Intrinsic Relationship between Matric Potential and Cation Hydration

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The origin of matric potential in the tightly adsorbed soil water retention (SWR) regime, where matric potentials are generally less than −150 MPa, remains unsettled. Surface tension in soil pores and van der Waals attraction (VDW) near particle surfaces are known, respectively, as the sources of matric potential for capillary and adsorbed film water. However, theories based on VDW fail to predict the SWR for matric potentials less than −150 MPa. Recent studies show that cation hydration occurs at matric potentials much lower than those predicted by considering a particle surface hydration originating from the VDW forces. With this basis, a theoretical soil water retention curve (SWRC) model for drying path is proposed to quantify matric potential and its retained water by accounting for all water sorption mechanisms on or within soil particles, particularly the cation–water molecule or charge–dipole interaction. Clays at very low soil water content, typically less than a few percentage gravimetric charge–dipole interaction energy, dominate matric potential. Experimental SWR data for various cation-exchanged soils confirms the validity of the theoretical SWRC model and its accuracy, indicating that cation hydration is mainly responsible for SWR for matric potentials less than −150 MPa. Furthermore, the predicted lowest matric potentials at zero water content for various soils agree well with experimental data. The lowest matric potential of a soil depends mainly on the type of exchangeable cations and thus is not a universal constant for all soils. These results have potential applications in using SWRC for the determination of cation exchange capacity and types of exchangeable cations in soils.

Abbreviations: CEC, cation exchange capacity; REV, representative elementary volume; RH, relative humidity; SSA, specific surface area; SWR, soil water retention; SWRC, soil water retention curve; VDW, van der Waals attraction; VSA, vapor sorption analyzer.

The total potential of pore water is the energy per unit volume of pore water with respect to the energy per unit volume of pure water under ambient air pressure and temperature conditions. The total potential consists of three forms of energy: matric, gravitational, and osmotic potential. Gravitational potential is not dependent on the constitutive characteristics of soils and varies as much as 1000 kPa for most geotechnical engineering problems (e.g., Lu and Khorshidi, 2015). Osmotic potential is the energy lowering as a result of the dissolution of salts in soil water and it can decrease total potential by as much as −4,000 kPa in shallow subsurface environments (e.g., Lu and Likos, 2004). Matric potential is the energy lowering as a result of the interaction between water and the soil matrix, and it can decrease total potential by as much as −1,200 MPa in shallow subsurface environments (e.g., Khorshidi, 2015). As such, for problems concerning total potentials less than −100 MPa, matric potential can be practically considered as total potential. The SWRC defines the relation between matric potential and soil water content (e.g., van Genuchten, 1980; Lu and Likos, 2004; Baker and Frydman, 2009). It is one of the most useful constitutive functions for describing soil moisture distribution and movement (e.g., Mualem, 1976; van Genuchten, 1980) and effective stress (e.g., Lu et al., 2010) in unsaturated soils.

All types of soils interact with water at very low matric potential down to approximately −1,200 MPa (e.g., Campbell and Shiozawa, 1992; Lu and Khorshidi, 2015). However, the
ability to retain water at very low matric potential, generally less than −100 MPa, varies greatly from soil to soil. For instance, the gravimetric water content at given low matric potential of −100 MPa can be much less than 1% in coarse-grained soils like Ottawa sand, whereas it can be as much as 25% in montmorillonite clay (Likos and Lu, 2006). We define the range of very low matric potentials in this study as −150 MPa as the upper bound with a lower bound of −1,200 MPa. Despite substantial effort to develop SWRC models for the entire matric potential range (e.g., Lebeau and Konrad, 2010; Jensen et al., 2015; Lu, 2016), the SWR relation over the very low matric potential range is still poorly defined primarily because of the lack of understanding of soil water interaction mechanisms and quantitative theories for the SWRC.

The prevailing quantitative understanding of soil water interaction is that water is attracted to soil either as adsorbed water on or within particles or as capillary water (e.g., Tuller et al., 1999; Frydman and Baker, 2009). As illustrated in Fig. 1, three water retention mechanisms are known (e.g., McQueen and Miller, 1974; Lu and Likos, 2004): tightly adsorbed water, adsorbed water, and capillary water. Starting from oven-dry conditions to full saturation during the wetting process, water is first adsorbed on particle surfaces or around exchangeable cations (Khorshidi and Lu, 2016). Generally, the first few layers of water molecules are bound to the cations or particle surfaces much more tightly than the subsequent layers; these first few water layers are referred to as tightly bound, whereas the subsequent layers are referred to as loosely adsorbed. The exact matric potential boundary between tightly adsorbed and adsorbed water is still unclear (e.g., Lu and Khorshidi, 2015). Once a cavitation matric potential value is reached by further adsorption of water, capillary condensation occurs and water menisci are formed in soil pores. Here, matric potential is appropriately expressed by an augmented Young–Laplace equation to include both adsorptive component (\( \psi_a \)) and capillary component (\( \psi_c \)) (e.g., Philip, 1977; Nitao and Bear, 1996; and Tuller et al., 1999):

