Intrinsic Relation between Soil Water Retention and Cation Exchange Capacity

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Abstract: The authors hypothesize that soil water retention (SWR) is dominated by cation hydration in soils possessing a cation exchange capacity (CEC) at high suction range. This hypothesis leads to the identification of a unitary maximum gravimetric water content \( w_{mc} \), up to which all water molecules should surround the exchangeable cations. The unitary \( w_{mc} \) can be obtained by using the CEC and hydration number of cations in soils. For a soil with an unknown CEC, the authors reveal that \( w_{mc} \) can be found independently from either the SWR based on the hysteretic behavior of a soil’s specific moisture capacity (SMC), or from the SWR curve interpreted by a Brunauer-Emmett-Teller (BET) sorption model. The authors demonstrate experimentally that \( w_{mc} \) computed independently from the previous approaches accord well with the calculated \( w_{mc} \), indicating the validity of the hypothesized unitary state and applicability of the SWR-based methodology in determining the CEC of soils. DOI: 10.1061/(ASCE)GT.1943-5606.0001633. © 2016 American Society of Civil Engineers.

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Introduction

The soil water retention curve (SWRC) describes the energy equilibrium conditions between the soil water content and its prevailing matric potential. The SWRC depends on two groups of soil characteristics: pore size distribution and air-solid-water interfacial physical properties (e.g., Tuller et al. 1999; Lu and Likos 2004; Revil and Lu 2013). Because each soil has its unique pore size distribution and interfacial properties, the SWRC is also called soil water characteristic curve (SWCC) in the literature (e.g., Fredlund and Xing 1994; Frydman and Baker 2009).

The aforementioned two groups of soil characteristics completely determine how soil and water physically interact with each other and the shapes of the SWRC. From a fundamental physics viewpoint, there exist two soil water retention mechanisms: capillarity and hydration. Capillarity refers to the interaction between bulk pore water, air, and soil particle surface, thus it can be well quantified by the equilibrium of surface tension, contact angle, and pore air and pore water pressure. As such, capillarity occurs in soil when matric potential is relatively high, likely greater than \(-400 \text{ kPa} \) (e.g., Frydman and Baker 2009; Lu and Khorshidi 2015). Here the pore water pressure concept is valid, and the commonly used definition of matric suction being the pressure difference between pore water and pore air, is incomplete. Therefore, matric suction, from the thermodynamic viewpoint, should be defined as the energy difference between air pressure and matric potential, or negative matric potential.

Like many other constitutive relations of soil, the SWRC also exhibits hysteresis (e.g., Khorshidi and Lu 2016a); here, the equilibrium water content could be different under the same matric potential, depending on soil initial water content. Like matric potential, the mechanisms for hydraulic hysteresis could also be quite different. In the capillary water retention regime, inkbottle pore neck and contact angle have been widely accepted as responsible for hydraulic hysteresis. Until recently, few physical mechanisms have been proposed for hydraulic hysteresis in the hydration water retention regime.

Hydraulic Hysteresis and Cation Exchangeable Capacity

Lu and Khorshidi’s (2015) hysteresis model is the first to explain hydraulic hysteresis in the hydration water retention regime at high suction range in clayey soil. The authors’ key concept is that hydraulic hysteresis in high suction range is dominated by the cation exchange capacity (CEC) of soils. The model is based on how cation hydration occurs differently in interlayers between wetting (adsorption) and drying (desorption) processes. Because of the
additional interaction between the exchangeable cations and their surrounding interlayers, the attractive interatomic force between the interlayers facilitates the desorption process, leading to the often observed strong stepwise or wavy shape of the SWRC. On the other hand, during adsorption, the attractive interatomic force between the interlayers is strong, leading to strong resistant forces against cation hydration and much less stepwise behavior with relatively lower water content in the SWRC. This striking difference between adsorption and desorption processes provides key information on the relative importance of cation hydration and interlayer surface hydration and in a subsequent section will be used to determine the boundary between cation hydration and interlayer surface hydration.

In soils with clay minerals, some cations can be exchanged or substituted by other cations without altering mineral structures. These cations play a vital role in hydration. The number of exchangeable cations a soil possesses is measured by the CEC in the units of milliequivalent electric charges per gram. The CEC of a soil has been long considered as a fundamental property for soil behavior. For example, the commonly used geotechnical engineering indexes such as Atterberg limits have been considered highly correlated to the CEC (e.g., Farrar and Coleman 1967; Sridharan and Rao 1975; Smith et al. 1985). The role of CEC in expansive soil behavior has been explored intensively in recent years (e.g., Christidis 1998; Thomas et al. 2000; Yilmaz 2006). The CEC also plays an important role in coupled fluid, and electric and chemical flows in clayey soils (e.g., Shainberg et al. 1980; Gaston and Selim 1990; Revil and Leroy 2004). Numerous methods have been established to measure the CEC of soils. Among them, the ammonium acetate method at pH = 7.0 (e.g., Schollenberger and Dreibleibs 1930), the sodium acetate method (e.g., Bower et al. 1952) or barium chloride (e.g., Bascoubm 1964) at pH = 8.2, and the ammonium chloride method (e.g., Shuman and Duncan 1990) have been widely used. In addition, Khorshidi and Lu (2016b) recently proposed a SWRC-based methodology for determination of CEC. Over the years, ammonium acetate has become the most popular method throughout the world; it has undergone several adaptations and will be used in this study.

