Novel Insights on Swelling and Dehydration of Laponite

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A B S T R A C T

This paper investigates water sorption and dehydration of model synthetic clay (Laponite) and highlights the large differences with natural Na-smectite clays. Measurements were done by combining for the first time thermogravimetric analysis and X-ray diffraction methods on Laponite powders stored in atmospheres with controlled relative humidity. Laponite exhibits a very good reproducibility of the sorption diagram and appears as the most hygroscopic among Na-smectites. The interlayer distance increases from 11 to 20 Å when the ratio $r = n_{H2O}/n_{Na}$ increases from 2 to 22, in agreement with recent numerical simulations. The desorption process, in this range of r, in isothermal conditions follows a first order kinetics with two regimes around $r^* = 7$ which is close to the coordination number of Na^+ ions in concentrated NaCl solution. Activation energies and frequency factors are derived for the two regimes of desorption and discussed in relation with stability of the cationic complex.

Smectite clays (Sm) are layered mineral nanostructures consisting of a central sheet composed of Li^+, Mg^{2+}, Al^{3+} or Fe^{3+} cations in octahedral coordination to oxygen atoms or hydroxyl groups. This central layer is sandwiched between two silicate layers where the silica atoms are in tetrahedral coordination to oxygen atoms. The presence of charge unbalance leads to an overall negative charge in the central layer, which is compensated by labile counterions, mainly Na^+ and Ca^{2+}, located at the surface of the silicate layers. The Sm group incorporates a variety of clays, the most common ones being montmorillonite (Mt) and hectorite (Ht) [1].

Laponite (Lap) (hydrous sodium lithium magnesium silicate) is a synthetic crystalline layered clay with structure and composition closely resembling Sm. Lap nanoparticles have a disk-shape with a thickness of approximately 1 nm, and a diameter of approximately 25 nm, much smaller than natural clays (microns). Lap disks possess a net negative charge which is balanced by the positive charge of sodium ions. Lap is used to modify rheological properties of liquids, cosmetics, paints, and inks [2].

More recently these anisotropic nanoparticles were also considered as building basic units of multilayered photonic crystals [3]. Lap and surface modified Lap can be used for adsorption of dyes [4], surfactants and biomolecules, to reinforce biopolymer based films [5] or as effective drug carrier [6].

Although the swelling of natural clays was broadly studied in the context of catalysis or environmental industries [7–9], few studies were devoted so far to the swelling and dehydration of Lap, which however presents the advantage over natural clays to have smaller particle size, lower structural polydispersity (dimension, surface charge) and better stability in water compared for instance to Mt.

This paper reports new results on Lap swelling under different relative humidities (RH) by combining for the first time thermogravimetric analysis (TGA), X ray diffraction and water desorption kinetics. We reveal the unusual characteristics of Lap upon dehydration and discuss the relation with the clay structure.

The synthetic clay is Lap RD (Southerm Clay Products Inc.) with molecular composition $(Si_8[Mg_{5.5}Li_{0.4}H_{4.0}O_{24.0}]^{0.7-}[Na_{0.7}]^{0.7+})$ [10]. Lap RD initially stored at room conditions was transferred to desiccators equipped with hygrometers containing silica gel with RH = 0.1%, 3% and saturated salt solutions for RH values of 31%, 45%, 71%, 89% and 94%. Powders were equilibrated during 4 days under each RH value (powders reached a constant weight). The equilibrium water content (moisture content) w_{equil} is given by:

$$w_{equil} = \frac{m_{water}}{m_{dry\ clay}} \tag{1}$$

The mass of dry Lap RD is determined after heating the powders at 150 °C using thermogravimetric analysis.

After equilibrium, Lap RD was analyzed using an X-ray diffractometer (Panalytical Empyrean, Cu Kα radiation) equipped with a

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multichannel detector PIXcel 2D solid-state detector (255 × 255 pixels, each pixel is 55 μm × 55 μm). X-ray diffraction patterns are in the 1.5–70° range, with a 0.025° step size and 30 s per step. Patterns were analyzed using Panalytical HighScore Plus software. The d_{001} value of basal reflection was calculated using Bragg law:

$$\lambda = 2d \sin \theta \quad (2)$$

where, λ is the wavelength of Cu Kα radiation (1.54187 Å), d is the spacing and θ, is the reflection angle. The overall duration of a measurement is about 10 min.