\[
\psi = \psi_a + \psi_c (r) \tag{1}
\]

where \( r \) is the principal curvature of water–air interface. The capillary component is equal to the difference in water and air pore pressure, expressed as follows:

\[
\psi_c (r) = - (u_a - u_w) \tag{2}
\]

where \( u_a \) is pore air pressure and \( u_w \) is pore water pressure. The quantity \((u_a - u_w)\) is often called matric suction, in the literature. In light of the possibility of soil water without capillary water defined by Eq. [1] and [2], such a definition of matric suction is incomplete. Matric suction should be defined as the negative of matric potential defined in Eq. [1].

The adsorptive potential \( \psi_a \) has been formulated based on VDW energy between particle surface and water (Tuller et al., 1999; Tuller and Or, 2005; Frydman and Baker, 2009). It can be expressed as follows:

\[
\psi_a = \psi_{vdw} = \frac{A}{6 \pi b^3} \tag{3}
\]

where \( A \) is the Hamaker constant for vapor–solid interaction through intervening liquid, and \( b \) is the water film thickness. The Hamaker constant is usually assumed as \(-6.0 \times 10^{-20} \) J for soils (e.g., Tuller and Or, 2005; Frydman and Baker, 2009; Leão and Tuller, 2014). The water film thickness \( b \) can be related to the gravimetric water content \( w \) (mass of water per mass of dry soil) and the specific surface area (SSA) of soil by the following equation (Tuller and Or, 2005; Frydman and Baker, 2009):

\[
b = \frac{w}{SSA \rho_w} \tag{4}
\]

where \( \rho_w \) is the mass density of water. Substituting Eq. [4] into Eq. [3] leads to the SWRC model (Tuller and Or, 2005; Frydman and Baker, 2009):

![Fig. 1. Soil water retention mechanisms for soils from oven-dried to full-saturation conditions (after Lu and Khorshidi, 2015).](image-url)
The above SWRC model typically describes SWR behavior down to matric potential of between −200 and −300 MPa. Below this range of matric potential values, large discrepancies (one to several orders of magnitude) between measured SWR data and SWRC models are evident. Frydman and Baker (2009) showed that measurements from kaolin and montmorillonite soils depart up to orders of magnitude from the theoretical predictions (using Eq. [5]) in the range of relative humidity (RH) between 5 and 30%, indicating that VDW might not be dominant. Tuller and Or (2005) recommended to use the above equation for soils with SSA >200 m² g⁻¹ (generally nonexpansive soils). Furthermore, Leão and Tuller (2014) derived an equation to calculate SSA as a fitting parameter for various nonexpansive soils using soil water sorption isotherms and Eq. [5]. Comparison between the measured soil water sorption isotherms and the predicted isotherms using the calculated SSA values reveals orders of magnitude deviation between predicted and measured isotherms at very low matric potentials (as discussed in Leão and Tuller, 2014). These observations imply that at very low matric potential range, particle surface hydration might not be the controlling factor. As shown below, another type of hydration (cation hydration) may play an important role in the adsorption of water for matric potentials less than −200 MPa or matric suctions >200 MPa.

During water adsorption on soil, hydration can occur at two locations: on exchangeable cation and on the interlayer particle surface (e.g., Xu et al., 2010; Lu and Khorshidi, 2015; Khorshidi and Lu, 2016). Several studies have indicated that the cation hydration mechanism dominates during water sorption at very low matric potentials (e.g., Quirk, 1955; Hu et al., 1995; Prost et al., 1998; Laird, 1999; Sposito, 2008; Xu et al., 2010). It was also shown that by normalizing the water content of soils by their cation exchange capacity (CEC), a unified curve at low RH range is obtained, demonstrating the substantial effect of cations on water adsorption (e.g., Woodruff and Revil, 2011; Revil and Lu, 2013). Recently, Khorshidi and Lu (2016) demonstrated quantitatively that prior to particle surface hydration, water molecules are first adsorbed by exchangeable cations in their hydration shell until the number of water molecules reaches the cation hydration number. They confirmed this notion by comparing the water content computed based on soil CEC and cation hydration number with the water contents obtained by two independent methods derived based on the measured water sorption isotherms. Therefore, the definition of matric potential at very high matric suction needs to be re-conceptualized and reformulated.

