Changes in water vapor adsorption and water film thickness in clayey materials as a function of relative humidity

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Abstract
Soil water, with adsorbed water being an important component, plays an important role in fluid flow and chemical movement in the unsaturated zone. The adsorbed water consists of water film and interlayer water, and its content is related to the relative humidity (RH). This study theoretically and experimentally focuses on the variation in adsorbed water content in clayey materials as the RH changes. Based on a slit-pore model, three types of water (water film, interlayer water, and capillary water) could be present in the water vapor adsorption process. The variation of water film is obtained from the analysis of interfacial forces, and then the total water content can be quantitatively subdivided into these three types of water for different RH values. The slit-pore adsorption model was used with experimental measurements (water vapor adsorption and N2 physisorption) to quantify the amounts and interrelationships of these three different types of water to six clayey materials, namely three clay minerals (kaolinite, montmorillonite, and illite-smectite mixed layer) and three clay-rich sediments from the Jianghan Plain in China. The main results are that (a) the volumes of water vapor adsorption are much greater than those of N2 adsorption except for kaolinite; (b) interlayer water largely dominates the growth of total water content in montmorillonite and results in a concentration of 0.090 ml g⁻¹ at 95% RH; and (c) the minimum thickness of water film is calculated to be 0.23 nm, and the maximum value is one-third of the pore width by considering the interfacial forces.

1 INTRODUCTION

Soil water supports plant growth, affects nutrient transport, and is involved in many geophysical and geochemical processes. Most soil water comes from the supply of atmospheric precipitation or groundwater, and its abundance and movement are recognized to be mainly controlled by gravity and capillarity (surface tension). However, there is another mechanism called adsorption by which the adsorbed water formed cannot be ignored (McQueen & Miller, 1974). Adsorption makes the properties of water different from bulk water, which may relate to some interesting phenomenon—for example, measurements of the...
saturated water content could be >100% in some soils (Villar & Lloret, 2004). However, adsorbed and capillary water in the unsaturated soil are significantly different but hard to distinguish (Baker & Frydman, 2009). Recognizing and distinguishing adsorbed and capillary water will contribute to a holistic understanding of the water–soil system.

The soil water retention curve is commonly used to describe the relationship between the soil matric potential and water content. There are many models to simulate this curve, but most models work poorly in the high-matric-potential part of the curve unless the capillary and adsorption are simulated separately (Lu, 2016; Revil & Lu, 2013). This is because the capillary water plays a dominant role in water contents at a matric potential that, in a specific pore size distribution, may be less than −400 kPa (Baker & Frydman, 2009; Khorshidi, Lu, & Khorshidi, 2016), and the adsorbed water becomes more prominent as water content decreases and matric potential increases. Based on the physical processes of water adsorption, Lu (2016) provided a unified model that divided the soil water retention curve into the adsorbed and capillary water for better matches, especially in the high-matric-potential part. However, this can be further improved, especially for clayey materials, since adsorbed water can be composed of surface and interlayer water.

Depending on the adsorption site on clay minerals, adsorbed water can be divided into surface water (water film) and interlayer water, which vary greatly in their physical properties and influence on fluid flow and chemical transport. In the vadose zone, the hydraulic conductivity of soil with low water saturation is mainly restricted by film flow (Zhang, 2011), and chemical diffusion is restricted by film thickness (Hu, Kneafsey, Roberts, Tomutsa, & Wang, 2004). The effective diffusion coefficient of a water film can be as low as $10^{-14}$ m$^2$ s$^{-1}$, compared to that of capillary water of $10^{-9}$ m$^2$ s$^{-1}$ (Tokunaga et al., 2017). Water films cover the solid surface and their physical properties change at different relative humidities (Tokunaga, 2009). Unlike water film, owing to the weak restriction of the 2:1 crystalline structure (two tetrahedrons and one octahedron) of expansive clay minerals (Bathija, Liang, Lu, Prasad, & Batzle, 2009; Katti & Katti, 2006), the type and hydration of interlayer cations (such as K$^+$ vs. Ca$^{2+}$) can lead to the formation of interlayer water in the mineral lattice layers (Zhang & Lu, 2018), a phenomenon known as intracrystalline (or interlayer) swelling (Laird, Shang, & Thompson, 1995). This swelling is mainly present in the smectite group clays (mainly montmorillonite) and the smectite within the illite–smectite mixed layer, and its process has been observed by X-ray diffraction (XRD) tests. The interlayer spacing could expand from 0.9 to 1.5 nm when water molecules are adsorbed (Carrier et al., 2013; Mooney, Keenan, & Wood, 1952; Norrish, 1954). Furthermore, the density of interlayer water was calculated by XRD analysis and molecular simulation and was found to be as high as 1.87 g cm$^{-3}$ (Zhang & Lu, 2018), compared with 0.995 g cm$^{-3}$ for capillary water (Fernández & Rivas, 2005; Jacinto, Villar, & Ledesma, 2012). In summary, these two types of adsorbed water have disparate physical properties and different impact on moisture storage, fluid flow, and chemical transport, but they are difficult to segregate and measure directly due to the challenging microscale studies.

