Studies in Surface Science and Catalysis 156
M. Jaroniec and A. Sayari (Editors)

Effect of exchangeable cation and hydration layer on the swelling property of 2:1 dioctahedral smectite clay – a periodic density functional study

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We used both localized and periodic calculations within the helm of Density Functional Theory (DFT) on a series of monovalent (Li^+, Na^+, K^+, Rb^+, Cs^+), and divalent (Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}) cations, to monitor their effect on swelling of clays. The activity order obtained for the exchangeable cations among all the monovalent and divalent series studied is: $Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+} > Cs^+ > Rb^+ > Na^+ > Li^+ > K^+$. We studied two type of clays Montmorillonite and beidellite, with different surface structure and with/without water using periodic calculation. We have calculated the layer spacing at the first, second and third hydration shell of exchangeable cation, to compare with the experimental d-spacing values to correlate with humidity. A novel quantitative scale is proposed by the relative nucleophilicity of the active cation sites in their hydrated state through Fukui functions within the helm of hard soft acid base (HSAB) principle. Finally, the swelling mechanism is proposed.

1. INTRODUCTION

Clays are lamellar alumino-silicates with a large variety of physicochemical properties, such as swelling, adsorption, surface acidity, ion exchange, etc. Smectites a member of 2:1 dioctahedral structural unit with one octahedral layer is sandwiched between two tetrahedral layers. Montmorillonite and beidellite are members of 2:1 dioctahedral smectite family. They share the common feature, that two tetrahedral sites sandwich a sheet of octahedrally coordinated metal ion. Substitution of a bivalent metal ion for octahedral aluminum in montmorillonite and substitution of a trivalent metal ion for tetrahedral silicon in beidellite results in a net negative layer charge, and the interaction with positive ions (exchangeable cation) to form an interlayer hydrated phase. There exists a high repulsive potential on the surface resulting from isomorphous substitution. Interlayer cation and charged clay surfaces interact strongly with polar solvents. As a result 2:1 clays expand in the presence of water in aqueous solution. This process is known as crystalline swelling [1]. The extent of swelling is controlled by a balance between relatively strong swelling forces, due to the hydration potential of the interlayer cations, charge sites, electrostatic forces of attraction between the positively charged interlayer cation [2] and negatively charged 2:1 phyllosilicate layer. The amount of water adsorbed by smectites is a function of the interlayer cations, is shown by Cuardos et al [3] using different experimental techniques such as B.E.T. surface area measurements, X-Ray Diffraction (XRD) and Thermo-gravimetric (TG) analysis. The equilibrium hydration state of a clay in integer-layer hydrates [4,5] regime is known to be a function of the magnitude and location of the clay layer charge, the applied pressure, the temperature, the interlayer ion identity and the water chemical potential as determined by vapor pressure or solution ionic strength using molecular dynamics. There is a consensus about the fact that swelling occurs through distinct steps forming one-, two-, and three-layer hydrates [6]. Many computer simulations have been directed to understand the swelling of clays or to study clay-water interface [7, 8-11]. In our earlier study [12, 13] we rationalized the structure property relationship in montmorillonite clays and observed that these hydroxyl groups expected to play a crucial role in the catalytic activity of dioctahedral clays. Pearson proposed the global HSAB principle [14] and a principle of maximum hardness (PMH) [15] which states that, for a constant external potential, the system with the maximum global hardness is most stable. Some DFT-based local properties, e.g. Fukui functions and local softness, [16] have already been used for the reliable predictions in various types of electrophilic and nucleophilic reactions. Now, it is known that, the reactivity of a chemical species depends on the solvent associated around the molecules [17]. Generally, when compared to a gas phase calculation, the solvent environment alters the charge distribution of a molecule and there is an increase in the dipole moment of the molecules. In addition to that, water enhances the intrinsic reactivity of polar molecules towards nucleophilic and electrophilic attack [17]. We in a recent study have used both localized reactivity index and periodic calculation on a series of monovalent and divalent cation in their monohydrated from to monitor their effect on the swelling of clays. A qualitative scale is proposed [18].