Water desorption rates of Lap RD were investigated by TGA (Q5000, TA Instruments, USA) in isothermal and non-isothermal modes operating with constant pure nitrogen gas flow (25 mL/min) and with open Pt pan with 10 mm diameter [11,12]. The initial sample weight was approximately 50 mg. The dehydration rates are analyzed in isothermal conditions at 35 °C and 45 °C during 120 min, heating rate + 1 °C/min, from 20 °C to 150 °C, continued by 60 min isothermal drying at 150 °C. Experiments were repeated at least two times for each sample and showed a good reproducibility.

After conditioning Lap RD under different RH values, we established using TGA the sorption isotherm at 25 °C presented in Fig. 1a. Our results are in good agreement with those reported by Fripiat et al. [14] at a temperature of 31 °C. A type II BET isotherm typical for multi layer adsorption of gases on non-porous solid surfaces [13] is obtained.

Our experimental isotherm (Fig. 1a) can be interpreted with the two parameter BET equation [13] with a good fit which identifies w_o, the amount needed to cover the surface with a monomolecular layer, $w_o = 0.09$ g water/g dry Lap and the C parameter, $C = 488$. The large C parameter is related to a large heat of adsorption of the first layer. The BET equation is close to the experimental data in the range $P/P_0 < 0.5$ and gives higher adsorption when $P/P_0 > 0.5$. The deviation was predicted by Brunauer et al. [18] for adsorption of gas on non-porous solids, when a limited number of layers are adsorbed at $P = P_0$ (instead of an asymptotic value). The meaning of such a deviation is based on the difference between liquid states of "bulk water" and of "last adsorbed layers". Accordingly, the BET model can be improved with a third parameter rescaling the relative pressure axis, to account for the "attractive force field of the adsorbent" (see Supplementary information for details on the BET equation fit and the domain of validity).

Fig. 1b shows the comparison between water sorption of Lap RD and Mt. and Ht clays converted to a homoionic sodium form (Na-Mt and Na-Ht) by treatment in ion-exchange columns. Lap RD appears much more hygroscopic than other Sm containing Na$^+$ exchangeable ions on the whole RH range and measurements are much more reproducible. This suggests that the equilibrium adsorption is acheived with Lap, which provides the best model system for testing the swelling mechanisms of Na-Sm type clays.

Fripiat et al. [14] determined graphically the Lap specific surface area to water 345.4 m^2/g, while with our procedure we find 450 m^2/g (see Supplementary information). Fripiat et al. [14] report for Na-Ht a much lower value, 79 m^2/g. Large specific surface areas can be interpreted as high proportion of active sites for water adsorption.

In order to elucidate the water adsorption mechanisms in Lap RD crystals, X-ray diffraction measurements were performed on the humid clays after equilibration at different RH values.

Distinct visible reflections appear in X-ray diffractograms (Fig. 2) at $3.7° \leq 2\theta \leq 7.7°$ ($d_{(001)}$) and $2\theta = 60.8°$ ($d_{(060)}$) which are related to the interlayer space and to the trioctahedral character of Lap, respectively [6,19,20]. Reflections with $2\theta < 10°$ are visibly shifted to the left with increasing humidity. Swelling of the clay modifies the distance $d_{(001)}$ related to the interlayer space. The $d_{(001)}$ values calculated from the position of the low angle diffraction peak increase linearly with w_{equil} (derived from Fig. 1a) following the equation:

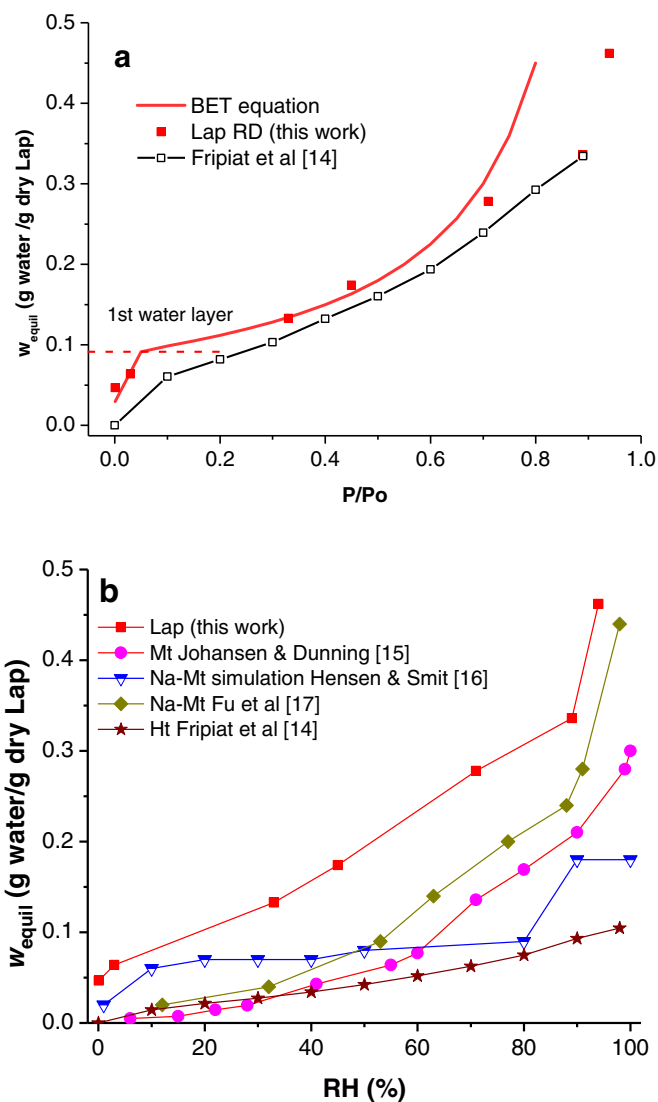$$d_{(001)}(\text{Å}) = 21.9 * w_{equil} + 10.2 \quad (3)$$

Fig. 1. a Sorption isotherm of Lap RD (full squares) conditioned under different relative humidities at 23 °C and results from Fripiat et al. [14] (open squares); water sorption is in g/g of dry Lap versus relative vapor pressure P/P_0 (P is the actual vapor pressure, P_0 is the vapor pressure at saturation) and the fit with BET equation is full line b. Comparison between the sorption isotherms of Lap RD (this work) versus RH and other Sm clays: Mt, full disc symbols [15]; Na-Mt simulations, semi-solid triangle symbols [16]; Na-Mt, full diamond symbols [17]; Na-Ht, star symbols [14].

suggesting that water molecules adsorb in interlayer space and produce a physical swelling. The distance extrapolated towards $w_{equil} = 0$ is $d_{(001)} = 10.2 \pm 0.2$ Å and predicts the interlayer space when Lap RD is completely dehydrated, very close to $d_{(001)} = 10.3$ Å reported by Hensen and Smit [16] from numerical predictions in dehydrated structures of Na-Mt. Eq. (3) shows that the interlayer spacing in Lap RD is due to a homogeneous hydration state, which is not the case in other Na-Sm [17].

Recent numerical simulations on Sm type clays follow two different strategies in interpreting the swelling process: Hensen and Smit [16] predict w_{equil} versus RH for Na-Mt, as shown in Fig. 1b and Morrow et al. [21] predict $d_{(001)}$ versus the ratio $r = H_2O/Na^+$ for Na-Ht.

Molecular dynamics and Monte Carlo sampling simulations [16] show that the crystalline swelling of Na-Mt is rigorously determined by the number of water molecules which enter the interlayers via the presence of the cation. Since water vapor adsorption and swelling are controlled by the cationic composition in Mt., it is interesting to calculate the ratio $r = H_2O/Na^+$ for Lap equilibrated in desiccators. With