According to the previously described findings, neglecting the impact of cation hydration on matric potential may not be accurate at very low water content in soil. The objectives of this study are to (i) distinguish the impact of different water retention mechanisms on matric potential and their operating ranges and (ii) derive a SWRC model suitable to describe matric potential in the very low range. As a corollary of the model, the matric potential at zero water content for any soil can be defined and quantified.

Theoretical and Experimental Methods

Thermodynamic Energy for Soil Water Retention at Low Water Content

Thermodynamics is used to define state variables controlling the multiphase transfer in porous media (e.g., Hassanizadeh and Gray, 1979; 1980; Sposito and Chu, 1981; 1982) and to identify and define forms of energy changes in the process of interest. Matric potential in soil can be defined as “the amount of work that must be done per unit quantity of pure water to transport reversibly and isothermally to the soil water at a considered point, an infinitesimal quantity of water from a reference pool” (Nitao and Bear, 1996):

\[ \psi = \frac{\partial G}{\partial V_w} \bigg|_{T,P} \tag{6} \]

where \( V_w \) is volume of soil water and \( G \) is defined as the Gibbs free energy for water retention (e.g., Nye and Tinker, 1977). For systems with constant temperature and pressure conditions, Gibbs free energy is a convenient representation of energy to define matric potential (e.g., Nitao and Bear, 1996). Matric potential can also be interpreted as the transferable or reversible energy per unit volume of water (e.g., Lu and Likos, 2004; Baker and Frydman, 2009).

Under the transferable or reversible energy concept defined by Gibbs free energy, several types of transferable work acting on water molecules during water sorption on a soil have been identified and formulated in the existing thermodynamic theories for unsaturated soil systems (e.g., Sposito and Chu, 1981; Iwata and Tabuchi, 1988). Below are synopses of the energy forms relevant to the three soil water retention regimes shown in Fig. 1 in the order from high to low matric potentials.

1. Surface tension work \( T_s \, dA \), where \( T_s \) and \( A \) are surface tension and interfacial area between air and water in soil volume, respectively. This form of energy is the most widely used in the literature for unsaturated soil problems; nearly all studies, whether implicitly or explicitly, consider surface tension as the major form of energy in unsaturated soils no matter what types of soils. However, as illustrated in Fig. 1, surface tension is only important in the capillary water retention regime.

2. Temperature work \( S \, dT \), where \( S \) is the entropy defining the heat energy change per unit temperature, and \( T \) is the temperature in Kelvin. If a system is considered to be in local thermodynamic equilibrium, then this term can be ignored, as the Gibbs energy is identical to the chemical potential or total potential within
a given representative elementary volume (REV) of soil. This is assumed in this study.

3. Van der Waals force field work ($\partial U_{vdw} / \partial h$) $dh$, where $U_{vdw}$ is the van der Waals potential interaction energy between particle surface and a layer of water, and $h$ is the distance of water layer from particle surface. This work operates within the adsorbed film regime shown in Fig. 1 and has been a focus of some recent studies (e.g., Nita and Bear, 1996; Tuller et al., 1999).

4. Compression work $V_w$ $dT$ within a REV, where $V_w$ is the volume of water within an REV, and $P$ is the pressure, which could be from either external or internal. The mechanism of matric potential from an external stress is called overburden effect in the literature (e.g., Coleman and Croney, 1952; Philip, 1969; Groenevelt and Bolt, 1972; Iwata and Tabuchi, 1988), and it is poorly understood. It is most pronounced in clayey soils but has negligible effect in sandy soils. Since in most geotechnical systems the overburden or load is less than a few thousands of kPa, the induced increase in matric potential is no more than 1000 kPa; it can be ignored for matric potentials varying within the tightly adsorbed regime shown in Fig. 1. While the internal pressure has been conceptually proposed for some years in soil physics (e.g., Sposito, 1972; Iwata and Tabuchi, 1988), only recently has it been proposed as the cause for hydraulic hysteresis in the tightly adsorbed water retention regime shown in Fig. 1 (Lu and Khorshidi, 2015). This work includes energies of cation and water molecule interaction and cation, water molecule, and intercrystalline particle surface interaction. The cation and water molecule interaction will be the focus of this study.