In the present study we therefore wish to extend the study for the same series of metal cations in presence of higher humidity to monitor the feasibility of two-layer or three-layer hydration using both reactivity index and periodic density functional calculation. We wish to compare the hydration behavior for all these cations and wish to propose a plausible mechanism of hydration. We have calculated the layer spacing at the first, second and third hydration shell of exchangeable cation, to compare with the experimental d-spacing values to correlate with humidity. A novel quantitative scale is proposed by the relative nucleophilicity of the active cation sites in their hydrated state through Fukui functions within the helm of hard soft acid base (HSAB) principle

2. THEORY

In density functional theory, hardness (η) is defined as [14]

$$\eta = \tfrac{1}{2}(\delta^2 E/\delta N^2)\ v(r) = \tfrac{1}{2}\ (\delta\mu/dN)_v$$

Where, E is the total energy, N is the number of electrons of the chemical species and μ is the chemical potential.

The global softness, S, is defined as the inverse of the global hardness, η.

$$S = 1/2\eta = (\delta N/\delta\mu)\ _v$$

Using the finite difference approximation, S can be approximated as

$$S = 1/\ (IE - EA) \qquad (1)$$

Where, IE and EA are the first ionization energy and electron affinity of the molecule, respectively.

The Fukui function f(r) is defined as mentioned in [18]

$$f(r) = [\delta\mu/dv(r)]_N = [\delta\rho(r)/\delta N]_v \tag{2}$$

The function 'f' is thus a local quantity, which has different values at different points in the species, N is the total number of electrons, μ is the chemical potential and v is the potential acting on an electron due to all nuclei present.

The local softness s(r) can be defined as

$$s(r) = (\delta\rho(r)/\delta\mu)_v \tag{3}$$

Equation (3) can also be written as

$$s(r) = [\delta\rho(r)/\delta N] v [\delta N/\delta\mu]_v = f(r)S \tag{4}$$

Thus, local softness contains the same information as the Fukui function f(r) plus additional information about the total molecular softness, which is related to the global reactivity with respect to a reaction partner, as stated in HSAB principle. Atomic softness values can easily be calculated by using eq 4, namely:

$$\begin{aligned} s_x^+ &= [q_x(N+1) - q_x(N)]S \\ s_x^- &= [q_x(N) - q_x(N-1)]S \\ s_x^0 &= S[q_x(N+1) - q_x(N-1)]/2 \end{aligned} \tag{5}$$

3. COMPUTATIONAL METHODOLOGY AND MODEL

The software package CASTEP (Cambridge Serial Total Energy package), which has been described elsewhere [19, 20] and associated programs for symmetry analysis were used for the calculations. Becke-Perdew parameterization [21,22] of the exchange-correlation functional, which includes gradient correction (GGA), was employed. The pseudo potentials are constructed from the CASTEP database. The screening effect of core electrons is approximated by LDA, while the screening effect for valence electrons is approximated by GGA. To obtain equilibrium structures for a given set of lattice constants, ionic and electronic relaxations were performed using the adiabatic or 'Born-Openheimer' approximation, where the electronic system is always in equilibrium with the ionic system. Relaxations were continued until the total energy had converged. In the present calculations kinetic cut-off energies between 600 and 1500 eV have been used. The Monkhorst-Pack scheme [23] was used to sample the Brillouin zone. The calculations were restricted to one special K point in the Brillouin zone, placed at (0.0, 0.0, and 0.0).

In the present study, all localized cluster calculations have been carried out with DFT [24] using DMOL^3 code of Accelrys Inc. A gradient corrected functional BLYP [25,26] and DNP basis set [27]was used through out the calculation. Basis set superposition error (BSSE) was also calculated for the current basis set in non-local density approximation (NLDA). Single point calculations of the cation and anion of each molecule, at the optimized geometry of the neutral molecule were also carried out to evaluate Fukui functions, global and local softness. The condensed Fukui function and atomic softness were evaluated using eqs 3 and 5, respectively. The gross atomic charges were evaluated by using the technique of electrostatic potential (ESP) driven charges.

