Dielectric Constant and Osmotic Potential from Ion-Dipole Polarization Measurements of KCl- and NaCl-doped Aqueous Solutions.

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ABSTRACT: This effort demonstrates how ion-dipole polarization affects the dielectric constant of saline aqueous solutions. When ion-dipole polarization is present, water's dielectric constant increases from 78 to 228 at 25 °C and low ionic concentrations. The onset of ion-dipole polarization is frequency and salinity dependent. The measurand is the capacitance-peak frequency which is linearly related to electrical conductivity for simple ionic solutions. For KCl and NaCl, the peak frequency ranges from 200 Hz for pure water to 3 GHz for saturated solutions at 25 °C. The onset of ion-dipole polarization is quantified graphically to aid in correcting water content measurements. The capacitance-peak frequency value is shown to be related to osmotic potential.

Key Words: Dielectric Spectroscopy, Ion-Dipole Polarization, Salinity Effects in Soils.

INTRODUCTION: This effort is motivated by the need to understand salinity effects when using changes in the dielectric constants to determine soil water content. Some instruments using this technique include Time Domain Reflectometry [1], Ground Penetrating Radar [2], Capacitance Devices [2], and Time Domain Transmission [3]. Such instruments typically operate in the 50 MHz to 1 GHz frequency range. This is the frequency range where salinity in soils causes the dielectric constant of water to increase and thus, complicates water content measurements.

The increase in the dielectric constant with salinity is explained by the onset of ion-dipole polarization. Experimental observation of ion-dipole polarization is shown in Figs. 1 and 2 where the phase angle and real capacitance spectra shift to higher frequencies as salinity increases. In Fig. 2 the high frequency portion of the curves is due to orientation polarization which has a dielectric constant of 78.36 [4] at 25 °C. At lower frequencies, the capacitance increase is due to the onset of ion-dipole polarization. The objective of this study is to quantify the ion-dipole effect on soil water content measurements by transforming the capacitance spectra into dielectric constant spectra. The key in the following figures lists the Date, EC [µS/cm], Temp [°C] and Nominal Concentrations [mM of KCl].
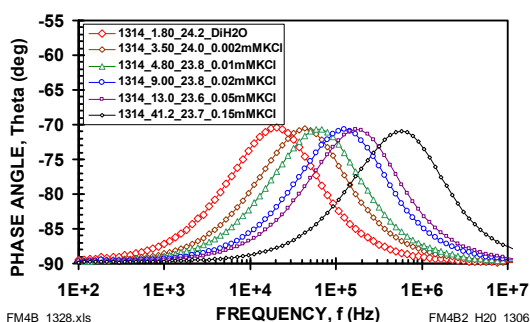

Fig. 1: Ion-dipole phase-angle spectra shift to higher frequencies with increased KCl concentration in water. DataSets: 47-52 (62)
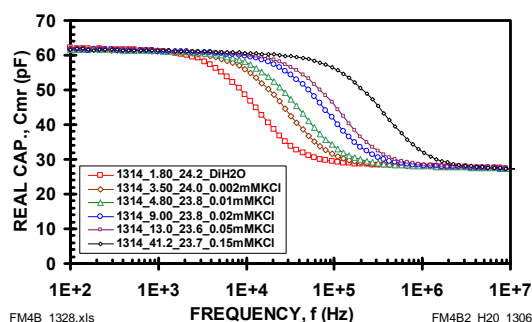
Fig. 2: Real capacitance increase at low frequencies due to the onset of ion-dipole polarization in KCl-doped water.

For low salinity soil, the water content is determined from the increase in the dielectric constant of the soil-water-air mixture using empirical relationships such as the Topp equation [1] which relates the

dielectric constant of the soil-water-air mixture to volumetric water content. However, when water becomes more saline, the Topp equation no longer holds [3]. Low salinity measurements assume the dielectric constant of water is due to orientation polarization which has a dielectric constant of 78.36 at 25 °C. However, as water becomes more saline, its dielectric constant increases due to the onset of ion-dipole polarization. As shown below, the onset concentration is frequency dependent. For low-saline water and low frequencies where both orientation and ion-dipole polarization are present, the dielectric constant of water is 228 at 25 °C.

Ion-dipole polarization is due to the formation of water shells that form around both cations and anions in aqueous solution [5]. Falkenhagen [6] calls the water shells, ionic atmospheres. The hydrated ions act as a polarizable unit. For low ionic concentrations, water shells are large and the relaxation frequency (or the onset of the effect) occurs at low frequencies. For higher ionic concentrations, water shells become smaller due to sharing of the water molecules with neighbor ions. In this case, relaxation occurs at higher frequencies.

