Maxwell-Wagner-Sillars, Adsorbed Water, and Free-Water Dielectric Relaxations within a Hydrated Arid-Zone Calcic Soil

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Abstract—We measured the broadband (40 Hz–20 GHz) relative dielectric permittivity of sieved surficial samples of an arid-zone soil. The soil samples were equilibrated at 25 °C with relative humidities of 43, 54, 84, and 97 %. Debye-like Maxwell-Wagner-Sillars (MWS) polarization relaxation times of 309, 227, and 73 ns were calculated for the soil samples equilibrated at relative humidities of 43, 54, and 84 %, respectively. Due to electrode polarization, MWS polarization relaxations could not be discerned on the soil sample equilibrated at 97 % relative humidity. The measured differences between the static and high-frequency relative permittivity (\(\varepsilon_s - \varepsilon_{\infty}\)) due to MWS polarization were between 25 and 45 times that of the oven dry soil. This would cause the MWS relaxation to increase radar-wave attenuation rates at frequencies as high as 1 GHz.

We found Debye-type relaxation times associated with adsorbed water of 13, 15, 17, 19, and 22 ps for an oven-dry sample and ones equilibrated at at relative humidities of 43, 54, 84, and 97 %, respectively. These frequencies are higher than previously thought. This progression with water contents may be due to the increase in soil solution salinity with increasing water contents. They were not likely caused by free water since a weakly resolved relaxation could be discerned corresponding to a relaxation time of approximately 8 ps, as expected for free-water.

Index Terms—Adsorbed water, dielectric permittivity, free water, Maxwell-Wagner-Sillars polarization, dielectric relaxation, soil.

I. INTRODUCTION

In earlier work based on time-domain reflectometry (TDR) measurements, we concluded that the anomalously high GPR attenuation rates found in some arid-zone soils were caused by Maxwell-Wagner-Sillars (MWS) polarization [2], [3]. Our ability to quantify the complex dielectric behavior of arid-zone soils suggestive of MWS polarization had been limited. This was because some of these TDR measurements were subject to electrode-polarization effects at frequencies below 1 MHz. Because the apparent relaxation frequency of MWS polarization was in this frequency range, we were compelled to estimate relaxation parameters with modeling results, which may have introduced extrapolation error in these estimates.

We report here broadband dielectric measurements made at low frequencies with a dielectric cell fitted to an impedance analyzer and at high frequencies with an open-ended coaxial probe fitted to a vector network analyzer. This approach extended the bandwidth and improved the precision over what could be achieved with TDR measurements. This composite approach should also provide more accurate estimates of attenuation rate over the entire GPR bandwidth. For most measurements it also shifted the onset frequency of electrode polarization far below that of the MWS, which allowed us to estimate relaxation parameters by non-linear regression fits to a simple Debye-type expression.

The complex relative dielectric permittivity of a soil can be represented by \(\hat{\varepsilon}(\nu)\) (1) where \(\nu\) is frequency (Hz). This quantity is defined by

\[
\hat{\varepsilon}(\nu) = \varepsilon'(\nu) - i \varepsilon''(\nu),
\]

\(\varepsilon'(\nu)\) being the relative dielectric permittivity, \(\varepsilon''(\nu)\), the relative dielectric loss, and \(i = \sqrt{-1}\). The attenuation rate (\(\beta\), dB·m\(^{-1}\)) of electromagnetic radiation through the soil may be estimated from \(\hat{\varepsilon}(\nu)\) via

\[
\beta = \left\{ 8.686 \omega \Im \sqrt{\hat{\varepsilon}(\nu)} \right\} / c_0
\]

where \(\omega\) is angular frequency (= \(2\pi\nu\), rad·s\(^{-1}\)) and \(c_0\), speed of light (m·s\(^{-1}\)) [2]. If the complex relative permittivity of a soil is measured or can be predicted, the attenuation rate can be calculated directly from equation (2). Analyses of soil permittivity data have led to a general conclusion that the dielectric permittivity of soils at low volumetric water contents will be close to those of the mineral phases and the influence of water is limited [1].

II. MATERIALS AND METHODS

A. Soil

The soil studied was collected from Yuma Proving Ground (YPG) at the location designated as “CM” by [8]. Detailed soil classification of YPG indicates that these soils were an intergrade of Gunsight and Christobal series [9]. The
properties of the soil itself, with a lower clay and rockfragment content, indicated that the soil should be classified as a Gunson series (a Loamy-skeletal, mixed, superactive, hyperthermic Typic Haplocalcid). We studied soil collected from the upper 15 cm of the soil profile. A sample was subjected to x-ray diffraction (XRD) and scanning electron microscopy/energy dispersive x-ray (SEM/EDS) analyses [6]. These yielded the approximate mineral proportions presented in Table 1.