In this study, the water contents of three water types (capillary water, water film, and interlayer water) are quantitatively divided by theoretical calculation from total water contents in six clayey materials. Water vapor adsorption experiments are then used to obtain the relationship between total water content and relative humidity (RH), which is an effective and commonly used approach to determining the dynamic changes of low water contents in soils. Finally, the relationships between the water content of three water types and RH are obtained. In addition, the water film thickness obtained from the analysis of interfacial forces is specifically discussed. Overall, this work contributes to a better understanding of the water adsorption process and the change in water types at low water contents for clayey materials.

2 | MATERIALS AND METHODS

2.1 | Slit-pore model

The micropore structure of clays is one of the basic factors controlling the location and shape of adsorbed water molecules. Recent experiments using scanning electron microscopy (SEM) on clays have shown that the pore shapes of illite and illite–smectite mixed layer mainly present in shales are similar to plate types (Li et al., 2017), which is consistent with the lattice shape of the clay minerals. Thus, a rigid slit-pore model is used in this study.

Core Ideas

- This work studies the variation of adsorbed water in clayey materials as a function of RH.
- Studied materials included clay minerals and clay-rich sediments in Jianghan Plain in China.
- Using a slit-pore model, water content was quantitatively divided into three types for RH changes.
- Both the minimum and maximum values of water film thickness were theoretically derived.
to simulate the pore structure of clays, with the water film adsorbed onto two plates parallel to each other (Figure 1). Although the original pore structure is much more complicated and even changes with clay swelling, this model normalizes all pores to a rigid and slit type and assumes that the swelling impact for slit pore space is ignorable, for purposes of providing a tentative approach and simplifying the calculation process. At a very low RH, water molecules are tightly adsorbed onto the solid surface to form the first layer of water film (Khorshidi et al., 2016; Lu, 2016), which means that the effective pore width is no longer the pore width without water ($D$) but is narrowed to the distance between the two water films (namely $D - 2f$, as shown in Figure 1). As the RH increases, the water film continues to thicken, resulting in a further decrease in the pore width; meanwhile, water vapor will start to condense in the nanopores of the clay to form capillary water (Evans, Marconi, & Tarazona, 1986; Iwamatsu & Horii, 1996). This condensation has been recently observed in nanoscale pores (Vitorino, Vieira, Marques, & Rodrigues, 2018), and some models are built to research this process (Barsotti, Tan, Saraji, Piri, & Chen, 2016; Cihan, Tokunaga, & Birkholzer, 2019). Thus, water films due to adsorption and capillary water from condensation simultaneously exist in nanopores. Condensation occurs after the formation of tightly adsorbed water film (Khorshidi et al., 2016; Lu, 2016); meanwhile, water molecules get into the lattice interlayers of expansive clay minerals to form the interlayer water, which results in the occurrence of interlayer water with an increasing RH.

Therefore, as the RH increases, three water types will form in clayey materials—namely, water film, interlayer water, and capillary water—and contribute to the change in total water content. As a result, the total water content $W_t$ by weight is the sum of these three components:

$$W_t = W_f + W_c + W_i$$

where $W_t$ is the water film content by weight; $W_c$ is the capillary water content by weight from condensation in pores; and $W_i$ is the interlayer water content by weight.

In this slit-pore model, the water molecules adsorb onto the flat solid surfaces, which makes the volume of water film easily calculated from the product of film thickness and surface area. In addition, both water film and capillary water occupy the pore space (space between two plates) after the condensation occurs, and hence water volume in the pore will be subdivided into water film volume and capillary water volume. Therefore, the water contents $W_f$ and $W_c$ can be expressed as

$$W_f = V_f \rho_f = fS \rho_f$$

$$W_c = (V_p - V_f) \rho_c$$

where $V_f$ and $V_p$ are the volumes of the adsorbed water film and the total volume of all water adsorbed in pores (i.e., film + capillary water); $f$ is the film thickness; $S$ is the specific surface area (SSA); $\rho_f$ and $\rho_c$ are the densities of water film and capillary water. Both $\rho_f$ and $\rho_c$ are different from that in the conventional liquid state due to the strong adsorption and surface tension under a high matric potential environment in the vadose zone (Van Honschoten, Brunets, & Tas, 2010; Zhang & Lu, 2018). In this study, the values of $\rho_f$ and $\rho_c$ are taken as 1.30 and 0.995 cm$^3$ g$^{-1}$, according to the work of Zhang and Lu (2018).

Equation 2a and 2b show that there are three parameters ($f$, $S$, and $V_p$) that need to be determined. As $W_t$ is the basic experimental data from water vapor adsorption experiments and changes with RH, the relationship between RH and these three parameters needs to be independently established. It should be noted that the water vapor adsorption test can also be used to calculate the pore volume $V_p$ (Zolfaghari, Dehghanpour, & Xu, 2017), but the polarity of water molecules and the existence of
interlayer water may bias the result. The N$_2$ physisorption test has similar adsorption principles (e.g., probing molecular adsorption consecutively from small to large pores) to the water vapor physisorption test and is used to accurately obtain the pore surface area and the pore volume in this study. However, the pore volume from the N$_2$ physisorption test is related to pore width $D$ instead of RH, but $V_p$ is the pore volume where condensation happens and is related to RH.