To characterize salinity effects in water, the dielectric constant as a function of frequency and salinity must be determined. This requires knowledge of the ionic concentration dependence of the parameters used in the Debye equation [7]. For orientation polarization, the relaxation time τ_{OR}, the static dielectric constant, ε_{ORs}, and the high-frequency dielectric constant, $\varepsilon_{OR\infty}$ are needed. Values for these parameters are found in the literature [4, 8]. For ion-dipole polarization, the relaxation time, τ_{ID}, and the static dielectric constant, ε_{IDs}, and the high-frequency dielectric constant, $\varepsilon_{ID\infty}$ are needed. The objective of this paper is to show how values for these parameters were obtained.

ANALYSIS: The shift in the measured capacitance-peak frequency, f_{mcp}, with molar ionic concentration, C^* [mol/L] is used to determine the ion-dipole relaxation time, τ_{ID}. To do this, the peak frequency was determined from the spectra shown in Fig. 3. To eliminate Maxwell-Wagner (MW) as an alternate mechanism, the logarithmic form is also shown in Fig. 3. The imaginary capacitance shows no increase at low frequencies [7, p.230] which is a characteristic of MW polarization.
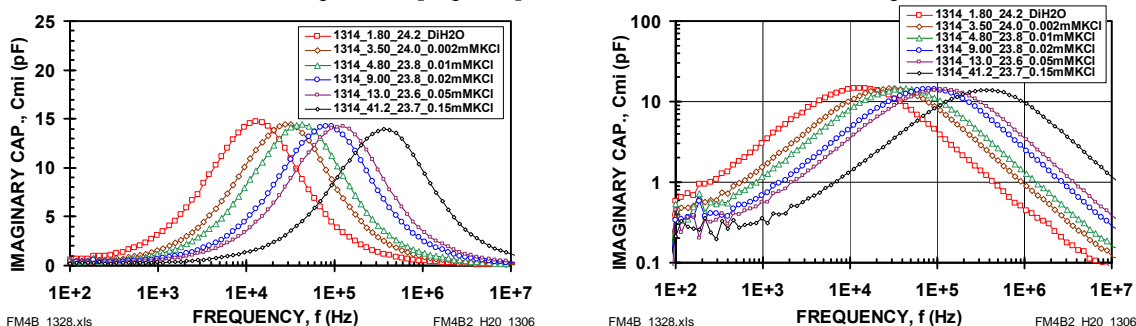

Fig. 3: Imaginary capacitance spectra shift to higher frequencies with increasing KCl concentration.

The sensing probe includes an integral blocking capacitor that is in series with the electrodes and solution. The blocking capacitor eliminates the Helmholtz double layer [9] found at metal electrodes and thus allows detection of low-frequency polarizations. When using a probe with a blocking capacitor the measured capacitance-peak frequency, f_{mcp}, is greater than the Debye peak frequency, f_{cp}. Later, the conversion between these frequencies is discussed. The relaxation time for a polarization process [10, p. 64] is related to the dielectric constant and the electrical conductivity, σ_∞, by:

$$\tau_{ID} = \frac{\varepsilon_0(\varepsilon_{IDs} - \varepsilon_{ID\infty})}{\sigma_\infty} = \frac{1}{\omega_{cp}} \tag{1}$$

where $\varepsilon_0 = 0.0885$ [pF/cm] and $\omega_{cp} = 2\pi f_{cp}$. Note that the relaxation time, τ_{ID}, is determined at $\omega = \omega_{cp}$ and the electrical conductivity, σ_∞, at $\omega = \infty$. The electrical conductivity is given by [5, p. 41]:

$$\sigma_\infty = \frac{\Lambda C^*}{1000} \tag{2}$$

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where Λ is the equivalent ionic mobility in S·cm^2/mol. The factor 1000 converts C^* in mol/L to mol/cm^3. The concentration dependence of Λ for KCl and NaCl is shown in Fig. 4. The data in Fig. 4 are plotted over the complete concentration range from pure water to ionic saturation at 25 °C. The data [5] in Fig. 4 was fitted with a fourth-order polynomial for KCl:

$$\Lambda = \Lambda^0_{KCl} - 91.01C^{*0.5} + 92.09C^* - 47.46C^{*1.5} + 8.57C^{*2} \qquad (3a)$$

where $\Lambda^0_{KCl} = 149.85$ S·cm^2/mol; the correlation coefficient is 0.9998. For NaCl the fitting polynomial is:

$$\Lambda = \Lambda^0_{NaCl} - 81.38C^{*0.5} + 71.03C^* - 36.86C^{*1.5} + 6.48C^{*2} \qquad (3b)$$

where $\Lambda^0_{NaCl} = 126.45$ S·cm^2/mol; the correlation coefficient is 0.9998.
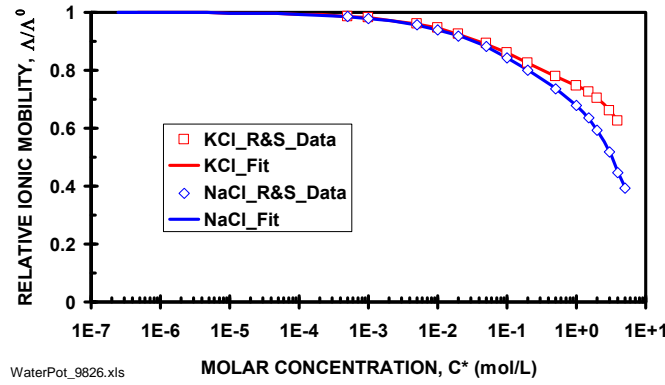

Fig. 4: Ionic mobility ratios for KCl- and NaCl-doped water at 25 °C. Data from [5, Appen. 6.3].

From the Λ concentration dependence, an expression for the ion-dipole dielectric constant, $\varepsilon_{IDs} - \varepsilon_{ID\infty}$, was determined by combining (1) and (2):

$$\frac{C^*}{1000\varepsilon_0\omega_{cp}} = \frac{\varepsilon_{IDs} - \varepsilon_{ID\infty}}{\Lambda} = \frac{(\varepsilon_{IDs} - \varepsilon_{ID\infty})_0}{\Lambda^0} \qquad (4)$$

where $(\varepsilon_{IDs} - \varepsilon_{ID\infty})_0$ and Λ^0 are evaluated at low ionic concentration. Rearranging this equation leads to an expression for the concentration dependence of the ion-dipole dielectric constant, namely:

$$(\varepsilon_{IDs} - \varepsilon_{ID\infty}) = (\varepsilon_{IDs} - \varepsilon_{ID\infty})_0 \frac{\Lambda}{\Lambda^0} \qquad (5)$$

To determine the $(\varepsilon_{IDs} - \varepsilon_{ID\infty})_0$ term, solutions were measured at low concentrations. To account for the probe's blocking capacitor, two correction factors were determined from a Cole-Cole [11] analysis of the experimental data. The measured peak frequency was adjusted using $\omega_{cp} = F_w \cdot \omega_{mcp}$ where $F_w = 0.685 \pm 0.010$. The measured conductivity, σ_{m0}, was adjusted using $\sigma_{\infty0} = \sigma_{m0}/F_s$ where $F_s = 1.993 \pm 0.042$. Combining the correction factor equations with (1) at low ionic concentrations leads to:

$$(\varepsilon_{IDs} - \varepsilon_{ID\infty})_0 = \frac{\sigma_{\infty0}}{\varepsilon_0\omega_{cp}} = \frac{\sigma_{m0}}{\varepsilon_0 F_s F_w \omega_{mcp}} = \frac{C'_{mcp}}{\varepsilon_0 F_s F_w} \qquad (6)$$

where $C'_{mcp} = \sigma_{m0}/\omega_{mcp}$ is the ratio of the solution electrical conductivity to the capacitance-peak frequency at low concentrations. Details for determining σ_{m0} and ω_{mcp} are given next.

MATERIALS AND METHODS: The impedance spectrometer (Wayne-Kerr 6500B) is shown in Fig. 5 and the sample chamber is shown in Fig. 6. The sensing probe with interdigitated fingers is mounted in the bottom of the chamber. The fingers are copper electrodes covered with a 76.2-µm FR-4 layer. Both KCl- and NaCl-doped water samples weighing 9 g were placed into the sample chamber. The weight of the samples was maintained at a constant value to stabilize the geometrical factor or cell constant. The conductivity, σ_{m0}, and temperature of the 9-g samples were measured with a conductivity meter (WTW Cond 315i with a TetraCon 325 probe). Sample temperatures were close to 25 °C and were corrected to 25 °C using an algorithm based on Wu [12] KCl data. Since FR-4 is