B. Sample Preparation

The soil was ground to pass through a No. 140 mesh sieve, but retained by a No. 270 mesh sieve. These particles had approximate effective diameters between 53 μm and 106 μm. Subsamples of these soils were wetted to approximately 10% gravimetric water content, then packed into either a dielectric cell similar to that described by [10] (for low frequency measurements) or a 15 cm³ polypropylene bottle (for high frequency measurements). The soils were packed to yield a dry porosity of 0.50 m³·m⁻³, which was verified by oven drying the samples after the dielectric measurements. These subsamples of the soil were equilibrated at 25°C under relative humidities of 43, 53, 84, and 97%, which were maintained by saturated aqueous solutions of K₂CO₃, Mg(NO₃)₂, KCl, and K₂SO₄, respectively.

C. Measurement of broadband dielectric permittivity

We measured dielectric permittivity of the hydrated soils from 40 Hz to 20 GHz. For the frequency range from 40 Hz to 110 MHz, we measured relative dielectric permittivity with an Agilent 4294A Impedance Analyzer fitted with a dielectric cell. Measurements from 1 MHz to 20 GHz were performed with an Agilent E5071C Network Analyzer fitted with an Agilent high-temperature open-ended coaxial probe.

1) Calibration for Impedance Measurements: Mazzeo and his coworkers found that small-area electrodes with a generous separation lowered the onset frequency of electrode polarization [10]. Following their general design we fabricated our dielectric cell from an acrylic body into which a 12.7 mm diameter well was drilled. Stainless steel electrodes with approximate diameters were fitted on opposite sides of the well.

We measured complex impedance, \( Z(\nu) = R(\nu) + jX(\nu) \), (Ω) where \( R(\nu) \) was electric resistance (Ω), and \( X(\nu) \), reactance (Ω). The complex capacitance (\( C(\nu) \), F) was calculated by

\[
\hat{C}(\nu) = \frac{1}{j\omega Z(\nu)},
\]

All measurements were made at 801 logarithmically-spaced frequencies between 40 Hz and 110 MHz. The cell was calibrated by measuring \( \text{Re}[\hat{C}(\nu)] \) for the following dielectric reference liquids: air, water, cyclohexane, ethanol, ethanedioil, 1-propanol, and 2-propanol. The reference values of these liquids were fitted to

\[
\text{Re}[\hat{\varepsilon}(\nu)] = a_0(\nu) + a_1(\nu) \frac{\text{Re}[\hat{C}(\nu)]}{C_0},
\]

where \( \hat{\varepsilon}(\nu) \) was the complex relative dielectric permittivity of the reference liquid (1) and \( C_0 \), the expected capacitance of an empty cell (F). The expected capacitance of an empty cell is calculated from the cell geometry via

\[
C_0 = \frac{\epsilon_0 A}{d}
\]

where \( \epsilon_0 \) was permittivity of vacuum (F·m⁻¹), \( A \), area of each of the two electrodes (m²), and \( d \), their separation (m). The dimension-one parameters \( a_0(\nu) \) and \( a_1(\nu) \), which varied with frequency, could be identified as the parasitic capacitance and the cell constant, respectively.

For the range of dielectric loss found in soils the dielectric cell could be calibrated based on conductance (\( G, S \)) of air, water and aqueous NaCl solutions having concentrations of 0.01, 0.1, 0.25, 0.5, 2, 3, 4, and 5 mmol·dm⁻³. The complex relative permittivity of aqueous electrolyte solutions (\( \hat{\eta}(\nu) \), 1) was modeled by

\[
\hat{\eta}(\nu) = \hat{\varepsilon}(\nu) - j\frac{\kappa}{\epsilon_{0,\nu} \omega}
\]

where \( \hat{\varepsilon}(\nu) \) is that of the pure solvent (1), and \( \kappa \), the dc conductivity of the electrolyte solution (S·m⁻¹). For dilute aqueous electrolyte solutions, the dielectric properties of the solvent may be represented by that of pure liquid [7].

\[
\hat{\varepsilon}(\nu) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + j\omega \tau}
\]

where \( \tau \) is relaxation time (s). The molar conductivity of NaCl solutions at 25°C from the reference literature was fitted by linear regression to the so-called Kohlrausch equation

\[
\Lambda_m = \Lambda_m^0 - K \sqrt{\varepsilon/\varepsilon_r},
\]

where \( \Lambda_m \) was molar conductivity (S·cm²·mol⁻¹), \( \kappa \), electrical conductivity (S·m⁻¹) \( c \), electrolyte concentration (mol·dm⁻³) and \( \varepsilon_r \), a normalizing constant (≈ 1 mol·dm⁻³) [4]. The parameters \( \Lambda_m^0 \) and \( K \) (both S·cm²·mol⁻¹) in Equation (8) were estimated by a linear regression fitted to tabular reference data presented in [11].