5. Electrical field work ($V_w(\partial \Psi / \partial h)$) $[(D / \varepsilon) - D]$ $dD$, where $D$ is the electric displacement, and $\varepsilon$ is the partial dielectric constant of the medium. It literally includes the electrostatic energy from the true charges of the particle surface, the elastic energy caused by the electric field, and the interaction energies between dipoles (water molecules) and surface charges between dipoles and polarized charges generated at the boundary between particle surface and dipole molecules and between dipole and dipoles. This work is most pronounced in the tightly adsorbed regime and it will be considered in this study. It is important to note that both $D$ and $\varepsilon$ depend on $V_w$.

The five forms of matric potential can be expressed in the differential form of the Gibbs free energy:

$$\text{d}G = V_w \text{d}P_{ext} - S \text{d}T + T \text{d}A + \frac{\partial U_{vdw}}{\partial h} \text{d}h + u_{c\rightarrow d} \text{d}N_t + \frac{V_w}{4\pi} \left( \frac{D}{\varepsilon} - D \right) \text{d}D \quad [7]$$

where $P_{ext}$ is the external pressure or load, and the internal pressure as a result of the cation hydration work is taken into account by multiplying the interaction energy $u_{c\rightarrow d}$ between one cation and one water molecule to the number of water molecules $N_t$ in a unit mass of soil. The matric potential from the internal pressure of cation–water–particle surface is not considered, as it is the reason for hydraulic hysteresis along the wetting path (Lu and Khorshidi, 2015). Thus, the SWR data and model here are for the drying state. The VDW work here corresponds to the conditions where layers of water molecules are formed on the entire particle surface. For the case of very low water content, where a monolayer of water has not fully formed, the VDW contribution may be obtained by multiplying $N_t$ to the interaction energy $u_{vdw}$ between the particle surface and one water molecule. Therefore, Eq. [7] for very low water content is as follows:

$$\text{d}G = V_w \text{d}P_{ext} - S \text{d}T + T \text{d}A + u_{vdw} \text{d}N_t + u_{c\rightarrow d} \text{d}N_t + \frac{V_w}{4\pi} \left( \frac{D}{\varepsilon} - D \right) \text{d}D \quad [8]$$

Assuming constant pressure and temperature condition during water sorption, the first two terms on the right hand side of the above equation can be ignored. In addition, the surface tension is not important in the tightly adsorbed water retention regime, as there is no curved interface between water and air (no capillary water exists). Hence, Eq. [8] is reduced to the following:

$$\text{d}G = u_{vdw} \text{d}N_t + u_{c\rightarrow d} \text{d}N_t + \frac{V_w}{4\pi} \left( \frac{D}{\varepsilon} - D \right) \text{d}D \quad [9]$$

Each unit layer within the crystalline structure can be considered as a plane surface made up of repeating units. Therefore, the attractive VDW energy between particle surface and one water molecule is calculated by the following (Israelachvili, 2011):

$$u_{vdw}(h) = -\frac{\pi C \rho}{6b^3} \quad [10]$$

where $C$ is the VDW energy coefficient ($10^{-77}$ J m$^6$), $\rho$ is the number density of soil molecules, and $h$ is the distance between the water molecule and the particle surface. The variation of $u_{vdw}$ vs. $h$ is plotted in Fig. 2. The plot is obtained using $\rho = 2.47 \times 10^{28}$ m$^{-3}$, which corresponds to a Hamaker constant of $-6.0 \times 10^{-20}$ J (Israelachvili, 2011) to represent the maximum possible interaction between water molecule and particle surface. The curve starts at the lowest distance 0.14 nm, which is half of the thickness of a monolayer of water (e.g., Moore and Reynolds, 1997; Mitchell and Soga, 2005).

Quantification of the interaction energy between cation and water molecules in soil is rarely addressed. To that end, water molecule can be considered as a dipole with one side (oxygen atom) attracting electrons more than the other side (hydrogen atoms). Thus, the interaction between a cation and a water molecule can be obtained by charge–dipole interaction energy ($u_{c\rightarrow d}$) given by (Israelachvili, 2011):

$$u_{c\rightarrow d}(r_1) = -E(r_1) p \cos \theta = -\frac{(V_c e) p \cos \theta}{4\pi \varepsilon_0 \eta r_1^2} \quad [11]$$
with \( r_1 \) as the distance between cation and water molecule (cation–oxygen distance), \( E(r_1) \) as the intensity of electric field due to cation at a point where water molecule is, \( V_c \) as the cation valence, \( e \) as the electron charge, \( p \) as the water molecule dipole moment \((6.172 \times 10^{-30} \text{C} \cdot \text{m})\), \( \theta \) as the angle between the axis of symmetry of the water molecule and the direction between the center of mass of the water molecule and the cation, and \( \varepsilon_0 \) as the permittivity of vacuum \((8.854 \times 10^{-12} \text{F/m})\). Variations of \( u_{c-d}(r_1) \) (for both monovalent and divalent cations) with regard to the distance \( r_1 \) are plotted in Fig. 2 as well. The parameter \( \theta \) in Eq. \([11]\) is assumed to be zero for water molecules within a monolayer around cation. Furthermore, the medium between cation and a monolayer water molecule is air, leading to \( \varepsilon = 1 \) in Eq. \([11]\).