In recent years, several researchers (e.g., Quirk 1955; Bérend et al. 1995; Chang et al. 1995; Hu et al. 1995; Chiou and Rutherford 1997; Prost et al. 1998; Laird 1999; Ferrage et al. 2005; Khorshidi et al. 2016a) explored the idea that water tends to form islands or clusters before complete surface coverage at very high suction values. Recent work by Woodruff and Revil (2011), and Revil and Lu (2013) clearly shed light into strong linkage between the CEC and SWRC. By normalizing the gravimetric water content (water content) by CEC of the soil, they demonstrated that the SWRCs of some clayey soils at high suction range (water sorption isotherm) can collapse within a very narrow band in the normalized water content and relative humidity space. Physically, this indicates that cation hydration is the dominant water retention mechanism for all soils with CEC at low relative humidity or high suction range.

On the other hand, according to the results from molecular dynamics simulations (e.g., Hensen and Smit 2002), the stepwise behavior of SWRC is all about the cations that change from not fully hydrated to fully hydrated. According to Hensen and Smit (2002), during this transition process, the hydrated cations will move toward to the center of interlayers and gradually make clay swell. However, this conclusion contradicts the fact that van der Waal interaction energy originating from surface hydration is the dominant mechanism to hold water below certain high suction values (e.g., Tuller et al. 1999; Frydman and Baker 2009). Furthermore, by considering the role of both hydration mechanisms and their sequences (cation hydration is followed by surface hydration) at high suction range, Khorshidi et al. (2016b) proposed a methodology to predict the specific surface area (SSA) of soils. The SSA obtained by this interpretation of water sorption on soil matches very well with the SSA measured by ethylene glycol monoothyl ether (EGME). These findings indicate the validity of the hydration mechanism sequence at high suction values.

The authors will show that soil water retention (SWR) is dominated by cation hydration prior to particle and interlayer surface hydration at high suction range in soils possessing a CEC. Specifically, the authors will show that the CEC dictates a SWRC or water desorption isotherm behavior at high suction range. The authors will confirm this hypothesis by comparing the water content at the completion of cation hydration obtained by three different approaches, a theoretical single-point method based on the soil’s CEC and two independently methods developed based on the measured SWRCs.

**Experimental Methods and Materials**

The SWRCs at high suctions (or water sorption isotherms for the current study) for different clays at high suction values greater than 8 MPa were obtained by using a Vapor Sorption Analyzer. This device is capable of dynamically measuring gravimetric water content and relative humidity for wetting and drying paths (e.g., Likos et al. 2011; Revil and Lu 2013; Akin and Likos 2014).

To minimize the uncertainties associated with unknown clay minerals, relatively known and pure clays were used. The tests were conducted on various mixtures of Georgia kaolinite and Wyoming bentonite (sodium montmorillonite), as well as Na⁺/Ca⁺⁺-bentonite specimens with various isomorphically substituted monocations. The end-member sodium montmorillonite and kaolinite materials are highly expansive and nonexpansive clays, respectively. Georgia kaolinite-sodium montmorillonite mixtures were prepared in seven oven-dried mass-controlled proportions corresponding to their respective Georgia kaolinite (GaK) and sodium montmorillonite (NaS) content (i.e., 100% GaK − 0% NaS, 80% GaK − 20% NaS, 60% GaK − 40% NaS, 40% GaK − 60% NaS, 30% GaK − 70% NaS, 20% GaK − 80% NaS, and 0% GaK − 100% NaS). In addition, the authors used the measured soil water sorption isotherms of the monocation Na⁺/Ca⁺⁺− bentonite specimens [reported in Akin and Likos (2014)]. These specimens were prepared by treating the clay with a saturated solution of the chloride of Li⁺, Na⁺, K⁺, Mg⁺⁺, and Ca⁺⁺⁺ (Akin and Likos 2014). All samples were oven-dried at 105°C and cooled down to ambient room temperature. The initial relative humidity for all tests was below 10%. Therefore, the sorption isotherms were obtained along the desorption path from initial condition down to 4% RH, followed by the adsorption path up to 95% RH, and then the subsequent desorption path down to 4% RH. All isotherms were obtained at 25 ± 0.2°C. A test for one specimen typically lasts between 24 and 48 h. Figs. 1(a and b) show the measured isotherms of various GaK and NaS mixtures as well as different monocation bentonite soils, respectively.

