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Isosteric heat of water adsorption and desorption in homoionic alkaline-earth montmorillonites

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ABSTRACT

The aim of the present work is to study by means of thermodynamic measurements and Infrared spectroscopy, the effect of the interlayer cations on the adsorption–desorption of water in the case of a montmorillonite exchanged with alkaline-earth metals. For the first time, the net isosteric heat of water adsorption and desorption is determined from isotherms recorded at three temperatures. The net isosteric heat is a very useful parameter for getting more insights into the sorption mechanism since it provides information about the sorption energy evolution which can be complementary to that obtained from structural or gravimetric measurements. The homoionic montmorillonite samples are prepared from purification and cationic exchanged in aqueous solution of the raw material, i.e. the reference SWy-2 Wyoming material. XRD at the dry state and elemental chemical analysis confirm that the treatment does not deteriorate the clay structure and yield the expected homoionic composition. The sorption isotherms measured at various temperatures show that the nature of the interlayer, i.e. exchangeable, cation changes the adsorbed/desorbed amount of water molecules for a given water relative pressure. The total amount of water adsorbed at $\frac{P}{P^s} = 0.5$ follows the cation sequence Ca $\sim$ Mg>Ba while the sorption isosteric heats follow a slightly different sequence, i.e. Ca > Mg>Ba. This discrepancy between the adsorption and desorption heat is due to the higher irreversibility of water sorption process in the Ca exchanged montmorillonite. Finally, analysis of the IR spectra recorded at room temperature and under a primary vacuum reveals that the amount of adsorbed water follows the same sequence as that of the isosteric heat of adsorption and shows the coexistence of liquid-like and solid-like water confined in the interlayer space.

1. Introduction

Clay minerals are among the most studied natural minerals. Their importance is related to their abundance, since they constitute 40% of the minerals in sedimentary rocks [1]. The rheology, colloidal, water retention, swelling and ion exchange properties of clays play an important role in many applications, i.e. hydrogeology, civil engineering, petroleum engineering, chemistry, environmental sciences and health [2,3]. As a typical example, the bentonite clay has long been used as a buffer material for the engineered barriers in disposal sites for nuclear waste due to its low water permeability when it is compacted and because of its ability to retain cations and to reduce or to delay the potential migration of radionuclides [4–6]. Another important application of clays, either natural or modified, is their ability to adsorb pollutants as heavy metal cations or many other kinds of organic compound contaminants in water [7,8]. Investigating the mechanisms of hydration is thus essential for the understanding of the physical and chemical properties of clays. Furthermore, it has been known for many decades that the water adsorption in smectites is much dependent on their chemical composition and more particularly on the nature of their metallic interlayer cations (IC). Many theoretical and experimental studies have then been carried out on the hydration phenomena as well as on the dynamics of the adsorbed water molecules inside the crystalline structure of the montmorillonite clay mineral [9–17]. However, due to its complexity and the uncertainty about the exact mechanism taking place at the

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molecular level, this topic remains a matter of fundamental and practical interest.

The purpose of the present study is to investigate the role played by the alkaline earth IC, i.e. Mg^{2+}, Ca^{2+} and Ba^{2+}, on the montmorillonite–water interactions using adsorption-desorption isotherms and middle range infrared (mid-IR) spectroscopy. The main novelty is that, for the first time, the adsorption–desorption isotherms at different temperatures, i.e. 25, 40, 60 °C, are measured and thus, the net isosteric heat of adsorption/desorption of water can be calculated from the Clausius-Clapeyron equation [9,18]:

$$\frac{d\left[\ln(\frac{P}{P°})\right]}{dT} = \frac{q_{st} - \Lambda}{RT^2} = \frac{q_{st}^*}{RT^2} \tag{1}$$

where P is the water partial pressure, $P°$ the atmospheric pressure, T the temperature, R the perfect gas constant. The net isosteric heat q_{st}^* which must be provided in addition to the heat of vaporization of pure water Λ, i.e. about 43.5 kJ.mol^{-1} [19].

Our thermodynamics data are then compared to the evolution of the basal spacing obtained at various relative water pressures for the same three homoionic montmorillonite materials as it was previously reported by others [10,11]. Finally, these thermodynamics and structural outcomes are compared to mid–IR measurements recorded at room temperature and under a primary vacuum. It is then clearly shown that the intensity of the IR signals assigned to the adsorbed water molecules follows the same trend as that of our thermodynamics data as well as that of reported for the dc conductivity [12] and hence confirms that IR spectroscopy is a useful tool for investigating water adsorption in this clay material.

