

Dielectric Relaxation of Bound Water versus Soil Matric Pressure

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ABSTRACT

The electrical permittivity of soil is a function of the water content, which facilitates water content measurements. The permittivity of soil is also a function of the frequency of the applied electric field. This frequency dependence can be described by the relationship between the dielectric relaxation frequency and the activation enthalpy of the water, which in turn is related to the soil matric pressure. The activation enthalpy or soil matric pressure is a measure of the binding forces acting on a water molecule in the soil matrix. Each water molecule is differently bound, varying from tightly bound to free water. The permittivity of the bulk soil results from the contribution of all the water molecules in the soil matrix. Therefore, the permittivity of soil as a function of frequency is related to the soil matric pressure. It is realistic to consider hygroscopic water as ice like. A relatively sharp transition can be observed from free to hygroscopic water at matric pressure -100 MPa corresponding to relaxation frequency $f_r \approx 8$ GHz. Therefore, for the interpretation of dielectric data using a dielectric mixture equation, the water content of soil can be split conveniently in “free” water and “hygroscopic” water.

FOR THE MEASUREMENT of the soil water content, the dielectric properties or complex permittivity, ϵ , of soil can be related to the water content θ . Apart from θ , this $\epsilon(\theta)$ relationship is also affected by the frequency of the applied electric field. Among others, Hoekstra and Delaney (1974) showed that this effect is higher at higher frequencies.

Two important factors that determine the frequency dependence of $\epsilon(\theta)$ are the intermolecular bonds between water molecules and the bonds between water molecules and soil particles. Therefore, the dielectric properties of bound water differ from that of free water. For clay, the bound water fraction is higher than for sand; this results in different $\epsilon(\theta)$ relations. This is one of the uncertainties in the use of a dielectric water content sensor for a soil of unknown composition and will be addressed in this paper.

THEORY

Soil is a three-phase system consisting of solid particles, water, and air. The solid phase forming the pore system is called the soil matrix. Water can be bound to the soil matrix. The degree of binding varies from unbound or free water which is at a great distance from the soil particle surface, to strongly bound or adsorbed water which is near the soil particle surface. According to Koorevaar et al. (1983) water is bound to the soil matrix by a combination of the following: (i) adhesive forces—binding between the solid phase and water

molecules, (ii) cohesive forces—binding between water molecules, and (iii) osmotic forces—binding due to gradients in chemical potentials in electric double layers (Bolt and Miller, 1958; Raythatha and Sen, 1986). Water-binding properties of a soil matrix can be described by its thermodynamic properties (Slatyer, 1967). If water becomes bound to the soil matrix, it is not capable of doing as much work as free water, hence it has lost energy. Similarly, a mix of water and cement or gypsum will generate heat during the process of hydration. This is an extreme example of the loss of energy for bound water analogous to the binding of water in soil.

By applying an alternating electromagnetic field to the soil matrix, energy will be stored and/or absorbed, depending on the frequency applied. At low frequencies, all energy applied will be stored and the soil becomes polarized. ϵ is a measure for this polarization. Because of binding forces, water molecules are prevented from following a rapid alternating field; this results in a decreased ϵ at high frequencies (Debye, 1929). The frequency for which ϵ is decreased to half its low frequency value is called the dielectric relaxation frequency, f_r . Thus, f_r is related to binding forces acting on a water molecule.

The frequency dependence of the polarization process can be described by the following complex representation of ϵ :

$$\epsilon = \epsilon' - j\epsilon'' \quad [1]$$

where the real part of the permittivity, ϵ' , is a measure of the polarizability of the soil. For a static E -field, ϵ' is usually referred to as dielectric constant. The imaginary part of the permittivity, ϵ'' , represents the energy absorption of dielectric loss.

The permittivity for a single relaxation process, according to experimental results of Kaatze (1996), is best described by the Debye (1929) relaxation function

$$\epsilon = \frac{\Delta\epsilon}{1 + jf/f_r} + \epsilon_{f \rightarrow \infty} \quad [2]$$

where $\Delta\epsilon = (\epsilon_{f \rightarrow 0} - \epsilon_{f \rightarrow \infty})$ is the dielectric increment or difference between polarization in the static E -field, $\epsilon_{f \rightarrow 0}$, and that at very high frequencies is $\epsilon_{f \rightarrow \infty}$. The subscripted $f \rightarrow 0$ denotes “for frequencies approaching zero” and $f \rightarrow \infty$ denotes “for frequencies approaching infinity”. For more details on the theory on electromagnetic fields and waves, one is referred to Lorrain et al. (1988).