Dielectric loss measurements with the dielectric cell were calibrated by fitting the following equation:

\[
G(\nu) = \gamma_0(\nu) + \gamma_1(\nu) \{-\text{Im}[\hat{\eta}(\nu)]\omega\}
\]

Both dimension-one parameters \( \gamma_0(\nu) \) and \( \gamma_1(\nu) \) were found to vary with frequency.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Approximate percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td>50</td>
</tr>
<tr>
<td>Calcite</td>
<td>15</td>
</tr>
<tr>
<td>Ca or Na feldspars</td>
<td>10</td>
</tr>
<tr>
<td>Mica</td>
<td>10</td>
</tr>
<tr>
<td>Smectite</td>
<td>10</td>
</tr>
<tr>
<td>Chlorite or kaolinite</td>
<td>5</td>
</tr>
</tbody>
</table>
2) Calibration for Open-Ended Coaxial Probe Measurements: The Agilent E5071C Network Analyzer was calibrated with the software provided with the Agilent 85070 high temperature probe and its attendant data-reduction software. Prior to measurements the probe was calibrated with a sequence of open, short, and load (double deionized water) measurements for 801 logarithmically spaced measurements from 1 MHz to 20 GHz [5]. Means of five measurements were calculated for every soil treatment. The standard errors of these means were negligible at frequencies above 10 MHz.

3) Contact Pressure of the Open-Ended Coaxial Probe: In preliminary studies we found that the broadband dielectric spectroscopy measurements of soils were affected by contact pressure. We determined that a contact pressure of 6.9 kPa yielded reproducible results, but did not compress the soil under test.

III. RESULTS

A. Water Contents

Tables II and III presented the porosities (\(\phi\), m\(^3\) m\(^{-3}\)) gravimetric (\(u\), kg·kg\(^{-1}\)) and volumetric (\(\theta\), m\(^3\)·m\(^{-3}\)) water contents for the soils studied. The water contents indicated slight discrepancies in the water contents between the soils equilibrated in the dielectric cells and the polypropylene bottles.

B. Dielectric Spectra

The dielectric spectra of the Gunsight series surface soil at five levels of hydration (i.e., the oven dry samples in addition to the four equilibration relative humidities) were presented in Figure 1. The relative dielectric permittivity of the oven dry samples were \(\approx 2\) across the entire spectrum.

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**TABLE II**

<table>
<thead>
<tr>
<th>RH</th>
<th>(\phi)</th>
<th>(u)</th>
<th>(\theta)</th>
</tr>
</thead>
<tbody>
<tr>
<td>%</td>
<td>m(^3)·m(^{-3})</td>
<td>kg·kg(^{-1})</td>
<td>m(^3)·m(^{-3})</td>
</tr>
<tr>
<td>43</td>
<td>0.535</td>
<td>0.055</td>
<td>0.060</td>
</tr>
<tr>
<td>53</td>
<td>0.535</td>
<td>0.057</td>
<td>0.070</td>
</tr>
<tr>
<td>84</td>
<td>0.535</td>
<td>0.078</td>
<td>0.097</td>
</tr>
<tr>
<td>97</td>
<td>0.535</td>
<td>0.122</td>
<td>0.151</td>
</tr>
</tbody>
</table>

**TABLE III**

<table>
<thead>
<tr>
<th>RH</th>
<th>(\phi)</th>
<th>(u)</th>
<th>(\theta)</th>
</tr>
</thead>
<tbody>
<tr>
<td>%</td>
<td>m(^3)·m(^{-3})</td>
<td>kg·dm(^{-1})</td>
<td>m(^3)·m(^{-3})</td>
</tr>
<tr>
<td>43</td>
<td>0.504</td>
<td>0.023</td>
<td>0.030</td>
</tr>
<tr>
<td>53</td>
<td>0.505</td>
<td>0.026</td>
<td>0.034</td>
</tr>
<tr>
<td>84</td>
<td>0.504</td>
<td>0.042</td>
<td>0.056</td>
</tr>
<tr>
<td>97</td>
<td>0.504</td>
<td>0.076</td>
<td>0.100</td>
</tr>
</tbody>
</table>

Figure 2 presented a rescaled view of the dielectric loss from 1 to 20 GHz. We discerned a Debye-type relaxation slightly below 10 GHz. These relaxations were found at all water contents, even the oven-dry samples. These relaxations appeared to be distinct from the relaxation due to free water, the relaxation of which could be noted also at approximately 20 GHz. Table IV presented the inferred relaxation times for the adsorbed water as a function of equilibration relative humidity. Unexpectedly, the inferred relaxation time increases with increasing water. One would expect the opposite to be true, that is that the increased water film thickness would reduce the rotational limitations on the adsorbed water molecules. A possible explanation could be found in the fact that dc conductivity increases with equilibration relative humidity. The most likely explanation for this progression was that the salinity increases with soil wetting. Previous studies have found that solvent relaxation times were depressed by increasing electrolyte concentrations.