The ideal formula of the clay montmorillonite, a member of 2:1 dioctahedral smectite family, is (M^+_x, nH_2O) ($Al_{4-x}Mg_x$) Si_8O_{20} $(OH)_4$ [12], where x = (12- a- b) is the layer charge, and the M is the balancing cation either monovalent or divalent. The desired structures of montmorillonite and beidellite have been generated from the structure of well-defined pyrophyllite [28]. They are having the formula $MSi_8Al_3MgO_{20}(OH)_4$ and $MAlSi_7Al_4O_{20}(OH)_4$, respectively. Hydrated phase calculations were performed with the minimum energy structures of the clays at the unhydrated phase. The interlayer structure was held fixed and the interlayer spacing was increased to accommodate the water molecule. Unhydrated respective clay structures were minimized using two steps: (1) the tetrahedral layers were allowed to relax with octahedral ions were kept fixed, and (2) all the ions were relaxed simultaneously relative to a fixed octahedral ion (magnesium or aluminum) until the total energies were converged. In both steps the interlayer cation is relaxed. For the hydrated phases we relaxed the cation water and the interlayer space, the lower part of the structure was kept fixed to compromise between CPU cost and accuracy.

The water complexes for the individual cations were generated from the optimized periodic structure. The geometries of the localized cations were isolated and then relaxed again for each neutral cationic and anionic form for the calculation of reactivity indices.

4. RESULTS AND DISCUSSION

This is known that at increasing humidity, smectites adsorb water vapor and form –one, -two and –three layer hydrates. The general swelling model within the interlayer of the smectite clay is shown in Figure 1. There exists bonded water molecule as shown in the fig and non-bonded water molecule, which acts as a bulk water, not shown here for visual clarity. We first compared the structure of two types of smectite namely montmorillonite and biedellite. For beidellite the negative charge associated with the tetrahedral layer substitution can be distributed over just three oxygens of one tetrahedron. This means that the water experiences a localized negative charge, which results in strong binding of water and interlayer cations. Whereas water experiences a more diffuse negative charge associated with octahedral substitution, for montmorillonite. It is as well observed that in terms of ionic radii the cations studied falls in the order $Cs^+ > Rb^+ > K^+ > Ba^{+2} > Sr^{+2} > Na^+ > Ca^{+2} > Li^+ > Mg^{+2}$.

Depending on the extent of increment in basal spacing between two smectite sheets, two types of swelling mechanism is proposed [18]; (1) crystalline swelling and (2) osmotic swelling. Crystalline swelling occurs for a situation with monolayer of water adsorption around cation, held by hydrogen bonding to the hexagonal network of oxygen atoms. This could result an increase of d-spacing in the range of about 10-20 Å. The osmotic swelling is the phenomenon when interlayer spacing increases abruptly to 30-40 Å with water content due to the interaction of the layer. We have chosen the model of the montmorillonite and beidellite type clays with structural formula $MSi_8Al_3MgO_{20}(OH)_4$ and $MAlSi_7Al_4O_{20}(OH)_4$, respectively, and optimized the structure in their unhydrated form. The internal coordinates matches with the available experimental values. The deviation is mostly at the basal oxygen atoms of the tetrahedral layer is due to the rotation of SiO_4 tetrahedral by 13.2° and tilted by 4.6° in average. It is observed that for montmorillonite the hydroxyl hydrogen attached with the octahedral aluminum makes an angle of 24.12° with a-b plane. We first optimized the

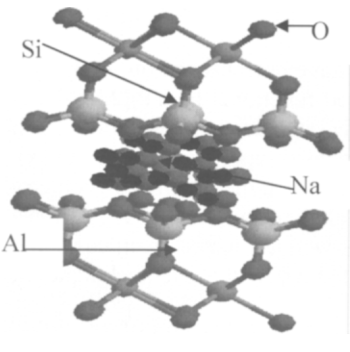


Figure 1: Smectite swelling model with type of atoms labeled.

montmorillonite / beidellite structure with different monovalent and divalent exchangeable cations. Then we added water around the cation center starting from first hydration shell to third hydration shell. We have used a cut off distance for this hydration shell, it is 2 Å for one layer, 3 Å for two layers and 4 Å for three layer of hydration. We have calculated the cell parameters after hydration to rationalize the swelling phenomenon.