For all validation tests, the CECs of soils were measured by the ammonium displacement method standardized in ASTM D7503 (ASTM 2010) and listed in Table 1 (data from Akin 2014). The CEC values of GaK and NaS mixtures are proportioned from the CEC of GaK and NaS soils. Moreover, due to the small difference between the CEC of cation-exchanged bentonites, their CEC values are assumed to be the same as Na⁺/Ca⁺⁺− bentonite. The CEC values and the cation hydration numbers found in the literature (Isrealachvili 2011) are used to validate the hypothesized concept of the unitary soil water retention state.
Unitary Soil Water Retention State by Cation Hydration

From clay mineralogy, three known sources for a negative particle charge and presence of exchangeable cations are: isomorphous substitution in tetrahedral and octahedral sheets, replacement of the exposed hydroxyl hydrogen, and broken bonds around particle edges (e.g., Mitchell and Soga 2005; Moore and Reynolds 1997). Because isomorphous substitution is the main source for CEC in smectite, exchangeable cations in Wyoming bentonite are mainly located between unit layers [Fig. 2(b)]. On the other hand, in kaolinite, broken bonds at particle edges can play a significant role in providing a source for the CEC (e.g., Grim 1968; Ma and Eggleton 1999); therefore, exchangeable cations are located on the particle edges and surfaces [Fig. 2(d)].

The stepwise and hysteretic behavior of SWR can be explained by considering the effect of cation hydration on SWR along the desorption path, as illustrated in Fig. 2.

![Gravimetric water content (%)](image)

**Table 1.** Comparison between the \( w_{mc} \) Values Obtained from the SMC Method, BET Plot Method, and CEC and Cation Hydration Number for All Soils

<table>
<thead>
<tr>
<th>Soil</th>
<th>Hydration number for cation (^a)</th>
<th>CEC (^b) (meq/g)</th>
<th>( RH_{mc} )</th>
<th>Primary shell coverage</th>
<th>Secondary shell coverage</th>
<th>( RH_{mc} )</th>
<th>Primary shell coverage</th>
<th>Secondary shell coverage</th>
<th>( RH_{mc} )</th>
<th>Primary shell coverage</th>
<th>Secondary shell coverage</th>
<th>( RH_{mc} )</th>
<th>Primary shell coverage</th>
<th>Secondary shell coverage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li(^+)-bentonite</td>
<td>5</td>
<td>0.77</td>
<td>13</td>
<td>—</td>
<td>0.059</td>
<td>—</td>
<td>0.056</td>
<td>—</td>
<td>—</td>
<td>0.069</td>
<td>—</td>
<td>—</td>
<td>0.069</td>
<td>—</td>
</tr>
<tr>
<td>Na(^+)-bentonite</td>
<td>4</td>
<td>0.77</td>
<td>23</td>
<td>—</td>
<td>0.055</td>
<td>—</td>
<td>0.058</td>
<td>—</td>
<td>—</td>
<td>0.055</td>
<td>—</td>
<td>—</td>
<td>0.055</td>
<td>—</td>
</tr>
<tr>
<td>K(^+)-bentonite</td>
<td>3</td>
<td>0.77</td>
<td>28</td>
<td>—</td>
<td>0.040</td>
<td>—</td>
<td>0.040</td>
<td>—</td>
<td>—</td>
<td>0.042</td>
<td>—</td>
<td>—</td>
<td>0.042</td>
<td>—</td>
</tr>
<tr>
<td>Mg(^{++})-bentonite</td>
<td>6</td>
<td>0.77</td>
<td>8</td>
<td>18</td>
<td>0.044</td>
<td>0.070</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>0.073</td>
<td>0.042</td>
<td>—</td>
<td>0.073</td>
<td>0.042</td>
</tr>
<tr>
<td>Ca(^{++})-bentonite</td>
<td>6</td>
<td>0.77</td>
<td>10</td>
<td>21</td>
<td>0.043</td>
<td>0.080</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>0.086</td>
<td>0.042</td>
<td>—</td>
<td>0.086</td>
<td>0.042</td>
</tr>
<tr>
<td>0% GaK–100% NaS</td>
<td>4</td>
<td>0.71</td>
<td>28</td>
<td>—</td>
<td>0.067</td>
<td>—</td>
<td>0.069</td>
<td>—</td>
<td>—</td>
<td>0.051</td>
<td>—</td>
<td>—</td>
<td>0.051</td>
<td>—</td>
</tr>
<tr>
<td>20% GaK–80% NaS</td>
<td>4</td>
<td>0.58</td>
<td>27</td>
<td>—</td>
<td>0.051</td>
<td>—</td>
<td>0.049</td>
<td>—</td>
<td>—</td>
<td>0.042</td>
<td>—</td>
<td>—</td>
<td>0.042</td>
<td>—</td>
</tr>
<tr>
<td>30% GaK–70% NaS</td>
<td>4</td>
<td>0.52</td>
<td>28</td>
<td>—</td>
<td>0.045</td>
<td>—</td>
<td>0.045</td>
<td>—</td>
<td>—</td>
<td>0.038</td>
<td>—</td>
<td>—</td>
<td>0.038</td>
<td>—</td>
</tr>
<tr>
<td>40% GaK–60% NaS</td>
<td>4</td>
<td>0.46</td>
<td>27</td>
<td>—</td>
<td>0.041</td>
<td>—</td>
<td>0.040</td>
<td>—</td>
<td>—</td>
<td>0.033</td>
<td>—</td>
<td>—</td>
<td>0.033</td>
<td>—</td>
</tr>
<tr>
<td>60% GaK–40% NaS</td>
<td>4</td>
<td>0.34</td>
<td>27</td>
<td>—</td>
<td>0.029</td>
<td>—</td>
<td>0.029</td>
<td>—</td>
<td>—</td>
<td>0.024</td>
<td>—</td>
<td>—</td>
<td>0.024</td>
<td>—</td>
</tr>
<tr>
<td>80% GaK–20% NaS</td>
<td>4</td>
<td>0.21</td>
<td>27</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>0.015</td>
<td>—</td>
<td>—</td>
<td>0.015</td>
<td>—</td>
<td>—</td>
<td>0.015</td>
<td>—</td>
</tr>
<tr>
<td>100% GaK–0% NaS</td>
<td>4</td>
<td>0.09(^c)</td>
<td>29</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>0.006</td>
<td>—</td>
<td>—</td>
<td>0.006</td>
<td>—</td>
<td>—</td>
<td>0.006</td>
<td>—</td>
</tr>
</tbody>
</table>