Each cation has a specific \( r_1 \) value for its hydration shell, therefore, a unique \( u_{c-d} \) value for each cation for the interaction between a cation and water molecules in its hydration shell can be found. Over the range of very low water content of soil, cations adsorb water molecules in the hydration shell similar to hydrated cations in aqueous solutions as illustrated in Fig. 3 (e.g., Quirk, 1955; Chang et al., 1998; Sposito, 2008, and Khorshidi and Lu, 2016). Therefore, the parameter \( r_1 \) in Eq. \([11]\) can be considered as the distance between cation and oxygen in aqueous solutions as listed in Table 1 and shown in Fig. 2 for \( K^+ \) and \( Ca^{2+} \) ions. The \( u_{c-d} \) corresponding to \( r_1 \) values of each cation listed in Table 1 are shown by markers in Fig. 2. Comparing the marked values of cation–water interaction energies by the interaction between particle surface and water reveals that the magnitude of the particle surface–water interaction is an order of magnitude smaller than the magnitude of the lowest (for \( K^+ \)) cation–water interaction. Hence, the contribution of the VDW energy in Eq. \([9]\) at very low water content in soil can be neglected, leading to the following:

\[
dG = u_{c-d} dN_t + \frac{V_c}{4\pi \varepsilon} \left( \frac{D}{\varepsilon} - D \right) dD \quad \text{[12]}
\]

Fig. 2. Plot of interaction energies between water molecule and different exchangeable cations as well as water molecule and particle surface in soil.

Fig. 3. Conceptual illustration of water molecule adsorption to exchangeable cations within the primary shell of radius \( r_1 \) in (a) nonexpansive soils at very low water content and (b) expansive soils at very low water content.
Material and Experimental Program

We used three types of natural silty and clayey soils in this study: Georgia Kaolinite (kaolinite), Bonny silt, and Na+/Ca2+ bentonite (bentonite). These soils cover different clay mineralogy ranging from kaolinite to montmorillonite (e.g., Likos and Lu, 2006; Akin and Likos, 2014; McCartney and Rosenberg, 2011). To have a control over the type of exchangeable cation in soil, the soils were treated with 1.0 M of NaCl, KCl, and 0.1 M of CaCl2 and MgCl2 to produce homoionic Na+, K+, Ca2+, and Mg2+ saturated soils. The bentonite soil was also treated with 1.0 M of LiCl to produce Li+-saturated form (Akin and Likos, 2014). The water sorption isotherms of these 13 soil samples were then measured using a vapor sorption analyzer (VSA, Decagon Devices) at 25°C.

The VSA works based on the concurrent dynamic measurement of RH and gravimetric water content, \( w \), of soils during both drying (desorption) and wetting (adsorption) paths (e.g., Likos et al., 2011; Khorshidi et al., 2016). All specimens were prepared in oven-dried powder form at 105°C and cooled to ambient room temperature. The initial RH for all tests was <10%. Therefore, the sorption isotherms were obtained along desorption path from initial condition down to 5% RH, followed by adsorption path up to 95% RH, and then the subsequent desorption path down to 3% RH; drying sorption path of the soils are shown in Fig. 4.

The CEC of natural Georgia kaolinite, Bonny silt, and Na+/Ca2+ bentonite were measured using the ammonium displacement method standardized in ASTM D7503 (ASTM, 2010) (Data from Akin, 2014). Though the CEC of cation-exchanged soils may slightly differ from the value of original soil, the CEC of cation-exchanged soils are assumed to be the same as those of natural soils, as listed in Table 2.

<table>
<thead>
<tr>
<th>Cation type</th>
<th>Cation valence, ( V^+ )</th>
<th>Cation hydration number†</th>
<th>Cation–water molecule distance, ( r_1 )</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li+</td>
<td>1</td>
<td>5</td>
<td>0.195</td>
<td>Chang et al., 1998; Mähler and Persson, 2012</td>
</tr>
<tr>
<td>Na+</td>
<td>1</td>
<td>4</td>
<td>0.240</td>
<td>Chang et al., 1998; Mähler and Persson, 2012</td>
</tr>
<tr>
<td>K+</td>
<td>1</td>
<td>3</td>
<td>0.275</td>
<td>Chang et al., 1998; Mähler and Persson, 2012</td>
</tr>
<tr>
<td>Mg2+</td>
<td>2</td>
<td>6</td>
<td>0.212</td>
<td>Bernal-Uruchurtu and Ortega-Blake, 1995</td>
</tr>
<tr>
<td>Ca2+</td>
<td>2</td>
<td>6</td>
<td>0.240</td>
<td>Bernal-Uruchurtu and Ortega-Blake, 1995</td>
</tr>
</tbody>
</table>

† From Israelachvili (2011).