According to the Kelvin and capillary rise equations, water molecules condense to form capillary water in pores of a certain width at a certain RH:

$$\frac{2\sigma V_m \cos \theta}{r} = -RT \ln \left( \frac{P}{P_0} \right)$$

(3)

where $\sigma$ is the surface tension of water of 0.072 N m$^{-1}$; $V_m$ is the molar volume of water of 1.8 $\times$ 10$^{-5}$ m$^3$ mol$^{-1}$; $\theta$ is the contact angle between water and solid surface; $R$ is the gas constant of 8.134 J mol$^{-1}$ K$^{-1}$; $T$ is the temperature (K); $P$ is the water vapor pressure in the gaseous phase (Pa), $P_0$ is the saturated vapor pressure of water (Pa), $P/P_0$ represents the RH ($\%$), and $r$ is the meniscus radius of curvature.

Due to the strong hydrophilicity between clays and water, in this study, we assume that the contact angle is 0, which means that $2r$ is equal to the effective pore width $D - 2f$; therefore, Equation 3 changes to

$$D = 2f - \frac{RT}{4\sigma V_m} \ln \left( \frac{P}{P_0} \right)$$

(4)

Thus, the pore volume from N$_2$ physisorption experiments can be related to RH by Equation 4 when $f$ is defined. As $S$ is an inherent property of the solid, the value of water film thickness becomes the key to obtain three types of water content. However, it is very difficult to directly measure the water film thickness. Gee, Healy, and White (1990) used ellipsometric measurements of water films on fully hydroxylated quartz plates, and the measured thicknesses ranged from 1.0 to 12.5 nm as the RH increased from 55 to 98%; however, the forces on the water film surface in pores of porous media are more complicated than on a single plate. Over recent years, nuclear magnetic resonance, in conjunction with N$_2$ physisorption, has been used to measure water film thickness, and the results were reported to be from 1.07 to 2.73 nm in shales of the Lower Silurian Longmaxi Formation (Zhang et al., 2019); however, the existence of capillary water in the nanopores cannot be eliminated, which results in an overestimation of the actual volume of water film. In this study, according to the mechanism of water film formation, the interfacial force analysis of water film is used to obtain the water film thickness, as described below.

### 2.2 Water film thickness

#### 2.2.1 Interfacial forces on water film

The Derjaguin–Landau–Verwey–Overbeek (DLVO) theory is widely used to study interfacial forces in colloids and interface sciences (Kim Tokunaga, Bargar, Latimer, & Webb, 2013; Tokunaga, 2012; Xie, Saeedi, Poo andyousefey, & Liu, 2016). The theory holds that the interfacial forces are composed of van der Waals and electrostatic forces. In addition, an additional structural force is considered to be a part of interfacial forces for hydrophilic materials (Li et al., 2017; Takahashi & Kovscek, 2010; Tuller, Or, & Dudley, 1999). These three forces are generated by the adsorption of the water film at the solid surface, and the balance of these forces is called the disjoining pressure. These forces act perpendicular to the solid surface; in this study, to simplify the calculation, all forces are applied to a flat surface.

**van der Waals force**. The van der Waals force, also known as the molecular force arising from the interactions between all phases (solid, water, and air), contributes to the formation of very thin water films. For the processes of water vapor adsorption on a flat surface, the van der Waals force $\Pi_{vdw}(d)$ generated between the solid–water and water–air surfaces can be described by Equation 5 (Gregory, 1981):

$$\Pi_{vdw}(d) = -\frac{A_{gws}(15.96d/l + 2)}{12\pi d^3(1 + 5.32d/l)^2}$$

(5)

where $A_{gws}$ is the Hamaker constant in a gas–water–solid system (J), $l$ is the London wavelength (nm), and $d$ is the distance between two surfaces (nm). When the two interfaces are very close with $d \ll l$, $\Pi_{vdw}$ is approximately proportional to $d^{-3}$. The value of the Hamaker constant $A_{gws}$ is about $-1.2$ to $-1.9 \times 10^{-20}$ J for a gas–water–quartz system, and $-3.2$ to $-4.9 \times 10^{-20}$ J for a gas–water–clay system (Li et al., 2017). In this study, $-4 \times 10^{-20}$ J is used as $A_{gws}$, and the London wavelength $l$ is assumed to be 100 nm, as suggested by Gregory (1981).

**Electrostatic force**. In addition to the van der Waals interactions, the imbalance of the surface charge provides an important mechanism to stabilize water film adsorption. Furthermore, electrolytes in solution play an important role in the adsorption of a water film layer (Binazadeh, Xu, Zolfaghari, & Dehghanpour, 2016; Tokunaga, 2011). However, for water vapor adsorption, the water film can be regarded to be very dilute (Li et al., 2017), and the electrostatic force $\Pi_e(d)$ in this special case can be expressed by (Langmuir, 1938)

$$\Pi_e(d) = \frac{\varepsilon_1 \varepsilon_0 (\pi k_B T)^2}{2(\varepsilon_0)^2 d^2}$$

(6)
where $\varepsilon_0$ is the permittivity in a vacuum, $8.85 \times 10^{-12}$ F m$^{-1}$; $\varepsilon_r$ is the relative permittivity of water (dimensionless); $k_B$ is the Boltzmann constant, $1.38 \times 10^{-23}$ J K$^{-1}$; $T$ is the temperature (K); $e$ is the electron charge, $1.6 \times 10^{-19}$ C; $z$ is the ion valence (dimensionless); and $d$ is the distance between two surfaces (nm). The main cations in the Jianghan Plain sediment samples used in this study (described in Section 3.1) are Ca$^{2+}$ and Mg$^{2+}$ (Gan et al., 2014), with the value of $z$ in Equation 6 as 2. The value of $\varepsilon_r$ is 78.36 under the experimental temperatures ($T$) of 298.15 K.