known to absorb moisture, it was stabilized by saturating it with deionized water for a period of 24 hours before the start of the measurement cycle. Between measurements, the chamber was washed with deionized water and dried with a paper towel. Then a new sample was introduced. The order in which the samples were measured began with deionized water and progressed to higher conductivity samples to minimize chamber contamination.
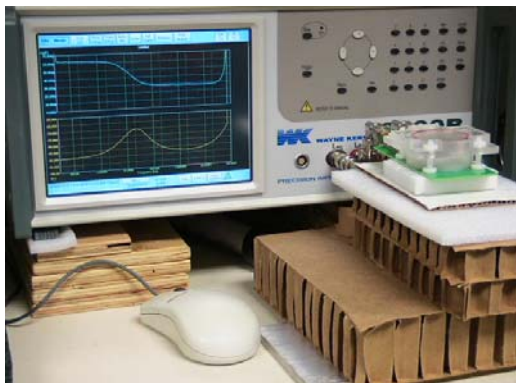

Fig. 5: Experimental apparatus showing spectra from a deionized-water sample. Upper trace shows the capacitance response; lower trace shows the phase angle response.
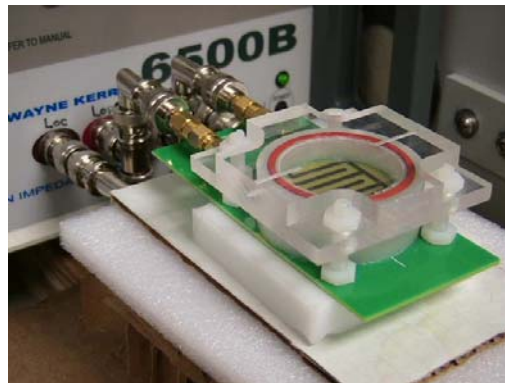

Fig. 6: Sample chamber is sealed with an O-Ring. Copper electrodes in the bottom of the chamber consist of interdigitated fingers embedded in FR-4.

The impedance and phase angle were measured at 100 frequencies between 30 Hz and 100 MHz. The real and imaginary capacitances were then determined. The peak frequency of the imaginary capacitance, seen in Fig. 3, was determined using a five-point, second-order fitting algorithm. The results are shown in Fig. 7; the conductivities ranging from 1 to 1000 µS/cm.

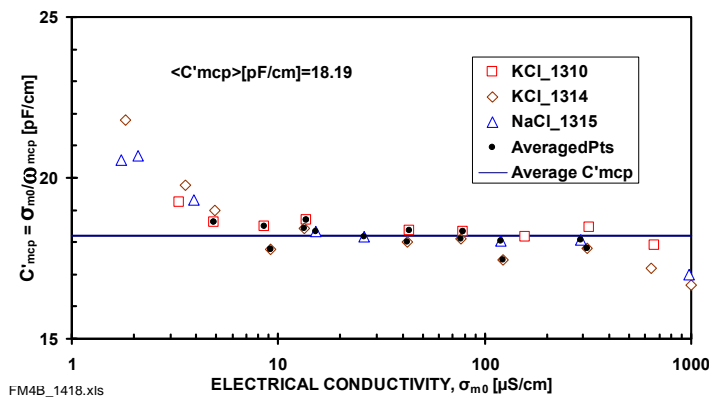Fig. 7: Experimental data from three data sets using KCl- and NaCl-doped water.

The points chosen for computation of $<C'_{mcp}>$ are marked with a dot. At the lowest conductivities the results are unreliable because measurements were at the detection limit of the conductivity meter. At the highest conductivities, the peak frequencies approached the upper frequency capability of the spectrometer where cable effects are important; thus, these data points were not included in the average. The average value for $<C'_{mcp}>$ = 18.19 ± 0.35 pF/cm at 25 °C. The value for the ion-dipole dielectric constant at low ionic concentrations using (6) is $(\varepsilon_{IDs} - \varepsilon_{ID\infty})_0$ = 150.1 ± 1.9. Results in Fig. 7 indicate that C'_{mcp} does not depend on ion type since results for KCl and NaCl overlap.

DIELECTRIC CONSTANTS: The orientation-polarization dielectric constant as a function of concentration was determined from Chen [8] for KCl-doped water:

$$\varepsilon_{ORs} = \varepsilon_{ORs0} - 8.9067 \times C* \tag{7}$$

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where ε_{ORs0} = 78.36 at 25 °C [4]. This dielectric constant is the sum of electronic, atomic and orientation polarizations. The orientation-polarization high-frequency dielectric constant is $\varepsilon_{OR\infty}$ = 5.2 at 25 °C [4].

