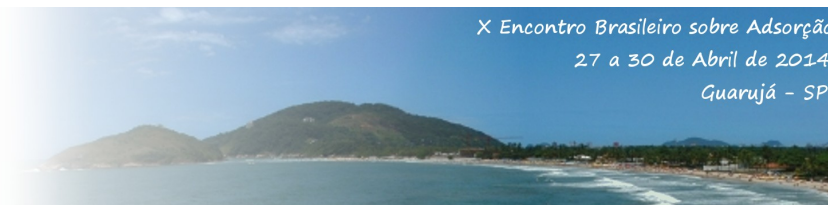
Anionic exchange	ΔG	ΔH	TAS
ZHC → ZHF	-7.64	-4.52	3.12
ZHC → ZHC	-9.55	-7.87	1.68
ZHF → ZHB	-7.55	-8.14	-0.59
ZHC → ZHI	-11.17	-12.48	-1.31

4. CONCLUSIONS

The values of the enthalpy, Gibbs free energy variations and the TAS could be calculated for the anionic exchange of the ZHC and ZHN compounds with fluoride, bromide, chloride and iodide. The results showed that the chlorides could only be exchanged with iodides and the resulting compounds are isostructural. The simulation of the anionic exchanges of the ZHN compound informed that the nitrates are exchanged with all studied anions. But the anions replace the water molecules which are coordinated to the tetrahedral zinc. So one water molecule remains in the interlayer region and the other one is released from the bulk. Unfortunately, the resulting structures of the experimentally exchanged compounds were not refined.

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