**Structural force.** In general, the positively charged ends of hydroxyl groups on the surface of the clay tend to attract the negatively charged ends of the water dipoles, thus hydrating the surface (Butt & Kappl, 2010; Starov & Velarde., 2019). The force generated by the wetting medium is called the structural force $\Pi_s$ or hydration force, which was described by Hirasaki (1991):

$$\Pi_s (f) = ke^{-\frac{f}{\lambda}}$$

where $k$ is the coefficient for the structural force (Pa); $\lambda$ is the characteristic decay length (nm); and $f$ is the water film thickness. In this study, the values of $k$ and $\lambda$ in this exponential model are assumed to be $1.5 \times 10^{10}$ Pa and 0.05 nm, as suggested by Hirasaki (1991).

**Disjoining pressure.** The interactions of the three forces mentioned above are the main reasons for maintaining the water film stability, and the balance of these three forces is called disjoining pressure. In a gas–water–solid system and the absence of solutes, the formation of a water film can be considered as a thermodynamic equilibrium process, and the disjoining pressure $\Pi$ can be expressed as Equation 8 (Tuller et al., 1999):

$$\Pi V_m = -RT \ln \left(\frac{P}{P_0}\right)$$

### 2.2.2 Water film stability

If the water film is adsorbed onto a single plate, such that the forces are only between the water film and one solid surface, then the distance $d$ is equal to the water film thickness $f$, and the interfacial force equation can be expressed as

$$\Pi = \Pi_{vdw} (f) + \Pi_e (f) + \Pi_s (f)$$

However, in the slit-type pore, water molecules adsorb onto the pore walls to form water films, and this creates four surfaces: Surface 0, Surface 1, Surface 2, and Surface 3 (Figure 2). Surfaces 0 and 2 are opposing gas–water film surfaces, whereas Surfaces 1 and 3 are opposing pore wall surfaces. In this study, the interfacial force analysis is performed on Surface 0, and the other three surfaces all have interactions with Surface 0 as discussed below.

Surface 1 is the adsorption surface for water on a solid, and the interface force between Surface 0 and Surface 1 includes all three forces mentioned above, namely van der Waal’s, electrostatic, and structural forces. Surface 2 is the water film surface opposite to Surface 0, and its interfacial force consists of van der Waals force only, because there are no hydroxyl groups and no surface charges. Surface 3 is the opposite adsorption surface, which is not in direct contact with Surface 0, so the structural force between them does not exist. Therefore, depending on the positional relationship, the disjoining pressure can be expressed by the following formulas:

$$\Pi = \Pi_{1-0} (f) - \Pi_{2-0} (f) - \Pi_{3-0} (f)$$

$$\Pi_{1-0} (f) = \Pi_{vdw} (f) + \Pi_e (f) + \Pi_s (f)$$

$$\Pi_{2-0} (f) = \Pi_{vdw} (D - 2f)$$

$$\Pi_{3-0} (f) = \Pi_{vdw} (D - f) + \Pi_e (D - f)$$

where $\Pi$ is the disjoining pressure on Surface 0; $\Pi_{i,j}(f)$ is the interfacial force between Surfaces $i$ and $j$; $\Pi_{1-0}(f)$ is the interfacial force between Surfaces 0 and 1; and $\Pi_{3-0}(f)$ is...
the interfacial force between Surfaces 0 and 3. It should be noted that the Hamaker constant changes to \( A_{\text{wgw}} \) in Equation 5 when being substituted into Equation 11b, as there is a two-phase (water and gas) interaction between Surfaces 0 and 2, and the value is \( 3.7 \times 10^{-20} \) J (Li et al., 2017).

### 2.2.3 Parameter analyses

Combining Equations 8, 10, and 11a–11c, an explicit relationship of four parameters \( (P/P_0, \Pi, f, \text{ and } D) \) can be obtained that \( P/P_0 \) is uniquely related to \( \Pi \) and \( \Pi \) is related to \( f \) and \( D \). Among these parameters, \( P/P_0 \) (RH) is a basic experimental value from water vapor adsorption experiments and has a clear and unique correspondence with \( \Pi \) from Equation 8. Thus, in order to calculate the water film thickness \( f \) from experimental data, the effect of pore width \( D \) has to be considered. Firstly, five values of the pore width \( D \) (2, 5, 10, 25, and 50 nm) are assumed and inserted into Equations 10 and 11a–11c. Thus, the relationship between the water film thickness \( f \) and the disjoining pressure \( \Pi \) is shown as Figure 3.