The water binding can be expressed in terms of the activation enthalpy, ΔH^* . In soil science, it is customary to express these binding forces in terms of the matric pressure of soil water, p_m . The $\Delta H^*(f_r)$ relationship is known from the theory on aqueous dielectrics (e.g., Hasted, 1973; Grant et al., 1978). For example for free water $\Delta H^* = 20.5$ kJ mol⁻¹ resulting in $f_r = 17$ GHz at 20°C and for ordinary ice at 0°C $\Delta H^* = 55$ kJ mol⁻¹ with $f_r = 9$ kHz. Apart from f_r , p_m is also related to ΔH^* (Slatyer, 1967). From this, the relationship between p_m and f_r , $p_m(f_r)$, can be derived.

Potential of Soil Water

The energy status of soil water is given by the difference in Gibbs' free energy between its ground or reference state (free water) and its actual state (bound water). It is simply called the total water potential ψ_t . Under thermodynamic equi-

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librium conditions, ψ_t represents the amount of energy per unit mass (J kg^{-1}) that is needed to transport, reversibly and isothermally, an infinitesimal quantity of water, from a pool of pure water, at atmospheric pressure $p_0 = 0.1$ MPa, at a temperature of 20°C and at specified elevation, to the soil water at the point under consideration. Total potential ψ_t is the summation of pneumatic, gravitational, matric, and osmotic potential (Koorevaar et al., 1983; ISO/TC, 1996).

For a small soil sample under equilibrium conditions, the pneumatic and gravitational potentials can be neglected. The osmotic potential of the equilibrium soil solution is considered the same everywhere and thus will not cause water binding to the soil matrix. However, osmotic gradients in an electric double layer at a soil particle surface (for instance around negative charged clay platelets) results in osmotic forces causing water to adhere to the soil matrix. This kind of water binding is included in the matric potential, ψ_m . The matric potential thus represents all forces that retain water to the soil matrix. If the density of water, ρ_w , is constant, the soil matric potential can be expressed as a pressure. This pressure equivalent of the soil matric potential, p_m , is defined as the amount of energy per unit volume (J m^{-3} or Pa); it is related to ψ_m as $p_m = \rho_w \psi_m$.

If soil is exposed to air, it will dry or wet, until a thermodynamic equilibrium is reached, depending on the potentials on both sides of the liquid-vapor interface. p_m is related to the relative humidity of air, e/e_s , by (Slatyer, 1967)

$$p_m = \frac{RT}{V} \ln(e/e_s) \quad [3]$$

where T is the absolute temperature, R the universal gas constant, and V the partial molar volume of water. The relative humidity of air is the ratio between the vapor pressure, e , and the saturation vapor pressure, e_s , of water at temperature T .

If the relative humidity is low, a monomolecular layer of water will exist at the surface of a material like the soil matrix. (De Boer, 1953). New layers of water will be formed if the relative humidity increases. Dirksen and Dasberg (1993) showed for a broad range of soil types only a small difference between the water content calculated for the first layer of water molecules on the particle surface, and the water content measured for air-dried soil samples. In the experiment of Dirksen and Dasberg, $e/e_s \approx 0.50$, corresponding with $p_m = -100$ MPa. For this paper, the amount of water adsorbed to soil at ambient conditions with $e/e_s = 0.50$ is defined as the hygroscopic water content, θ_h . θ_h is a function of the specific surface area, S_A , of the soil matrix. S_A and consequently θ_h increase with increasing silt or clay content. For the experiment of Dirksen and Dasberg, θ_h varied between 0.02 for sandy soils with low S_A , and 0.12 for a Vertisol and a Bentonite with high S_A .

The two limits for p_m between which a monomolecular layer of water can exist depends to a large extent on the mineral composition of the soil particles. The lower limit is where the first layer of adsorbed water will escape from the particle surface. A soil is assumed to be completely dry if this layer of water molecules is removed by the oven-dry method at 105°C corresponding with $p_m > -2 \times 10^3$ MPa at 20°C (Koorevaar et al., 1983). The upper limit for p_m for which the number of water layers starts to increase depends on the particle material and according to the foregoing may be assumed to have $p_m > 100$ MPa. The highest value of p_m , $p_m = 0$ MPa, applies to a soil saturated with water. No energy is needed to add or remove water at great distance from a soil particle surface. Note that in soil physics the atmospheric pressure, p_0 , is taken as reference for the matric pressure. Thus, $p_m = 0$ MPa corre-

sponds with the matric pressure of a water saturated soil at $p_0 = 0.1$ MPa.