Upscaling of the Cation Hydration Energy to the Soil Water Retention Curve

The dielectric displacement \( D \) is generated because of a polarization effect induced in the electric field originated from both exchangeable cations and particle surfaces:
where \( E' \) is the intensity of electric field from both cations and particle surfaces. The total charge of electronegative particle surfaces and that of cations have the same values. Therefore, the electric field \( E' \) induced by both cations and particle surfaces and the electric field \( E \) induced by cations only, are proportional:

\[
E' = \alpha E
\]

where \( \alpha \) is a constant. Subsequently, \( D \) can be expressed as follows using Eq. [11] for \( \theta = 0 \), Eq. [13], and Eq. [14]:

\[
D = -\frac{\tau_0 \alpha \mu_{c-d}}{\rho} \tag{15}
\]

By substituting \( D \) from the above equation into Eq. [12], we have the following:

\[
d\mathcal{G} = u_{c-d} \left[ dN_t + \frac{V_w \alpha^2 \tau_0 (1 - \tau)}{4 \pi \rho^2} d\tau \right] \tag{16}
\]

The number of water molecules \( N_t \) can be determined based on either gravimetric water content, \( w \) and molar mass of water \( (w_w) \) or \( V_w \) and molar volume of water \( (v_w) \) as follows:

\[
N_t = \frac{w}{w_w} N_A = \frac{V_w}{v_w} N_A \tag{17}
\]

where \( N_A \) is Avogadro’s number \((6.022 \times 10^{23})\). The differential free energy changes given by Eq. [16] should then be integrated to find the total change of the Gibbs free energy. Finally, the matric potential as defined by Eq. [6] is derived as follows:

\[
\frac{d\mathcal{G}}{d\rho} = u_{c-d} N_A \frac{1}{\rho} \left[ 1 + \frac{\tau_0}{4 \pi \rho^2} \int_0^{\tau_0} \frac{V_w \alpha^2 \tau_0 (1 - \tau)}{4 \pi \rho^2} d\tau \right] \frac{d\tau}{d\rho} \tag{18a}
\]

or:

\[
\frac{1}{\kappa} = \left[ 1 + \frac{\tau_0}{4 \pi \rho^2} \int_0^{\tau_0} \frac{V_w \alpha^2 \tau_0 (1 - \tau)}{4 \pi \rho^2} d\tau \right] \frac{d\tau}{d\rho} \tag{19}
\]

The adsorptive component of matric potential \( \psi_a \) for very high matric suctions can be arrived at by substituting Eq. [18b] into Eq. [6] and using Eq. [11] to upscale \( u_{c-d} \):

\[
\psi_a = -\frac{(V_c \rho \cos \theta) N_A}{4 \pi \rho^2} \frac{1}{\kappa} \frac{d\tau}{d\rho} \tag{20}
\]

Feeding the values of known parameters mentioned following Eq. [11] into Eq. [20] gives the following:

\[
\psi_a = -3 \times 10^{-10} \frac{V_c}{\kappa \rho^2} \tag{21}
\]
where the units of $\psi$ and $r_1$ are Pascal (N m$^{-2}$) and meter, respectively. Equation [21] quantifies the matric potential at very low water content.

The term $1/\kappa$ in Eq. [21] contains an integral over a soil’s REV that may be calculated analytically through applications of some averaging techniques such as homogenization and theory of mixture. The integral depends on the volume of soil water REV $V_w$ through $\tau$. Specifically, $\kappa$ depends on the volume of water in soil, that is, the number of water molecules around cations ($N$) and much less so on other factors such as types of exchangeable cations and clay minerals. Further assumptions such as pore structure and particle distribution are needed to obtain analytical form of the $1/\kappa$ term. Alternatively, the dependence of $\kappa$ on water content can be quantified experimentally as follows.