As shown in Figure 3, when the disjoining pressure is greater than 7,000 kPa (RH < 95%), there is no significant difference between the curves generated for different pore widths \( D \), which means the water film thickness is controlled by the RH and the effect of \( D \) is negligible under this condition. Additionally, \( D - f \) as well as \( D - 2f \) are much larger than \( f \) when RH < 95%, which means that \( \Pi_{2,0}(f) \) and \( \Pi_{3,0}(f) \) are much smaller than \( \Pi_{1,0}(f) \). Therefore, the water film thickness \( f \) can be obtained for all pores when RH < 95% using Equation 10, while Equations 11b and 11c can be omitted.

### 2.3 Clayey materials and physisorption experiments

#### 2.3.1 Samples

In this work, the behavior of water vapor adsorption in six hydrophilic materials (three clay minerals and three clay-rich sediment samples) was investigated using water vapor and \( N_2 \) physisorption isotherm experiments. The three clay minerals are kaolinite, montmorillonite, and the illite-smectite mixed layer (I/S). Kaolinite and Na-montmorillonite were obtained from Ward's Science, and their origins are Twiggs County, Georgia, and Clay Spur, Wyoming, respectively. With an origin from Slovakia, the I/S (70/30 ordered, ISCz-1) was from Source Clays Repository at Purdue University. As a naturally occurring material, ISCz-1 [structural formula: \( K_{0.95}Na_{0.20}(Al_{3.35}Mg_{0.47}Fe_{0.18})(Si_{7.32}Al_{0.68})O_{20}(OH)_4 \)] has a purity of 93% with 2% quartz, 4% feldspar, and a trace amount of kaolinite (Chipera & Bish, 2001; Geramian, Osacky, Ivey, Liu, & Etsell, 2016).

Three clay-rich sediments were collected from the Jianghan Plain in Hubei Province in China, where there is arsenic contamination in the soil and groundwater (Duan et al., 2015, 2017; Gan et al., 2014). Two 10-m-deep boreholes named A and B were dug in Shahu Town, Xiantao City, in Jianghan Plain. Borehole A was near a pond with little sedimentary change in the core, so sample A17 was taken from 5.0-m depth in the middle of the core. Borehole B was drilled close to a river, and two core samples were taken at 1.0 and 9.5 m, named B1 and B42, respectively. Duan, Gan, Guo, Ding, and Deng (2014) indicated that the grain sizes are very fine, and that grain sizes of <0.01 mm make up >50% of the study area. The three clay-rich sediment samples were sieved to <75 \( \mu \)m and dried at 60 °C for 48 h, and the mineralogical compositions were measured using XRD (XRD-7000, Shimadzu Corporation) at 40-kV voltage, 30-mA current, and scanning from 2 to 70° at intervals of 0.02°.

#### 2.3.2 Water vapor adsorption

Most water vapor adsorption experiments use an oversaturated solution in a tightly closed container to maintain one level of RH (Hu, Trautz, & Wang, 2004; Zolfaghari et al., 2017), but this has the following disadvantages: (a) it is time consuming to reach equilibrium and much space is needed for many containers; (b) it is difficult to reach the target RH.
by saturated salt solution, especially a low one such as 10% RH; and (c) it is disruptive to the equilibration process to take and return the samples to weigh periodically, and thus equilibration must be reestablished.

In this study, the dynamic water vapor adsorption isotherm was obtained using a gravimetric water vapor adsorption analyzer (Aquadyne DVS, Quantachrome/Anton Parr). The instrument controls the RH in the sample chamber by mixing a dry gas (N\textsubscript{2}) with saturated steam. The RH range is from 2.0 to 95.0%, with a precision of ±0.1%. The sample was loaded onto the weighing pan connected to a weighing device with a high precision (±0.1 μg), and real-time sample weights were automatically recorded every minute.

Prior to the measurements, granular samples of size 500–841 μm (20–35 mesh) were dried at 60 °C for 48 h before starting experiments to remove most of the moisture in the connected pores in the samples. The sample chamber was kept at 25 °C during the experiments. When the rate of change in the weight (the ratio of the weight change per minute to the initial weight of the sample) for a given RH was <0.01%, it was deemed to have reached an equilibrium state, and then the experiment proceeded to the next step with a higher RH value. The RH values used were from 5 to 95% for the adsorption process, and then back to 5% for desorption.

### 2.3.3 Nitrogen physisorption isotherm

Nitrogen physisorption isotherm tests were used to obtain the SSA and pore size distribution, which are then used to determine the values of \( S \) and \( V_p \) in Equations 2a and 2b.

In this work, the isotherm was obtained at 77 K with relative pressures ranging from 0.001 to 0.995, using a specific surface and porosity analyzer (ASAP 2460, Micromeritics Instruments). Before the beginning of experiments, all the granular samples were dried in an oven at 60 °C for 48 h and then outgassed under a high vacuum at 110 °C for 12 h. The Brunauer-Emmett-Teller (BET) model (Brunauer, Emmett, & Teller, 1938) and Barrett-Joyner-Halenda (BJH) model (Barrett, Joyner, & Halenda, 1951) were used to calculate the SSA and pore size distribution, respectively.