The Relationship between Soil Matric Pressure and Dielectric Relaxation

Comparison of the thermodynamic properties of water with those of other liquids, suggests that hydrogen bonds greatly affect the properties of water (Eisenberg and Kauzmann, 1969). The cohesive forces between water molecules are extraordinarily strong. The most likely cause is the hydrogen bonding between molecules in the liquid. In soil, a water molecule is also bound to the particle surfaces by one or more hydrogen bonds. Hydrogen bonds prevent molecules from reorienting in a rapidly changing electromagnetic field. As can be deduced from the kinetic rate theory (Glasstone et al., 1941), the relaxation frequency, f_r , is related to the probability of making or breaking hydrogen bonds during the time $\tau = 1/(2\pi f_r)$ of one period. According to this theory, the dielectric relaxation frequency for water is given by

$$f_r = \frac{kT}{2\pi h} e^{\frac{\Delta G^*}{RT}} \quad [4]$$

where ΔG^* is the change in molar Gibbs' free energy required to break an $\text{OH}\cdots\text{O}$ bond, h is Planck's constant, k is Boltzmann's constant, T is the absolute temperature, and R the universal gas constant. When a molecular bond is broken, it is almost immediately followed by the creation of a new bond.

The Gibbs' function is defined as $G = H - TS$, where H is the enthalpy, S the entropy, and T the absolute temperature. Thus, $\Delta G^* = \Delta H^* - T\Delta S^*$, where ΔH^* is the molar activation enthalpy and ΔS^* the molar activation entropy. According to Kaatze and Uhlendorf (1981) and Grant et al. (1978), the weak temperature dependency of ΔH^* and ΔS^* is negligible between -5°C and 60°C . For liquid water, ΔS^* is approximately independent of the binding forces. Thus, ΔH^* corresponds approximately with the energy required to make or break a hydrogen bond. The expression may be rewritten in terms of activation enthalpy as follows:

$$f_r \approx \frac{kT}{2\pi h} e^{\frac{\Delta H^*}{RT}} \quad [5]$$

In the following, the subscript 0 denotes values for free water at a reference atmospheric pressure $p_0 = 0.1$ MPa and 20°C , while values without this subscript refer to molecules experiencing a certain level of binding force at the same temperature.

Any binding force acting on a water molecule will add to ΔG^* , i.e., $\Delta G^* > \Delta G^*_0$. From Eq. [4] or its approximation of Eq. [5], the ratio between f_r and f_{r0} becomes

$$\frac{f_r}{f_{r0}} = e^{\frac{\Delta G^*_0 - \Delta G^*}{RT}} \approx e^{\frac{\Delta H^*_0 - \Delta H^*}{RT}} \quad [6]$$

The difference $(\Delta G^*_0 - \Delta G^*)$ or $(\Delta H^*_0 - \Delta H^*)$ can be related to the soil matric pressure, p_m . Consider a water molecule located exactly at the vapor-liquid interface anywhere in the matrix. p_m is related to the difference between the chemical potential or partial molar free enthalpy of the water molecule in the reference state, μ_0 , and its actual potential μ , by Slatyer (1967) as follows:

$$p_m V = \mu_0 - \mu \quad [7]$$

Assume the water at the location under consideration to be pure. It is shown in textbooks on thermodynamics (e.g., Harrison, 1963; Roos and Wollants, 1995) that the chemical poten-