2. Materials and methods

2.1. Montmorillonite starting material

Montmorillonite is a clay mineral commonly used in a wide range of industrial and environmental applications. It is a well-studied smectite, a 2:1 layered aluminosilicate [2]. The structure consists of a central octahedral sheet sandwiched between two tetrahedral ones. The tetrahedra contain dominantly Si(IV) central atoms with some Al(III) substitutions. The octahedral sites are mainly occupied by Al(III) partly substituted with Fe(III) and Mg (II). Because of these nonequivalent isomorphous substitutions, the layers bear a negative charge, which is balanced by exchangeable cations located in the interlayer space, i.e. the so-called interlayer cations (IC). The layer charge is an important criterion controlling the mineral's ability to retain cations and hence to adsorb water and/or various polar organic molecules [20]. The general formula of montmorillonite is: $X_{x/v}^{v+}(S\ i_{4-y}Al_y)\ [(Al, Fe^{3+})_{2-z}\ (Mg, Fe^{2+})_z]O_{10}(OH)_2$ with x = 0.2–0.6; x = y + z, and y ≪ z. $X_{x/v}^{v+}$ is the IC, e.g. Na^+, K^+, Ca^{2+}, or Mg^{2+} [21].

2.2. Homoionic clay preparation

The homoionic alkaline-earth montmorillonites investigated in this work originate from a montmorillonite extracted in Crook County (Wyoming) and purchased from the Source Clays Repository (Clay Mineral Society Ref.: Srce_Clay_SWy-2; for more information see [22]). This clay has the chemical formula $(Si_{7.98}, Al_{0.02})$ $(Al_{3.01},\ Fe_{0.41}^{3+},\ Mg_{0.54})$ $Na_{0.32}\ K_{0.05}\ Ca_{0.12}\ Mn_{0.01}Ti_{0.02}O_{20}$ $(OH)_4$. Its cation-exchange capacity (CEC) was reported to be about 76.4 meq/100 g [22]. The samples investigated here are composed of the ≤2 μm fraction of various alkaline-earth exchanged Wyoming montmorillonites. The fine fraction is obtained by dispersing 20 g of the original clay in one liter of distilled water. A 0.1 M NaOH solution is added to adjust the pH at 8 using a pH-meter. After 24 h of sedi-

mentation, the supernatant is centrifuged to yield a powder with an average grain size of 2 μm or less. The exchange with the different alkaline-earth metal cations is then obtained by dispersing and stirring this fine fraction in a 1 M XCl_2 solution (where X = Mg, Ca, and Ba) for 24 h, followed by centrifugation. This operation is repeated three times and finally the powder is washed until no trace of chloride ions is detected by testing with $AgNO_3$ [12,23]. Finally, the powder is separated from the liquid phase by centrifugation and air drying. The so obtained samples are here after referred to as MWy-X.

2.3. X-ray diffraction

XRD measurements are performed in the dry state using a X-ray diffractometer wide angle INEL CPS120 equipped with a conventional X-ray source (Cu Kα) and a 120° curved detector. First, the clay powder is poured into a capillary and heated at 200 °C for two hours (the reference dry state) in a Mettler FP52 type furnace. The capillary tube is then sealed without switching the oven off in order to avoid atmospheric water contamination. The interlayer distance is calculated, for each sample, from the position of the d_{001} peak.

2.4. Dynamic vapor sorption

Water adsorption-desorption isotherms are recorded on all the samples using an IGAsorp instrument from Hiden Isochema ltd, U. K. It directly measures the sample mass for a given relative water pressure at a given temperature. About 15 mg of the studied montmorillonite is placed in the IGAsorp microbalance and dried at T = 200 °C under a dry N_2 flow during 3 h before the sample mass variation is measured at various relative partial water pressures P/P^0. Overall, the total weight variation is in the order of 1 mg. The partial water pressure is adjusted by mixing a dry N_2 and a water saturated N_2 gas flow. The total gas flow is 250 ml.min^{-1}. The relative humidity and the mass of the sample are continuously recorded. Adsorption and desorption isotherms are recorded at 3 different temperatures, i.e. 25 °C, 40 °C, 60 °C. For each partial water pressure, the water uptake (adsorption) or loss (desorption) is measured after 6 h. If after this period the equilibrium state is not reached, the sample mass at equilibrium is estimated by extrapolation of the decay or growth curve at infinite time.

2.5. Isosteric heat

In order to get further insights into the sorption thermodynamics of our samples, we calculate the isosteric heat of adsorption and desorption from the isotherms obtained at the different temperatures. The isosteric heat of sorption q_{st}^* which gives by definition the heat of sorption considering a constant layer of the adsorbent surface can be calculated from the Clausius-Clapeyron (Eq. (1)). It shows that the value of q_{st}^* can be extracted from the experimental data obtained from the evolution of the partial water pressure corresponding to a given number of adsorbed molecules at different temperatures. The knowledge of q_{st}^* as a function of the loading is important for several reasons. First, it gives access to the energetics of sorption based on a given value of coverage, i.e. the quantity of adsorbed molecules, and therefore allows us to compare sample to sample. Second, the evolution of q_{st}^* with the loading tells us about the sorption mechanism, i.e. whether it follows a single or complex multi-steps route. Last but not least, the comparison between the adsorption and desorption curves gives insights into the reversibility of the phenomenon, i.e. whether adsorption and desorption phenomena follow a reverse route.