### 3 RESULTS AND DISCUSSION

#### 3.1 Physisorption isotherm experiments

The raw data obtained by N\textsubscript{2} and water vapor experiments are completely different (left ordinate axes in Figures 4a and 4b). Since the adsorbed volumes of N\textsubscript{2} isotherms are the gas volumes at standard temperature and pressure (STP), the water contents of water isotherms are converted to the adsorbed volumes of water vapor (right ordinate axis in Figure 4b) by dividing by water vapor density (8 × 10\textsuperscript{-4} g cm\textsuperscript{-3}) at STP for comparison. Obviously, the adsorbed volume of water vapor is much larger than that of N\textsubscript{2}. Comparing the highest point of each sample curve, which represents the adsorption capacity of samples in two experiments, Sample B1 is the lowest in both figures, but the highest values are different among other samples. Sample B1 only possesses ~10% clay minerals (Table 1), which is the lowest clay content in the six samples, but still shows a factor-of-two difference in its ability to adsorb N\textsubscript{2}.
over water vapor. As a comparison, the difference is about five times for montmorillonite, and minimal for kaolinite. These differences are present probably because water molecules are more easily adsorbed than N\textsubscript{2} on the surfaces of clay minerals, and they can also be hydrated by cations in the interlayer space of clay minerals where the N\textsubscript{2} cannot (Macht, Eusterhues, Pronk, & Totsche, 2011; Zhang & Lu, 2019). Furthermore, the maximum relative pressure (N\textsubscript{2}) for which measurements can be made is greater than the maximum RH (water); otherwise, the difference will be even larger. The RH is much more difficult to control at high values, which is a disadvantage of water vapor adsorption compared with N\textsubscript{2} adsorption and one of the reasons that N\textsubscript{2} is used more often than water vapor in gas physisorption.

Based on N\textsubscript{2} isotherms, the SSA and the average pore width were obtained from BET and BJH models, respectively (Table 2). The SSA values are in line with the external surface area of these clay-rich materials: for example, 16–35 m\textsuperscript{2} g\textsuperscript{-1} for the external area and 583–714 m\textsuperscript{2} g\textsuperscript{-1} for the internal (interlayer) area for five montmorillonite samples (Diamond & Kinter, 1956). On the other hand, the SSA results obtained by using different adsorbate of nonpolar N\textsubscript{2} gas vs. polar organics liquid (ethylene glycol monomethyl ether) capable of penetrating the interlayer surfaces of expandable clay minerals could yield a huge difference for montmorillonite (Macht et al., 2011). In this study of the N\textsubscript{2} physisorption test, the values of SSA represent the surface that adsorbs the water film and that N\textsubscript{2} molecules can access, without the interlayer area. In addition, the average pore widths of six samples ranges from 23.7 to 49.9 nm, and these nanoscale pores are also the main space in which the capillary condensation happens in water vapor experiments.

The shapes of the N\textsubscript{2} hysteresis loops are similar to type H3 in the International Union of Pure and Applied Chemistry (IUPAC) classification, indicating that the shape of the main pore structure in the samples is close to a slit or plate (Sing, 1985), which provides a favorable basis for the model in this work. The hysteresis loops for kaolinite are similar for both N\textsubscript{2} and water vapor adsorption. However, for all other samples, the water vapor isotherms do not overlap like N\textsubscript{2} isotherms in low-RH or -pressure regions, and the hysteresis loops appear wider and larger. In higher RH, the hysteresis may have multiple causes, including the “ink bottle” effect (Cohan, 1938; Morishige & Tateishi 2003) and the changes of contact angle for the adsorption and desorption branches (Joanny & De Gennes 1984; Johnson & Detre 1964). However, hysteresis still happens in low RH of water vapor isotherms, and the reason may be related to the clay minerals. The interlayer water widens the interlayer distance of clay minerals and then reduces the attraction force between crystal layers, which causes the interlayer cations to be less bound and to have stronger adsorption for water molecules (Lu & Khorshidi, 2015). This results in the hysteresis loops at low RH values, as shown in Figure 4b for all of six samples except for kaolinite, which does not have an interlayer structure for water molecules to access. Moreover, Lu and Khorshidi (2015) found that the higher the smectite content, the wider and larger the hysteresis loop will be, which is consistent with the results of this study.

### 3.2 Water vapor adsorption process

The process for dry clayey samples to increase water content is complex, as it includes changes in three water types (water film, interlayer water, and capillary water) (Figure 1). After a series of calculations (Section 2), the total water content from water vapor adsorption experiments has been broken into these three water types at every RH value (Figure 5). At low RH, the increase in total water is all due to water film increase. Water film content increases

| Sample | Quartz composition | Albite | Illite | Muscovite | Clinohlorop | Montmorillonite | Kaolinite |
|--------|--------------------|--------|--------|-----------|-------------|-----------------|----------|
| A17    | 66.4 ± 4.2         | 8 ± 0.7| 2.3 ± 0.5| 6.2 ± 0.5| 3.5 ± 0.3   | 6 ± 0.7         | --       |
| B1     | 64.8 ± 4           | 11.4 ± 0.9| 8 ± 0.6| --        | 2.1 ± 0.2   | --              | --       |
| B42    | 43.8 ± 2.6         | 18 ± 1.2| 21.6 ± 1.6| 10.1 ± 1.0| 1.5 ± 0.1   | 1.6 ± 0.3       | 3.4 ± 0.4|