To quantify the parameter $\kappa$ in Eq. [21], water sorption isotherms of different cation-exchanged bentonites (from Akin and Likos, 2014) are used to fit with Eq. [21] to back-calculate the parameter $\kappa$. The relationship between the parameters $\kappa$ and the number of water molecules around each cation $N$ is shown in Fig. 5. The $N$ value can be calculated from the gravimetric water content, $w$, of soil water sorption isotherm for homoionic soils by (Khorshidi and Lu, 2016):

$$N = \frac{V_w}{w_{mc} \text{CEC}}$$  \[22\]

Strikingly, a unified curve is observed for the relation between the parameters $\kappa$ and $N$ for all soils with different types of cations. As illustrated in Fig. 5, the unified relation between $\kappa$ and $N$ at 25°C is as follows:

$$\kappa = 4N + 9.3$$  \[23\]

The above equation implies that the parameter $\kappa$ only depends on the number of water molecules around each cation regardless of the type of cation.

By substituting $N$ from Eq. [22] into Eq. [23] and following substitution of the resultant into the Eq. [21], an explicit relation between matric potential and gravimetric water content of soil at very low matric potentials at 25°C is identified as follows:

$$\psi = \psi_a = - \frac{3 \times 10^{-10} V'_w w_{mc} \text{CEC}}{r_1^2 (4V'_w w + 9.3w_{mc} \text{CEC})}$$  \[24\]

Equation [24] is the SWRC model for water content of soil ranging from zero up to the monolayer cation hydration ($w_{mc}$). The $w_{mc}$ is the calculated $w$ in Eq. [22] when the hydration number of a cation (listed in Table 1) is used for the parameter $N$ (Khorshidi and Lu, 2016). The proposed equation for quantification of matric potential at very high matric suctions is validated by other soils, as described below.

Results

Experimental Validation of the Proposed Soil Water Retention Curve Model

To assess the applicability of Eq. [24] to predict water sorption isotherms of various soils, eight other homoionic soil samples were studied. Using CEC values from Table 2 and $V'_c$ and $r_1$ values from Table 1, the predicted water sorption isotherms using Eq. [24] are plotted and compared with the measured isotherms in Fig. 6. Close matches between the measured and predicted water sorption isotherms are observed. Figure 6(a) also reveals that there is a gradual increase in the difference between the water contents of predicted and measured isotherms of monovalent Georgia kaolinite (and to a lesser degree for monovalent Bonny silt as shown in Fig. 6[b]) soils as the RH increases. The effect of the particle surface hydration mechanism on matric potential gradually increases as water content increases. The adsorption energy of the particle surface on water molecules is less than that from the cation. Therefore, the isotherms predicted based on cation hydration show a greater amount of water content than the measured isotherms, and the discrepancy increases with the increase of RH. Nonexpansive soils (such as Georgia kaolinite) possess a low amount of exchangeable cations, hence, the portion of water adsorbed on particle surface becomes comparable with cation hydration water as water content increases. The cation hydration mechanism still dominates for RH values less than ~15%.

In bentonite soils, because of the high amount of exchangeable cations, the amount of cation hydration water is much greater than the amount of water adsorbed on particle surface. This
results in the good agreement between predicted and experimental water sorption isotherms over the range of RH values shown in Fig. 6(c). Kaolinite and bentonite are the end members of clays in their structure and properties. Therefore, it can be concluded that cation hydration is absolutely dominant for RH values <15% in all soils. The RH region of cation hydration dominancy extends beyond 15% with the increase in CEC of soil.

Close matches between measured and predicted soil water sorption isotherms in Fig. 6 support the validity of the proposed Eq. [24], established based on the charge–dipole interaction energy for cation hydration in soil, for matric potential at very low water content.

**Prediction of the Highest Matric Suction**

Identification of the highest matric suction in soil has both theoretical and practical applications. Different models have been developed for SWRC prediction either for capillary water or adsorbed water to describe various phenomena in unsaturated porous media. Some models are constructed based on the consideration of highest matric suction (matric suction at zero water content) as the upper bound of the SWRC. In all models, it is assumed that the highest matric suction is a unique value for all soils independent of soil type. The matric suction at zero water content is generally accepted as 1.0 GPa (e.g., Croney and Coleman, 1961; Ross et al., 1991; Campbell et al., 1993; Webb, 2000; Khlosi et al., 2006), although values of 900 MPa (e.g., Cui et al., 2008) and 800 MPa (e.g., Jensen et al., 2015) are also reported. Recently, Chen et al. (2014) and Lu and Khorshidi (2015) indicated that highest matric suction does depend on soil type and cannot be identified uniquely for all soils.