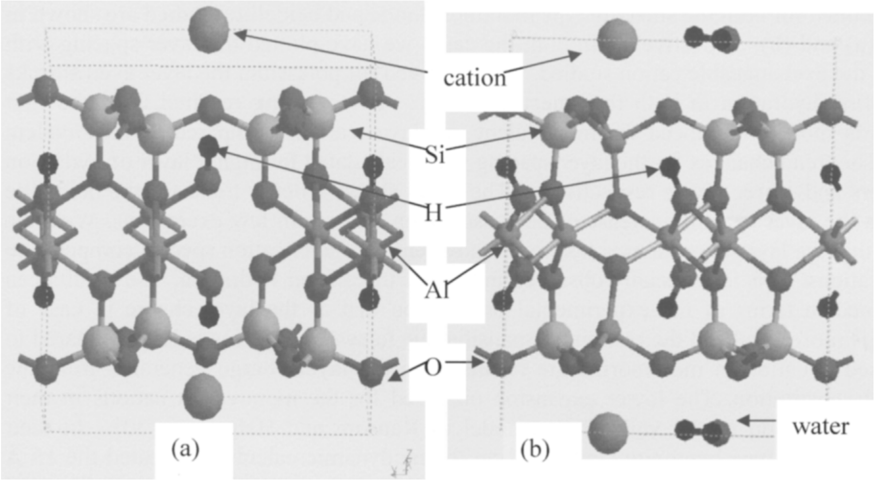
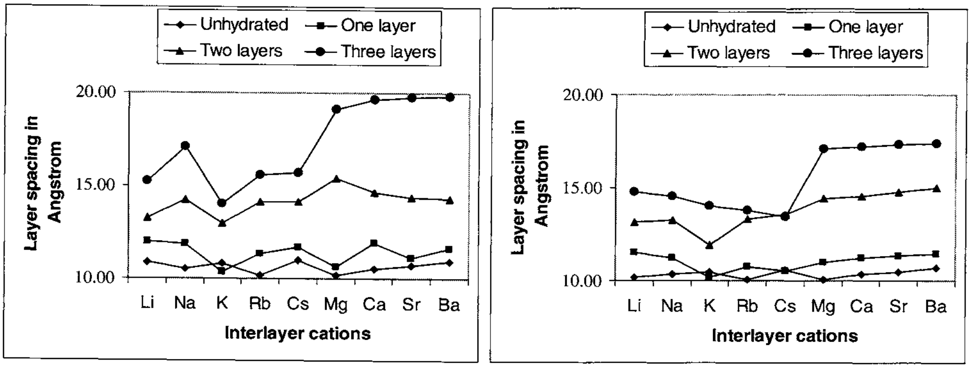


Figure 2: (a) Optimized structure of the sodium cation over the montmorillonite type clay structure, where octahedral aluminum is substituted by magnesium. (b) Model clay structure with exchangeable cation to show water addition inside a radius of 2 Å as an example.



(a) (b)

Figure 3: The effect of layer spacing in (a) montmorillonite and (b) beidellite in presence of different interlayer cations with varying layer of hydration.