### Table 2

Pore structure results from N\textsubscript{2} isotherms using Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) models

| Sample name | A17 | B1 | B42 | Kaolinite | I/S\textsuperscript{a} | Montmorillonite |
|-------------|-----|----|-----|-----------|----------------|----------------|
| Specific surface area, m\textsuperscript{2} g\textsuperscript{-1} | 18.4 | 10.3 | 23.6 | 17.7 | 29.9 | 22.0 |
| Avg. pore width, nm | 24.5 | 26.2 | 29.3 | 46.2 | 23.7 | 49.9 |

\textsuperscript{a}\text{I/S, illite–smectite mixed layer.}
FIGURE 5 The variation of three water types in each sample as a function of increasing relative humidity (RH) values; total water lines are the experimental data ($W_t$) from water vapor experiments, water film lines ($W_f$) are obtained from Equation 2a, capillary water lines ($W_c$) are obtained from Equation 2b, and interlayer water lines ($W_i$) are calculated from Equation 1. I/S, illite–smectite mixed layer.

rapidly at this stage, but the increase is slowed after a certain RH (e.g., this RH is 50% for kaolinite), which indicates the completion of the first-layer water film. This RH is the monolayer coverage RH, and some researchers expected to find a uniform value of it and thereby used it to calculate the SSA of clay minerals (Arthur et al., 2013; Leão & Tuller, 2014; Newman, 1983; Quirk, 1955). However, such a method is obviously not widely applicable, as different samples exhibit a distinct monolayer coverage RH (Figure 5). At a RH condition higher than this value, the adsorption transitions into the second stage with the emergence of interlayer water and capillary water. The total water grows gradually as RH increases, and it consists of these three types of water. The increase in interlayer water behaves differently in different samples; in some (montmorillonite and A17) it grows fast, but in others (B1, B42, and I/S) it grows fast initially then slows down, and in one (kaolinite) it does not grow. Afterwards, an inflection point in the
total water curve is reached at a higher RH value for all samples, and thereafter every water type increases rapidly, and even the water film increases at high RH values. Furthermore, the proportions of different water types in different samples changes with RH. Overall, the capillary water dominates the rapid growth in total water for kaolinite, whereas the interlayer water plays the dominant role for montmorillonite.

In fact, the different adsorption capacity of three water types is due to the different physical properties of samples. The water film and capillary water are mainly limited by surface area and pore size distribution, respectively. The interlayer water relates to the swelling ability of samples, and its content has a positive change with montmorillonite content. The interlayer water content of A17 is the second largest (next to that of montmorillonite) due to the smectite content of ~6% (Table 1). Furthermore, based on the density of 1.872 g cm$^{-3}$ (Zhang & Lu, 2018), the volumes of interlayer water of A17, B1, B42, I/S, and montmorillonite at 95% RH are 0.021, 0.003, 0.004, 0.016, and 0.090 ml g$^{-1}$, and these values represent the volume in addition to the pore volumes obtained from the N$_2$ physisorption isotherm. It should be noted that B1 has no montmorillonite but still shows interlayer water; this may be because the illite in B1 is illite–smectite mixed layer. Finally, adsorption in the expansive clay minerals proceeds in a stepwise manner (Khoshshidi et al., 2016; Mooney et al., 1952; Zhang & Lu, 2019), which means that the interlayer water forms layer by layer, and this could be the physical interpretation of the inflection points in the interlayer water curves.

### 3.3 Bounding thickness of water film

#### 3.3.1 Minimum thickness of water film

During the process of water vapor adsorption, the water film plays an important role in the total water content, especially initially. Its thickness influences the pore width and hence the capillary water content. Although the tightly adsorbed water film forms first and increases slowly, its thickness reaches the minimum value at monolayer coverage RH without much subsequent change. Based on the slit-pore model and Equation 2a, the minimum thickness of the water film ($f_{\text{min}}$) can be obtained from the weight of the water film ($W_{\text{mf}}$) by Equation 12:

$$f_{\text{min}} = \frac{W_{\text{mf}}}{S\rho_f}$$

Furthermore, as Figure 6 shows, the weight of the water film at monolayer coverage RH has a linear relationship with the SSA, which indicates that the ratio of $W_{\text{mf}}$ to $S$ is the same for each clayey sample, and $f_{\text{min}}$ could be a fixed value. Dividing the slope shown in Figure 6 by the water film density $\rho_f$, the thickness of monolayer water film is obtained as 0.23 nm, close to the monolayer thickness ($\sim$0.25 nm) measured through water next to oxide surfaces (Antogniuzzi, Humphris, & Miles, 2001; Israelachvili & Pashley, 1983). Thus, the first stage of water vapor adsorption could be a process of monolayer adsorption like the Langmuir adsorption.

In this study, since the monolayer coverage RH determines the value of $W_{\text{mf}}$ and thereby influences the value of $f_{\text{min}}$, an approach is provided to verify the monolayer coverage based on the experimental data. During the monolayer adsorption, the water molecules experience the processes of diffusion in pores and then adsorption onto the surface wall, and the latter is considered to occur instantaneously (Suzuki, 1990). Therefore, the diffusion is the rate-limiting process to control the adsorption rate, and the monolayer adsorption rate of water vapor for a mineral should be constant. Moreover, because the diffusion is influenced by temperature, connected pathways, and pressure differential inside and outside of sample, the diffusion rate is expected to be the same when these conditions are well controlled.