\(^a\)From Israelachvili (2011).

\(^b\)Data from Akin (2014).

\(^c\)Data from Woodruff and Revil (2011).

\(^d\)\( RH \) and \( w \) values are at the completion of primary/secondary water coverage around cations.
Mooney et al. (1952) and Lu and Khorshidi (2015), the desorption path is more representative for inferring exchangeable cation and surface related properties because the effect of intermolecular forces and hysteresis sources are less prominent in the desorption path than the adsorption path. Therefore, the drying paths of the soils are used to reveal the relation between SWR and CEC in this work. Wyoming bentonite shows strong hysteresis and stepwise SWR behavior, whereas these behaviors are barely observed in Georgia kaolinite (Fig. 2). The stepwise behavior of SWR of expansive soils (such as Wyoming bentonite) is discussed as follows: Exchangeable cations have a smaller size than oxygen and hydroxyl ions of particle surface and have more charge compared to the surface layer charge. Therefore, dehydration occurs first on an interlayer surface, followed by dehydration around cation. Starting from point A in Fig. 2(a) moving toward point B on the drying path of Wyoming bentonite, water content decreases linearly and slightly as the relative humidity decreases. This can be interpreted as the process of interlayer surface dehydration, as illustrated from panel a to panel b. At point B (in panel b), the end of interlayer surface dehydration, all the exchangeable cations are hydrated by all the water molecules. This point is defined here as the monolayer cation hydration water content ($w_{mc}$), where all soil water molecules surround the exchangeable cations. It exists for all soils possessing a CEC.

For soils with dominating 1:1 minerals (one tetrahedral and one octahedral sheet in each unit cell) such as Georgia kaolinite, shown in Fig. 2, the monolayer water coverage around the exchangeable cations and the monolayer coverage on the particle surface are completed at point C (Fig. 2(c)). As discussed earlier, the dehydration process from point C to point D removes water molecules first from the particle surface, leading to water coverage only around the exchangeable cations [Fig. 2(d)]. Therefore, for a monocation soil with cation $i$, cation hydration number $I_{i}$, cation valence $N_{i}$, and exchangeable cation CEC$_{i}$ (which is equal to CEC), the gravimetric water content at the first complete layer of cation hydration $w_{mc}$ can be uniquely expressed as

$$w_{mc} = \omega_{w} I_{i} \text{CEC}_{i} / N_{i}$$

(1)

For a soil consisting of multiple cation species, the preceding equation can be generalized by the principles of superposition and the local thermodynamic equilibrium as

$$w_{mc} = \omega_{w} \sum_{i} I_{i} \text{CEC}_{i} / N_{i}$$

(2)

Here, $i$ represents different types of exchangeable cations in soil (i.e., Na$^{+}$, K$^{+}$, Ca$^{++}$, and Mg$^{++}$).

The validity of the previous hypothesis [Eq. (1)] will be examined later by other independent methods for identifying the monolayer cation hydration water content ($w_{mc}$). The authors will show that, in general, the $w_{mc}$ of a soil can be determined independent of the CEC and cation hydration number, either from the SWR based on the hysteretic behavior of a soil’s specific moisture capacity (SMC), or from the SWR curve interpreted by a Brunauer-Emmett-Teller (BET) (Brunauer et al. 1938) sorption model, taking into account the effect of cation hydration. These two methods are described in detail in the following sections.