The model for the calculation is shown in Figure 2. Water molecules are added until there is a constant rise in the stabilization energy to propose the maximum number of water molecule to reside in the first hydration shell is reached. For monovalent cations the number of water molecules surrounding the cations is 5 and that for bivalent cations is 3 in the first hydration shell as observed at the forced boundary condition. This result matches with our earlier Grand Canonical Monte Carlo GCMC simulation [29]. The general trend exhibits that, for all the cases there is a swelling along c-direction after hydration except for potassium. This can be explained by the fact that, in these types of clays one tetrahedral sheet of one unit layer is adjacent to another tetrahedral sheet of another layer. The oxygen atoms here are opposite to one another and the bonding between the layers is weak. Also there exists a high repulsive potential on the surface of layers resulting form isomorphous substitution. These factors contribute to the increase of the unit cell in c-direction due to the penetration of water. The results obtained for both the smectite type montmorillonite and beidellite studied are shown in Figure 3 (a) and (b), respectively. In both the cases we have plotted the layer spacing with respect to the exchangeable cation studied. It is observed for potassium the layer even shrinks after the first hydration in both the smectite variety. The swelling resulted from the first hydration is more pronounced for monovalent interlayer cations compared to the bivalent cations. The trend changes for the layer spacing when calculated for higher layer of hydration –two layers and –three layers respectively. The result shows a better trend for the beidellite variety, as the layer spacing increase or decreases in an order with few exceptions. We have observed that the layer expansion is less for monovalent interlayer cation species compared to bivalent cations. This is especially observed in case of three layer hydration. The results can be explained in terms of the experimental proposition that as the layer charge in case of beidellite is more localized the resulting expansion due to swelling forces is less compared to the diffused situation in montmorillonite results from the layer charge generated from the octahedral substitution. The lower expansion observed for the monovalent cations in their three-layer hydration model validate the model of Ransom and Helgesson [30]. In their model for sodium type bentonite clay based on thermodynamic calculation treated the 15 Å hydrate and the anhydrate as the end members of a solid solution series and chose to disregard the 19 Å regimes because they assumed that water content has thermodynamic properties about the same as those of bulk water. This effect is contradicted by Basett et al [31], where they show that this 19 Å regime holds good for bivalent metal cations e.g. Ca and Mg. The order of swelling in terms of layer spacing as observed for –one, -two and –three layer hydration for all the interlayer cations studied are as follows, respectively: Li > Ca > Na > Cs > Sr > Rb > Ba > Mg > K; Mg > Ca > Ba > Sr > Na > Cs > Rb > Li > K; Sr > Ba > Ca > Mg > Na > Cs > Rb > Li > K. The order is given only for the montmorillonite as there are no experimental results available for comparison with beidellite. It is observed that experimentally [3] in terms of d-spacing the order is Mg > Ca > Sr > Rb > Ba > Li > Na > Cs > K. This order is obtained at a fixed humidity and so the expansions were related with the number of water layer present at that humidity. Our layer spacing results are therefore have we only a partial match with experimental findings, and can reproduce the lowest expansion of potassium as observed by experiment very well. Whereas, considering the humidity of 30% the energetic characteristic obtained from the periodic calculations reproduces the trend of experiment. This trend is therefore mostly for the monolayer hydration, the effect for increased humidity condition cannot therefore be obtained though the periodic calculations. We can not see any pronounced difference between the monovalent and divalent cation to account for the difference in swelling phenomenon at higher humidity. This shows that the bulk calculation is unable to match the experimental trend of swelling. Hence, it seems it will be nice to monitor the localized water environment around the cation, which, may then be able to reproduce the experimental trend and as well can foresee the mechanism of multilayer hydration situation for a specific exchangeable cation. We need to answer the question, why one set of cation (bivalent) has shown increased swelling at the same humidity when the other cation (monovalent) cannot. We therefore have started with the cation water complexes for each monovalent and divalent cation to emphasize on their localized environment. We have performed a localized calculation with each cation water complex with the number of water molecules present in their cut off used in the periodic calculation we have just taken out the cation water complex from the model and optimized to calculate the relative nuceophilicity as described elsewhere [13]. The models and the results are shown in Figure 4 and figure 5, respectively.