The addition of a small amount of water, 2–5% on a
permittivity, particularly at frequencies below 100 MHz. Electrode polarization for the soil equilibrated at 43, 54, 84, and 97 % relative humidity precluded elucidating the relaxation-model parameters for the dielectric phenomena for this hydration state. As presented in Figure 3, the Cole-Cole diagram of the real and imaginary parts of complex relative permittivity indicated that the relaxation phenomena in soils is captured well by our combined measurement systems.

We fitted the data for soils for the soils equilibrated at 43, 54, 84 % relative humidity by nonlinear regression to the Cole-Cole equation

\[ \varepsilon(\nu) = \varepsilon_\infty + \frac{\varepsilon_a - \varepsilon_\infty}{1 + (\omega\tau)^{1-\alpha}} \]  

(10)

Nonlinear regression was calculated with PROC NLIN statement in the SAS/STAT statistical analysis package [12]. These parameter estimates were presented in Table V, in which the relaxation frequency, \( f_r = 1/(2\pi\tau) \). The parameter estimates showed that the relaxation times were much lower than those associated with a liquid solvent molecule, supporting the idea that these soils over a broad frequency range. The increase in conductivity with water content suggested that at higher water contents this behavior dominates the dielectric signature of these soils over a broad frequency range. so that dielectric loss was due to dc conductivity effects at higher water contents, though electrode polarization in our measurements prevented a definite conclusion.

IV. CONCLUSION

We believe that the combination of impedance and open-ended coaxial measurements can yield accurate soil dielectric permittivity measurements from 40 Hz to at least 20 GHz. These allow us to calculate precisely the expected attenuation rates for these soils at various hydration states. For example, the expected one-water attenuation rates for these soils at 100 MHz would be 4.8, 7.4, 11.0, and 20.1 dB·m\(^{-1}\) for soils hydrated at 43, 54, 84, and 97 % RH. For the particular case of hydrated arid-zone soils, this approach yielded accurate resolution of three relaxation phenomena, with very precise description of the MWS polarization phenomena. The two most obvious future applications for this capability would be to discern if MWS polarization is found also in water-saturated, as opposed to hydrated, soil samples and to investigate the dielectric permittivity of frozen soil samples.

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REFERENCES


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**TABLE IV**

DC conductivities and adsorbed water relaxation frequencies measured on the soil samples at their equilibration relative humidities.

<table>
<thead>
<tr>
<th>RH</th>
<th>( \kappa ) (mS·m(^{-1}))</th>
<th>( \tau ) (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.55 × 10(^{-6})</td>
<td>13.45</td>
</tr>
<tr>
<td>43</td>
<td>1.13 × 10(^{-3})</td>
<td>15.96</td>
</tr>
<tr>
<td>53</td>
<td>0.013</td>
<td>17.43</td>
</tr>
<tr>
<td>84</td>
<td>0.14</td>
<td>18.66</td>
</tr>
<tr>
<td>97</td>
<td>5.3</td>
<td>22.32</td>
</tr>
</tbody>
</table>

**TABLE V**

Maxwell-Wagner-Sillars polarization relaxation parameters fitted to the Cole-Cole equation.

<table>
<thead>
<tr>
<th>RH</th>
<th>( \tau ) (ns)</th>
<th>( f_r ) (MHz)</th>
<th>( \varepsilon_\infty )</th>
<th>( \varepsilon_a )</th>
<th>( \alpha )</th>
</tr>
</thead>
<tbody>
<tr>
<td>43</td>
<td>309</td>
<td>0.315</td>
<td>2.40</td>
<td>55.41</td>
<td>0.1194</td>
</tr>
<tr>
<td>53</td>
<td>227</td>
<td>0.701</td>
<td>3.05</td>
<td>77.11</td>
<td>0.2188</td>
</tr>
<tr>
<td>84</td>
<td>72.8</td>
<td>2.19</td>
<td>2.81</td>
<td>90.65</td>
<td>0.1823</td>
</tr>
</tbody>
</table>