Fig. 2. Conceptual illustration of different soil hydration mechanisms for three mixtures of Georgia kaolinite and Wyoming sodium montmorillonite; desorption isotherms of mixtures with (a) interlayer cation hydration and interlayer surface hydration; (b) interlayer cation hydration; (c) cation hydration and particle hydration; (d) cation hydration
Determination of Monolayer Cation Hydration Water Content by the SMC Method

As conceptualized in Lu and Khorshidi (2015) and evidenced in some clayey soils (e.g., Likos and Lu 2003), the stepwise SWR behavior is more pronounced along the desorption path rather than the adsorption path. This is a characteristic behavior of the exchangeable cations in soils with 2:1 minerals (two tetrahedral and one octahedral sheet in each unit cell) as well as other expansive soils, quantified through the SMC \[ C(w) \] as Eq. (3)

\[
C(w) = \left[ \frac{\partial w}{\partial RH} \right] = \left[ \frac{\partial w}{\partial \psi} \right] \frac{\partial RH}{\partial \psi}
\]

where \( RH \) = relative humidity; \( w \) = gravimetric water content; and \( \psi \) = total potential that is equal to the negative matric suction. The SMC reflects the amount of change in water content per unit change in total suction. The total potential (\( \psi \)) can be directly related to relative humidity through Kelvin’s equation (e.g., Lu and Likos 2004)

\[
RH = \exp\left( \frac{\omega \psi}{RT} \right)
\]

where \( R = \) universal gas constant; and \( T = \) temperature in Kelvin. By substitution of Eq. (4) into Eq. (3), SMC can be rewritten in terms of relative humidity as

\[
C(w) = -\frac{\omega}{RT} RH \frac{\partial w}{\partial RH}
\]

The main reason for hysteresis in SWR at low relative humidity is crystalline swelling (Lu and Khorshidi 2015). As discussed in the introduction, in clayey soils, two adjacent unit layers are held together by van der Waals forces and hydrogen bonding between layers of oxygen and hydroxyls or between layers of hydroxyls. The effect of these forces on water molecules during adsorption and desorption processes on soil are completely different. During wedgelike penetration of water molecules into the interlayer space along adsorption path, the interlayer bonding hinders water adsorption around exchangeable cations; as discussed in the previous section, water molecules first hydrate the exchangeable cations. On the other hand, during desorption, these forces promote water removal from the interlayer space. Consequently, water molecules can move more freely during desorption than adsorption. Therefore, the value of SMC on the desorption path is greater than the corresponding value on the adsorption path. After the interlayer space being opened due to the hydration of water molecules around exchangeable cations, further water molecules can be drawn into and hydrate the interlayer surfaces at the vacant spaces between the hydrated cations (e.g., Bérend et al. 1995; Chiou and Rutherford 1997). These two hydration mechanisms are the reasons for the intensified stepwise and hysteresis behaviors of SWR as the bentonite content of soils increases (Fig. 2).

In contrast, during water adsorption and desorption processes on the interlayer surface, the SMC of the adsorption path is almost equal to that of the desorption path. The reason is that during adsorption/desorption of water molecules on the interlayer surface, the distance between unit layers almost remains constant; thus, van der Waals forces have little contribution to the SMC. The same situation and reasoning are also valid for adsorption/desorption of water molecules on the particle surface (the SMC on the adsorption path is almost equal to that of the desorption path, as observed in the isotherm of GaK in Fig. 2). Based on the preceding interpretation for the sequences of hydration mechanisms in soil, Khorshidi et al. (2016b) proposed a SWRC-based methodology for determination of specific surface area that agrees well with the specific surface area measured by ethylene glycol monoethyl ether (EGME).

Taking into account the two previously mentioned statements for the SMCs during adsorption and desorption processes, one can figure out the dominant hydration mechanism in a certain range of relative humidity. Fig. 3 illustrates the variations of the SMC during the adsorption and desorption paths for a typical expansive soil. At low relative humidity, the value of SMC on the desorption path is greater than the corresponding value on the adsorption path, indicating that the water is adsorbed around cations. After the completion of hydration around the cations, water molecules are adsorbed on the interlayer surface. Therefore, the SMC on wetting and drying paths becomes about the same. The relative humidity at which SMCs during desorption and adsorption processes intersect each other is referred to as \( RH_{nc} \). This relative humidity corresponds to the unitary state water content \( w_{mc} \), being the maximum water content that can be held by exchangeable cations in the monolayer coverage (also called primary shell coverage).

In general, while monovalent cations are able to form only a primary water shell around themselves, divalent cations can form a secondary water shell as well (Israelachvili 2011). Secondary water shell coverage around cations can be determined using the slope of the SMC curve. When a new layer of water molecules is gradually forming around cations, the distance between the unit layers keeps increasing and, subsequently, the attractive forces between them keep decreasing. As a result, water molecules are freer to be adsorbed or desorbed, leading to a gradual increase of the SMC as illustrated in Fig. 3. Similarly, the distance between the unit layers and the number of water layers around cations are directly proportional. It follows that, with an increase in water layer, the water molecules are set to be freer in adsorption/desorption processes. It causes the slope of the SMC-RH curve to increase compared to the SMC-RH curve slope for the previous water layer around cations. On the other hand, during hydration on the interlayer surface, the SMC values are almost constant due to the invariable spacing between the unit layers. The three features of the SMC-RH curve mentioned previously are employed in the identification of the secondary water shell coverage around cations (following the primary water shell coverage).