One of the valuable features of the new model is that it directly relates matric potential to the water content of soil at zero water content. Substituting zero water content in Eq. [24], the lowest matric potential of a soil is reduced to the following:

$$\psi_{\text{min}} = -\frac{3.2 \times 10^{-11} \mu_{c}}{\eta^2}$$  

[25]

The above equation shows the highest matric suction along the drying path only depends on the type of cations in soil. Note that this may not be correct for the wetting path because of the energies that would need to overcome the intermolecular forces between interlayer.

Given the accurate and contiguous measurement of soil water sorption isotherm over the range of RH very close to oven-dry conditions (down to 3–4%) with the current technology of VSA, it is possible to identify the highest matric suction. The highest matric suction values of the tested soils were identified by extrapolating the end part of their water sorption isotherms to zero water content. These values are also estimated using Eq. [25] and are listed in Table 2. The values of the experimental highest matric suction of different soils with the same cation are very similar to each other, unlike the values obtained for soils with different cations (see Fig. 7). This confirms that the highest matric suction depends exclusively on cation type in soil rather than soil mineral type, and in a soil with multispecies cations, where one species is dominant, the
The highest matric suction is close to the highest matric suction of the same soil saturated with that dominant exchangeable cation. The comparison between the experimental and theoretical values of the highest matric suction of different soils is also plotted in Fig. 7. Good agreement between measured and predicted results \( R^2 = 0.90 \), excluding Mg\(^{2+}\)-saturated soils are obtained. The deviation for Mg\(^{2+}\)-saturated soils (~50%) could be due to the high charge and small radius of the cation, leading to the Mg\(^{2+}\) cation having the highest energy density among all cations. As implied by Fig. 5, it seems that for RH very close to zero (corresponding to \( N < 4 \) for Mg\(^{2+}\)-saturated bentonite), which is beyond the measurement range of VSA and thus was not accounted for in our experimental data, the effect of cation energy density is more pronounced on the parameter \( k \). It follows that at this range of RH, \( k \) depends not only on \( N \) but also on the type of cation. Therefore, Eq. [23], and consequently matric suction at zero water content obtained using Eq. [25], may deviate from experimental results for Mg\(^{2+}\)-saturated soils.

To show the importance of cation hydration and its relation with matric potential, the SWRC model of this study is developed for homoionic soils. The model can be used for prediction of soil CEC (unpublished data, 2016). It can also be applied to predict soil water sorption isotherms of thermodynamically equilibrated systems composed of multiple cation species. If the CEC of soil for each cation species is known, then the water content corresponding to each species at any matric potential can be determined using Eq. [24]. Consequently, total water content of soil is obtained by summing up partial water contents associated to all cation species at the given matric potential. Inversely, composition of exchangeable cations in soil can be identified by Eq. [24] given soil water sorption isotherm and CEC (unpublished data, 2016).

**Summary and Conclusion**

Soil water retention curve consists of three regimes, namely, capillary, adsorbed water, and tightly adsorbed water. In the range of tightly adsorbed water, cation hydration and particle surface hydration are responsible for soil water retention. Although VDW energy density for particle surface hydration can well represent matric potential of some soils in particular ranges of RH, it fails to predict matric potential and water sorption isotherms at very low RH range (<25%). In this study, we show that within this range, cation hydration (as opposed to particle surface hydration) plays the dominant role. Water molecules are first adsorbed in the primary hydration shell of cations with a certain fixed distance from the exchangeable cations prior to be adsorbed on particle surface.

Accordingly, a theoretical model has been proposed to represent matric potential by considering all mechanisms retaining water molecules, particularly the charge–dipole (cation–water molecule) interaction energy. The measured soil water sorption isotherms of several homoionic-saturated soils match very well with the isotherms predicted based on the new matric potential model. It is concluded that at very low matric potential, because of the dominance of cation hydration over particle surface hydration, soil water sorption isotherms can be well quantified by the charge–dipole interaction energy.

The proposed SWRC model also provides quantitative predictions of matric suction at zero water content. The predictions are in good agreement with the experimental values. The experimental
highest matric suction values for different soils vary between 455 and 1100 MPa. It is found that different types of soils saturated with the same mono-cation have very close values of the highest matric suction, indicating that the highest matric suction is mainly controlled by type of cation and not much so by type of mineral. It is concluded that the highest matric suction is not universal for all soils and depends on type of exchangeable cations of soil.

One important conclusion from the conceptualization of water retention regimes and their corresponding energy magnitudes is that the constitutive theories describing mechanical and hydraulic behavior of unsaturated silty and clayey soils should not just consider surface tension but also consider VDW and cation hydration energies. This has not been shown previously using existing theories.

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This research is funded by a grant from the National Science Foundation (NSF CMMI 1233063).

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