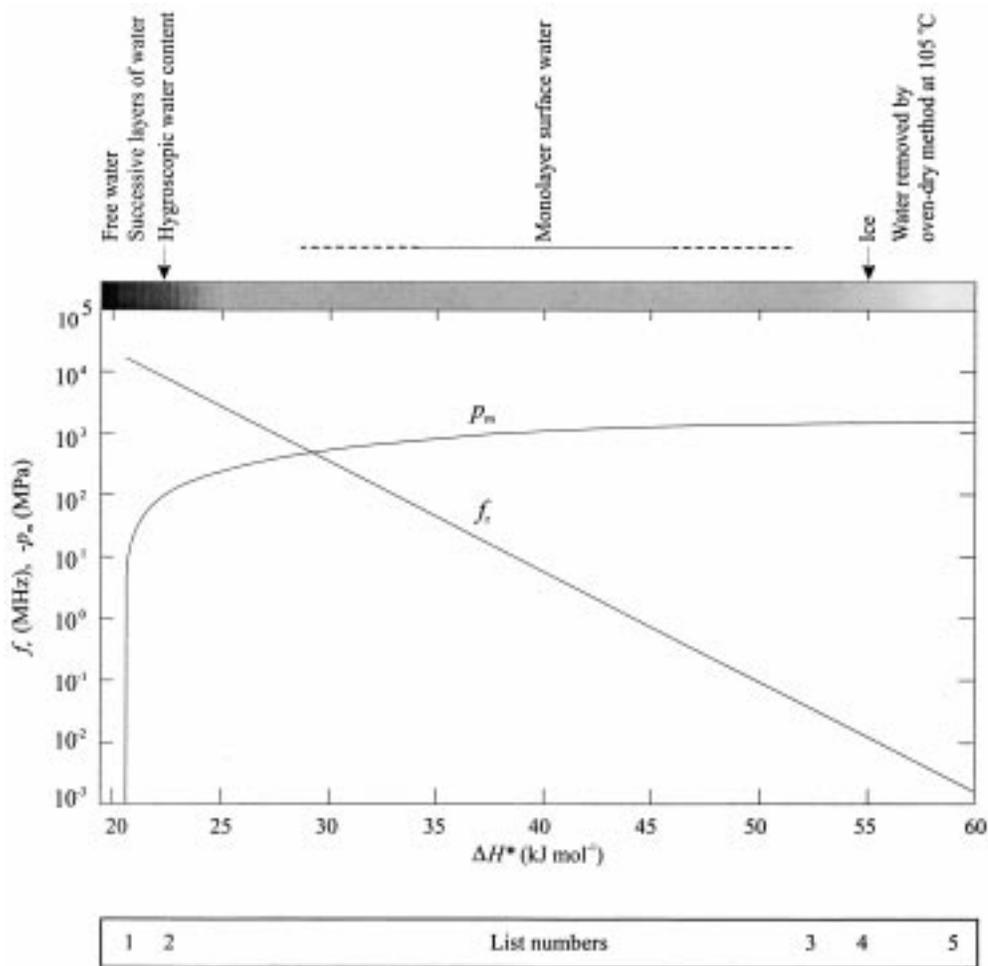


Fig. 1. An overview of the relationship between the different energy states of bound water in soil. The relaxation frequency, f_r , and the soil matric pressure, p_m , are plotted as a function of activation enthalpy, ΔH^* . The bar on top of the graph is an indication of the number of water layers bound to a soil particle. White represents no water and black a large amount of water layers. The bar at the bottom refers to the numbers of the list in the text.

tial, μ , of a pure substance is equivalent to ΔG^* ; that is

$$p_m V = \Delta G^*_0 - \Delta G^* \approx \Delta H^*_0 - \Delta H^* \quad [8]$$

Then $p_m V$ may be substituted in Eq. [6] and the relationship between f_r and p_m becomes

$$f_r = f_{r0} e^{\frac{p_m V}{RT}} \quad [9]$$

Consider a water molecule located at the vapor–liquid interface somewhere in the soil matrix near a particle surface. As p_m is defined at the liquid surface, it applies only to molecules at the vapor–liquid interface. The impact of p_m , and thus of ΔH^* on f_r for the molecule at this location, can be found from Eq. [9]. If this interface is moved to a greater distance from the particle surface, by adding water to the soil matrix, p_m and $(\Delta H^*_0 - \Delta H^*)$ will increase (they become less negative). For a water molecule at this new location, ΔG^* and f_r are closer to values for free water. However, ΔH^* and therefore f_r for the molecule at the first location is not changed since the force fields acting on this molecule are still the same.

The relationship between ϵ and θ is well known for soil. For each successive layer of water molecules in the matrix, the impact of ΔH^* on f_r can be totaled by means of an applicable dielectric mixture equation which results in the dielectric spectrum, $\epsilon(f)$, of the soil. Thus ϵ is related to both p_m and θ . For this paper, however, we will concentrate on $f_r(p_m)$. The

advantage is that it relates dielectric properties to the energy status of soil water in terms very common in soil physics.

Comparison with Data Found in Literature

In the following, an overview is given of data found in the literature for the relationship between the activation enthalpy, ΔH^* , the relaxation frequency, f_r , and the soil matric pressure, p_m . These data are interpreted with Eq. [3], Eq. [5], or Eq. [9]. The following observation can be made and compared with Fig. 1 (see list numbers), where the curves for f_r and p_m are shown as a function of ΔH^* .