The usage of the SMC for the determination of the \( w_{mc} \) is most suitable for the soils whose difference between the SMCs
of adsorption and desorption paths is obvious (as in expansive soils). For other soils whose difference between the SMC paths is small or negligible, the BET plot method can be used to find the \( w_{mc} \), as described next.

**Determination of Monolayer Cation Hydration Water Content by the BET Plot Method**

The \( w_{mc} \) can be identified by implementing the BET model. Some previous work (e.g., Keren and Shainberg 1979; Likos and Lu 2002) showed that the SWRCs of clays in high suction or low relative humidity (e.g., less than 40%) can be predicted by the BET model. A linear relation between \( RH/(1 - RH)w \) and \( RH \) is assumed in the BET model:

\[
\frac{RH}{(1 - RH)w} = c - \frac{1}{cw_m} RH + \frac{1}{cw_m}
\]

where \( w_m \) = water content corresponding to the monolayer of water on particle surface; and \( c \) = BET sorption constant pertinent to the sorption enthalpy of the first layer water adsorption on particle surface. For more details on how the BET constant is related to the sorption enthalpy of the first layer water adsorption on particle surface, see Lu and Khorshidi (2015).

The basic assumption of the BET model is that the surface is homogenous; therefore, plotting the experimental values of \( RH/(1 - RH)w \) versus \( RH \) gives a straight line, as illustrated in Fig. 4(a). By using the slope of this line and its intersection with the vertical axis, the BET parameter \( c \) can be determined. For the majority of soils, however, the assumption of being perfectly linear does not exist. For small values of \( RH \), the value of \( RH/(1 - RH)w \) obtained from the BET equation is usually smaller than the experimental value (Ponec et al. 1974). As illustrated in Fig. 4(b) for a typical soil, it generally gives a nonlinear (curve) segment followed by a linear one. The reason is that the particle surface is nonhomogenous, and there are some active sites with the heat of adsorption values different from the adsorption heat on the particle surface. In the range of low relative humidity, water molecules are adsorbed first by exchangeable cations. Thus, the adsorption heat can be related to cation hydration rather than particle surface hydration. As such, the difference in adsorption heat of cations and particle surface can be used to determine the \( w_{mc} \) value.

In order to find the \( RH_{mc} \) (and consequently its corresponding water content \( w_{mc} \)), the boundary between hydration on cation and particle surface should be identified. To this end, the experimental values of \( RH/(1 - RH)w \) and \( RH \) are plotted first (BET curve), as shown in Fig. 4(b). Afterward, by drawing a line passing through the linear segment of the BET curve (line AB), both nonlinear and linear segments of the BET curve can be delineated. These segments correspond to the adsorption around exchangeable cations and on interlayer/particle surface, respectively. The relative humidity at the boundary of nonlinear and linear segments of the BET curve (point A) is the \( RH_{mc} \). For some soils in which the contrast between the two parts is not obvious (i.e., the BET curve is nearly a straight line), Eq. (6) can be used to find the \( w_m \) [as depicted in Fig. 4(a)], which can be used as the \( w_{mc} \).

**Validation of the Unitary State of SWR at High Suction**

To validate the authors’ hypothesis that the cation hydration occurs prior to the interlayer/particle surface hydration in soils with CEC, the results of the \( w_{mc} \) obtained are based on the three methods described earlier: the CEC and cation hydration number [Eq. (1)], the SMC [Eq. (3)], and the BET plot are then compared.

The SMC values for different ranges of relative humidity during adsorption and desorption paths for NaS, 70% NaS–30% GaK, and GaK soils are plotted and compared in Figs. 6(a–c), respectively. In the range of low relative humidity shown in Figs. 5(a and b) where \( C_{des} > C_{ads} \), hydration occurs around the exchangeable cations. It is then followed by hydration on the interlayer surface \( (C_{des} = C_{ads}) \). The \( RH_{mc} \) is the relative humidity at the boundary of these two distinct hydration mechanisms. In Fig. 5(c), the SMCs during the adsorption and desorption paths are nearly equal to each other for the entire range, indicating that the hydration occurs on the particle surface. Since GaK is a nonexpansive soil, the BET plot method should be used to determine the \( RH_{mc} \) value.

Figs. 6(a–c) illustrate the way to obtain the \( RH_{mc} \) for 100% NaS–0% GaK, 70% NaS–30% GaK, and 0% NaS–100% GaK soils, respectively, based on the BET plot method. A straight line passing through the linear portion of the BET curve is drawn to
distinguish between linear and nonlinear segments. The \( RH_{mc} \) is identified as the relative humidity at the boundary of the nonlinear and linear segments of the BET curve.