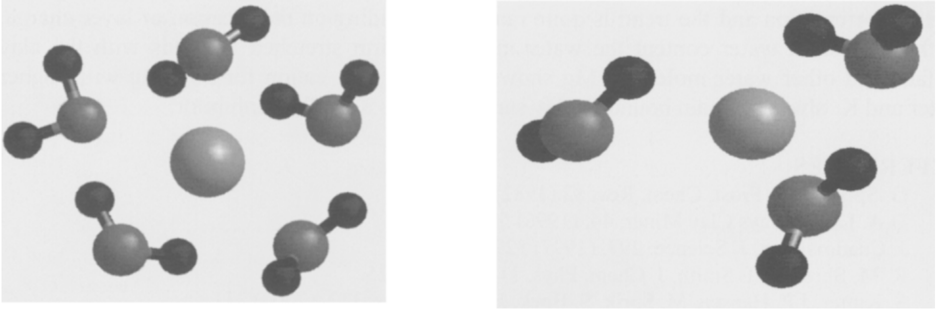


Figure 4: The model for (a) monovalent cation mono hydrated complex with 5 water molecules and (b) bivalent cation complex with 3 water molecules as obtained from periodic calculation.

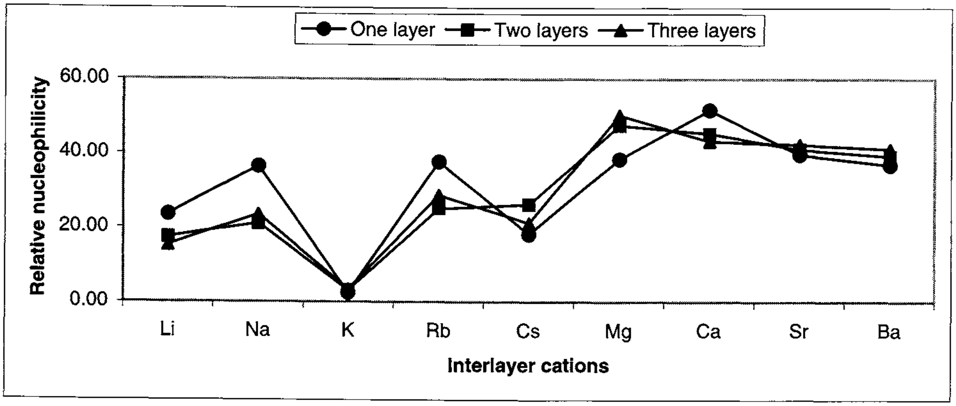


Figure 5: The plot of relative nucleophilicity with respect to the interlayer cations.

The result show that in terms of relative nucleophilicity (which is the ratio of nucleophilicity of a particular atom center) the order of activity for –one, -two and –three water scenario for montmorillonite is as follows: Ca > Sr > Mg > Rb > Ba > Na > Li > Cs > K; Mg > Ca > Sr > Ba > Cs > Rb > Na > Li > K; Mg > Ca > Sr > Ba > Rb > Na > Cs > Li > K. This activity order is in close resemblance with the experimental d-spacing results. We have as well seen from the optimized geometry of the cation water complex, the most stable bivalent hydrate complex Mg is surrounded by 6 water molecule in a two layer hydration with a cut off radius of 3 Å. One of the H atoms of each water molecule is pointed directly towards an oxygen atom of the adjacent clay layer. This is also confirmed that a tetrahedral network of water molecule similar to pure ice or water does not form due to complicated influence of clay sheets and the interlayer cation. The difference in behavior of monovalent and divalent cation is mainly therefore due to localized cation-water interaction.

5. CONCLUSIONS

In this communication we have studied a range of monovlent and divalent interlayer cations and their interaction with water during the swelling process for 2:1 dioctahedral smectite clay with a special emphasis on montmorillonite for their all possible –1, -2 and –3 hydration layer situation. A quantitative order of activity comparable with the experimental d-spacing is obtained. It is observed that at low hydration the water molecules try to squeeze in a flat orientation and the trend is quite random depending on the location of layer charge. With increase in water content the water molecules form stretched H-bonds with the clay surface and other water molecule. Mg shows to be the best cation for swelling with higher water and K always remain bound to clay surface acts as a swelling inhibitor.

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