We used kaolinite to investigate, as it lacks interlayer mineral sites and has the presence of both quite hydrophilic (the octahedral sheet) and relatively hydrophobic (the tetrahedral sheet) basal surfaces (Tenney & Cygan, 2014). As shown in Figure 7a, the step change of RH is controlled to be 10% by water vapor adsorption instrument to obtain the same relative pressure difference under the controlled temperature of 25 $^\circ$C. Additionally, each granular sample at 500–841 μm has a fixed path.
of diffusion, so the adsorption rate should be the same among each step change of RH. For kaolinite tests, its curves of adsorption rate change are shown to almost coincide when RH values are < 50% (four lines between 10 and 50% RH, Figure 7b). This value is the same as the monolayer coverage RH of kaolinite obtained above; hence, the monolayer coverage RH from theoretical calculation is justified. In addition, there are several noticeable trends about Figure 7b. The adsorption rates increase and then decrease, as the instrument takes 5 min to raise and maintain the desired RH value, which causes the differential pressure to increase in the first 5 min and then decrease gradually afterwards (the inflection point at 5 min in Figure 7b). Finally, the adsorption reaches an equilibrium gradually and the adsorption rate reaches zero when the experimental time is ~ 60 min. When RH is > 50%, three curves of each RH step change are lifted due to the multilayer condensation in kaolinite, in addition to water film formation, which leads to increased adsorption rate.

3.3.2 Maximum thickness of water film

For a certain pore width, as the RH continues to increase with an accordingly decreasing disjoining pressure Π, the thickness of the adsorbed water film finally reaches a maximum value $f_{\text{max}}$. For instance, when the humidity reaches 95%, the water film in the 2-nm-wide pores reaches the maximum thickness of 0.58 nm (Figure 3). Theoretically, based on the slit-pore model, the maximum thickness is given by Equation 13 (Tuller et al., 1999):

$$\frac{\partial \Pi}{\partial f} = 0$$

As mentioned above, Π is related to pore width D and water film thickness f, so a functional relationship between D and $f_{\text{max}}$ can be established. Using just the molecular force in the parallel-plate model, Tuller et al. (1999) gave the approximate solution of $f_{\text{max}} \approx D/3$. In this work, Equation 13 becomes more complex with the addition of electrostatic and structural forces, so only several certain pore widths (from Figure 3) are used to calculate the maximum thickness of water film, and calculations assume a rigid particle spacing (results are shown in Figure 8). The pore width and the maximum thickness have a significant linear relationship, and the slope of 0.33 is the same as the approximate solution of Tuller et al. (1999), even considering three interface forces.

As mentioned about the equations of interfacial forces, the structural force is only one term in Equations 11a–11c and decreases exponentially as the thickness increases; thus, it could be ignored. The van der Waals force and
the electrostatic force both have increasing and decreasing terms in Equations 11a–11c, but the former is more sensitive to distance (d) than the latter (e.g., $\Pi_{vdW} \propto d^{-2}$, whereas $\Pi_e \propto d^{-3}$). Furthermore, the direct result of increasing the water film thickness is the proximity of the opposing water film, that is, the reduction in $D - 2f$, as well as in $D - f$. This results in the van der Waals force having two increasing terms (while the electrostatic force only has one) that increase faster than the electrostatic force. Therefore, van der Waals force becomes the main factor in controlling the water film thickness as its thickness increases. However, the controls on the maximum thickness are much more complicated than those calculated in this model. For example, a greater curvature of finer mineral particles will lead to an increased curvature-dependent water film force (Tokunaga, 2009), and a continuous thickening of the water film makes gravity non-negligible (Israelachvili, 2011); therefore, the prediction of $f_{max}$ in this study is only suitable for the slit-pore model in a water vapor environment.

4 | CONCLUSIONS

With the development of modeling and experimental capabilities, research on soil water becomes more and more microscopic, and water types in soil can be discretely divided for a mechanistic understanding. A slit-pore model is built to confirm three water types (water film, interlayer water, and capillary water) composing the total water content during water vapor adsorption. Using interface force analysis in a slit-pore and two gas (water vapor and N$_2$) experiments, a new approach is provided for quantification of these three water types at each RH. The results show that the interlayer water content strongly relates to smectite content and also give the monolayer coverage RH of water film.

At low water vapor pressure (around RH < 60%), adsorbed water (water film and interlayer water) accounts for most of the total water content; on the contrary, capillary water gradually dominates the water content at higher RH values. This may lead soil water to possess different physical properties at different water contents, especially for high interlayer water that does not actively participate in flow and transport, causing the illusion that the available water is abundant at high water contents. However, it is still very challenging to accurately recognize the changes in soil water at different water contents. For this study, the shape of pores may be tubular rather than slit, the water film density depends on RH rather than a fixed value, and the clay swelling may have a great influence on pore structure but was not included in our model in this work. These are the directions that can be studied in the future.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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