The values of the \( RH_{mc} \) determined from the SMC or BET plot method, as described previously, are tabulated in Table 1 for all

**Fig. 5.** Comparison between SMC during desorption and adsorption paths for (a) Wyoming sodium montmorillonite; (b) 30% Georgia kaolinite–70% Wyoming sodium montmorillonite; (c) Georgia kaolinite

**Fig. 6.** Determination of \( RH_{mc} \) based on BET plot method for (a) Wyoming sodium montmorillonite; (b) 30% Georgia kaolinite–70% Wyoming sodium montmorillonite; (c) Georgia kaolinite
soils (for the first 10 soils, the SMC-$RH_{mc}$ values are presented, as are the BET-$RH_{mc}$ values for the last two soils). Given the values of the $RH_{mc}$ from either the SMC or BET plot method for each soil, the $w_{mc}$ can then be read from the measured water sorption isotherms shown in Fig. 1(a). These values of the $RH_{mc}$, as well as the $w_{mc}$ obtained from the CEC and cation hydration number [Eq. (1)], are also listed in Table 1. The cation hydration number varies roughly by $\pm 1$ (Israelachvili 2011), while the values of the $w_{mc}$ given in Table 1 computed from the CEC and cation hydration number correspond to the average hydration number of each cation.

In Fig. 7, the $w_{mc}$ values resulted from the SMC and BET plot methods are compared with the values of the $w_{mc}$ obtained from the method of CEC and hydration number. Note that the horizontal coordinates of the data points shown by the markers and solid points are calculated by the BET plot and SMC methods, respectively. The error bar around each data point is related to the $\pm 1$ uncertainty in the cation hydration number value. Note that good agreements exist between the $w_{mc}$ values obtained independently from different methods of the SMC, BET plot, or CEC and hydration number for all soils (Table 1 and Fig. 7), particularly for various cation exchanged-bentonite soils shown in Fig. 7(a). Fig. 7(b) shows some degree of error in the $w_{mc}$ values obtained from the CEC and cation hydration number for various mixtures of GaK and NaS soils. Note that GaK and NaS are composed of multiple cation species, such as Na$^+$ and Ca$^{++}$ (e.g., Rollins and Pool 1968; Dohrmann et al. 2012; Marchuk et al. 2012). For these soils, the $w_{mc}$ values from CEC and hydration number are obtained from Eq. (1) by considering only the dominant cation in soil, Na$^+$; the authors used $I_{Na}$ and $CEC_{Na}$ equal to the soil’s CEC in the calculations. Thus, using the single-species, Eq. (1) instead of the multispecies, Eq. (2) may contribute to the error.

The $RH_{mc}$ values for various cation-exchanged bentonites shown in Table 1 are crucial ones that are found in this study. As hypothesized, up to the relative humidity value of the $RH_{mc}$, water molecules are adsorbed only around exchangeable cations. This indicates that the $RH_{mc}$ exclusively depends on the types of the exchangeable cations in soils (via their hydration energies), and not on the particle surface (type of soils). Therefore, regardless of soil type, the $RH_{mc}$ values of all monocation soils possessing the same exchangeable cation should be identical. This implies that the $RH_{mc}$ values for various cation-exchanged bentonites listed in Table 1 can be used for any other soils with the same monocations, including kaolinite. The $RH_{mc}$ values determined in this study for Mg$^{++}$, Ca$^{++}$, Li$^+$, Na$^+$, and K$^+$-saturated bentonites are, respectively, 8, 10, 13, 23, and 28%. This order is consistent with the reverse order of the hydration energy of these cations (1,910 > 1,580 > 506 > 397 > 314 kJ/mol) (Bohn et al. 1985). Orchiston (1955) found that the monolayer for K$^+$, Mg$^{++}$, and Ca$^{++}$-saturated bentonites were completed at the relative humidity of 34, 16, and 17%, respectively. It is interesting that these values are close to 28% for the $RH$ value at the primary water shell coverage around K$^+$, 18% for the $RH$ value at the secondary shell coverage around Mg$^{++}$, and 21% for the $RH$ value at the secondary coverage around Ca$^{++}$ obtained here (Table 1). Furthermore, the $RH_{mc}$ value for the monolayer water coverage around cations in the Na$^+$-saturated bentonite as well as the $RH$ values for the monolayer and double-layer water coverage around cations in Ca$^{++}$-saturated bentonite, obtained from the SMC method and shown in Table 1, are comparable with the corresponding $RH$ values determined from the X-ray diffraction method provided by Brindley and Brown (1980).