1. Kaatzte and Uhlendorf (1981) found $\Delta H^*_0 = 20.5 \text{ kJ mol}^{-1}$ and $f_{r,0} = 17 \text{ GHz}$ for free water at 20°C and atmospheric pressure. Free water corresponds with the very last fraction of water for which $p_m \approx 0$ needed to saturate the soil.
2. Dirksen and Dasberg (1993) showed that for soil, a monomolecular layer of water exists at $e/e_s \approx 0.50$. According to Eq. [3], $e/e_s = 0.50$ corresponds to $p_m = -100 \text{ MPa}$ for which $f_r = 8 \text{ GHz}$ according to and $\Delta H^*_0 = 22.3 \text{ kJ mol}^{-1}$ according to Eq. [5].
3. Rolland and Bernard (1951) found $\Delta H^* \approx 52.5 \text{ kJ mol}^{-1}$ for water adsorbed to silica gel (approximately one layer)

which corresponds to $f_r \approx 32$ kHz and $p_m \approx -2 \times 10^3$ MPa at 20°C according to Eq. [3] and Eq. [9], respectively.

4. Hasted (1973) found $\Delta H^* = 55$ kJ mol⁻¹ with $f_r = 9$ kHz for ordinary ice at 0°C. Soil is assumed to be completely dry if the first, ice-like layer of water molecules is removed from the particle surface, by the oven-dry method at 105°C. It may be assumed that this water layer has $\Delta H^* \approx 55$ kJ mol⁻¹ corresponding to $f_r \approx 10$ kHz and $p_m < -2 \times 10^3$ MPa at 20°C, according to Eq. [3] and Eq. [9], respectively.
5. Iwata et al. (1995) reported for water bound to the surface of clay $\Delta H^* > 55$ kJ mol⁻¹. For water adsorbed to settled concrete, most of the literature (Van Breugel, 1991) shows values for $\Delta H^* > 60$ kJ mol⁻¹. These values for ΔH^* corresponds to $f_r < 10$ kHz and $p_m < -2 \times 10^3$ MPa at 20°C, according to Eq. [3] and Eq. [9], respectively.

DISCUSSION AND CONCLUSIONS

The impact of bound water on f_r , as described by Eq. [7] can be calculated from p_m . This conclusion was illustrated by means of the dielectric and water retention properties of porous materials as found in the literature.

A relationship between the matric pressure and the dielectric properties of soil implies that the hysteresis (i.e., the difference between adsorption and desorption) observed for the soil water retention characteristic, also applies to the dielectric spectrum. As shown by Dirksen and Dasberg (1993), at relative humidity $e/e_s = 0.5$, a monomolecular layer of water exists at a soil particle surface corresponding to a soil matric pressure $p_m = -100$ MPa and relaxation frequency $f_r \approx 8$ GHz. This is the water that is still bound to the soil matrix for air dry soils and defined as the hygroscopic water content θ_h . The measurements of Dirksen and Dasberg (1993) are carried out by means of time-domain reflectometry (TDR), for which the dominant measuring frequency was around 150 MHz. They found a reasonable match for most soils between the expected effect on the permittivity due to θ_h and the measurements. From this, it may be concluded that $f_r < 150$ MHz for θ_h is more realistic than 8 GHz. Hoekstra and Delaney (1974) showed that for a low-conductive Goodrich clay, there was almost no decrease in permittivity for frequencies between 10 MHz and 100 MHz and a continuously declining permittivity for 100 MHz and higher. From this, it is likely that $f_r < 10$ MHz for θ_h is a realistic expectation.

The permittivity of bulk soil results from a mixture of different layers of water, each with its own dielectric properties resulting from the water-binding energy status. In Fig. 1, a relatively sharp transition can be observed from “free” to “hygroscopic” water at $p_m \approx -100$ MPa. From the foregoing observations, it seems to be realistic to consider θ_h as ice like. According to data of Hasted (1973), the permittivity at the two extremes of the frequency spectrum of ice at 0°C are respectively

$\epsilon_{icef \rightarrow 0} = 92$ and $\epsilon_{icef \rightarrow \infty} = 3.2$. These values of free water at 20°C are respectively $\epsilon_{water, f \rightarrow 0} = 80.2$ and $\epsilon_{water, f \rightarrow \infty} = 5.6$, where f is the frequency of electromagnetic waves and ϵ the relative complex permittivity.

For the interpretation of dielectric data using a dielectric mixture equation the water content of soil can be split conveniently in “free” water and “hygroscopic” water.

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