In the following, with the aid of the preceding theory, consistency between the results of the $w_{mc}$ values identified based on the SMC method and Eq. (1) is further investigated for kaolinite soils by using the data provided in Martin (1959), where the water sorption isotherms of K$^+$, Na$^+$, Li$^+$, and Mg$^{++}$-saturated kaolinites were obtained. Using the $RH_{mc}$ values of Table 1 (determination based on the SMC method) and the water sorption isotherms of Martin (1959), the $w_{mc}$ of K$^+$, Na$^+$, Li$^+$, and Mg$^{++}$-saturated kaolinites during drying path are 0.44, 0.48, 0.36, and 0.43%, respectively. The CEC of the soils were not measured in Martin (1959); therefore, the CEC values for the soils are herein assumed to be the same at the ambient temperature. However, Martin’s water sorption isotherms were obtained after drying the soils at 70°C in a vacuum [approximately equivalent to air drying at 115°C (Keenan et al. 1951)]. Thus, the effect of heat on the reduction of the soils’ CEC should be considered. During the measurements of water sorption isotherms, according to Pennel et al. (1991), the CECs of Li$^+$ and Na$^+$-saturated kaolinites must be decreased by about 50 and 20%, respectively, compared to the CEC at the ambient temperature. However, the CECs of K$^+$ and Mg$^{++}$-saturated kaolinites do not change by heat. By normalizing the ratio of $w_{mc}$/CEC of the soils relative to the ratio of $w_{mc}$/CEC of K$^+$-saturated kaolinite, as shown in Table 2, their CEC values are then not needed to be

![Fig. 7. Comparison between $w_{mc}$ values obtained based on SMC/BET plot method and $w_{mc}$ values obtained from CEC and cation hydration number for (a) various cation-exchanged bentonites; (b) various mixtures of Georgia kaolinite, and Wyoming sodium montmorillonite.](image-url)
known. The normalized values of $w_{mc}/CEC$ obtained from the SMC method as well as Eq. (1) are given in Table 2. Comparison between the tabulated results clearly shows an excellent agreement between the $w_{mc}$ obtained from the SMC method and Eq. (1) for various cation exchanged-kaolinites, further confirming the validity of the hypothesis and the establishment of Eq. (1).

**Summary and Conclusions**

In this work, it is hypothesized that the hydration of cation occurs prior to the hydration of particle or interlayer surface. Based on this hypothesis, a unitary state that links the SWR and the CEC and cation hydration number of soils is established for any soil possessing the CEC. To validate the existence of the unitary state, it is shown that the $w_{mc}$ can be found independently from either the SWR based on the hysteretic behavior of a soil’s CEC, or from the SWR curve interpreted by a BET sorption model. Comparison between the values of the $w_{mc}$ calculated from the CEC and cation hydration number, and from the SMC or BET plot method shows the validity of the unitary state.

The crystalline swelling that has been recently proposed by Lu and Khorshidi (2015) as the main cause for hysteresis in adsorbed water content can be used to determine the $w_{mc}$ based on the SMC method. When water molecules are adsorbed around exchangeable cations, the SMC value on the desorption path is greater than the corresponding value on the adsorption path. Furthermore, the SMC increases as cation hydration proceeds. However, the SMC values during desorption and adsorption processes are almost equal and constant when water molecules are adsorbed on particle or interlayer surfaces. These three features of the SMC-RH curve are used for determination of the $RH_{mc}$.

The applicability of the BET model to arrive at the $RH_{mc}$ (and the corresponding $w_{mc}$) is discussed by taking into account the cation hydration. Adsorption heat of water around cations is different from that of the particle surface, thus the curve of $RH/(1 - RH)w$ versus $RH$ is generally composed of a nonlinear segment followed by a linear segment at low values of $RH$. Following the proposed unitary state hypothesis, the nonlinear and linear parts of the curve are related to the adsorption of water around exchangeable cations and on the particle or interlayer surface, respectively. The $RH_{mc}$ is considered to be the relative humidity at the boundary of the nonlinear and linear segments. The $w_{mc}$ value corresponding to the $RH_{mc}$ obtained from either the SMC or BET plot method can then be found from the measured water sorption isotherm of the soils.

The $w_{mc}$ for different soils is obtained from the SMC, BET plot, and independently from the CEC and cation hydration number. Consistent agreement between the $w_{mc}$ values (shown in Table 1) obtained from these three methods confirms the validity of the unitary state hypothesis; cation hydration occurs prior to particle or interlayer surface hydration at low values of relative humidity during wetting and drying paths. The practical implication of the existence of the unitary state is that the SWRC and the CEC can be quantitatively linked together for all soils possessing a CEC.

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**References**


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**Table 2.** Comparison between the Results of Normalized $w_{mc}/CEC$ for Various Cation-Exchanged Kaolinites Obtained from the SMC Method, and CEC and Cation Hydration Number

<table>
<thead>
<tr>
<th>Normalized $w_{mc}$ by CEC</th>
<th>SMC method</th>
<th>CEC and Cation Hydration Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[w_{mc}/(0.8CEC)]<em>{Na^+}/[w</em>{mc}/CEC]_{K^+}$</td>
<td>1.36</td>
<td>1.33</td>
</tr>
<tr>
<td>$[w_{mc}/(0.5CEC)]<em>{Li^+}/[w</em>{mc}/CEC]_{K^+}$</td>
<td>1.64</td>
<td>1.67</td>
</tr>
<tr>
<td>$(w_{mc}/CEC)<em>{Mg^{2+}}/[w</em>{mc}/CEC]_{K^+}$</td>
<td>0.98</td>
<td>1.00</td>
</tr>
</tbody>
</table>