The ion-dipole polarization high-frequency dielectric constant is equal to the low-frequency orientation-polarization's dielectric constant; that is, $\varepsilon_{ID\infty} = \varepsilon_{ORs}$. The ion-dipole dielectric constant, $\varepsilon_{IDs} - \varepsilon_{ID\infty}$, was calculated from (5) using the previous determined value for $(\varepsilon_{IDs} - \varepsilon_{ID\infty})_0$ = 150.1. The low-frequency ion-dipole dielectric constant was calculated from:

$$\varepsilon_{IDs} = (\varepsilon_{IDs} - \varepsilon_{ID\infty}) + \varepsilon_{ID\infty} \tag{8}$$

At low concentration, ε_{IDs0} = 228.5 ± 1.9 at 25 °C which is the sum of electronic, atomic, orientation, and ion-dipole polarizations. The ion-dipole dielectric constants are shown in Fig. 8 where $\varepsilon_{ID\infty}$ is salinity sensitive above 0.1 S/cm; however, ε_{IDs} is salinity sensitive above 0.0001 S/cm.
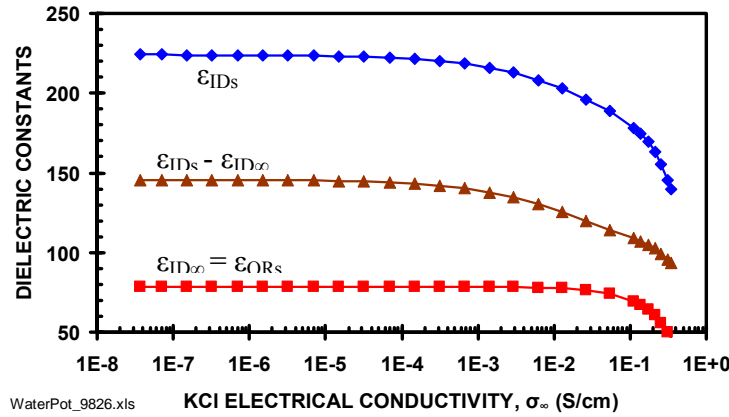

Fig. 8: Ion-dipole dielectric constants showing their roll off at higher conductivities.

RELAXATION TIME: To determine the onset of a polarization mechanism, the relaxation time is needed. The onset occurs at a critical angular frequency. Below this frequency the polarization mechanism contributes to the dielectric constant and above the critical frequency, it does not contribute. The ion-dipole relaxation time was determined by combining (1), (2), and (4):

$$\tau_{ID} = \left(\frac{1000\varepsilon_0(\varepsilon_s - \varepsilon_\infty)_0}{\Lambda^0} \right) \frac{1}{C^*} \tag{9}$$

This expression appears in Falkenhagen [6, p. 213] and Harned and Owens [10, p. 130]. A footnote in Falkenhagen [6] indicates that this equation was first mentioned by Schiele [13] in 1931. The equation indicates that τ_{ID} is inversely proportional to C^*. Since τ_{ID} = $1/\omega_{cp}$, then ω_{cp} is proportional to C^*. The relaxation time for orientation polarization was obtained from Chen [8] for KCl-doped water:

$$\tau_{OR}[ps] = \tau_{OR0} - 0.7569 \times \sqrt{C^*[mol/L]} \tag{10}$$

where τ_{OR0} = 8.33 ps.

APPLICATIONS: Four examples are discussed in this section. The first example shows that the electrical conductivity can be determined from the capacitance-peak frequency. Combining (1) and (5) leads to:

$$\frac{\sigma_\infty}{f_{cp}} = 2\pi\varepsilon_0(\varepsilon_{IDs} - \varepsilon_{ID\infty})_0 \frac{\Lambda}{\Lambda^0} = 8.35 \times 10^{-11} \frac{\Lambda}{\Lambda^0} \tag{11}$$

This equation is plotted in Fig. 9 for KCl- and NaCl- doped water. It shows that $(\varepsilon_{IDs} - \varepsilon_{ID\infty})_0$ is the major factor where the Λ/Λ^0 ratio (see Fig. 4) describes the slight roll off at high conductivities.

For a given conductivity, the Debye frequency, f_{cp}, is the lowest measurable frequency. When a blocking capacitor is used, the measured peak frequency, f_{mcp}, will be higher than f_{cp} or $f_{mcp} = f_{cp}/F_w$. For the sensing probe where F_w = 0.685, the measured-peak frequency is 1.46 times the Debye

frequency or $f_{mcp} = 1.46 \cdot f_{cp}$. For a blocking capacitance that is large compared to soil capacitances, F_w approaches unity.
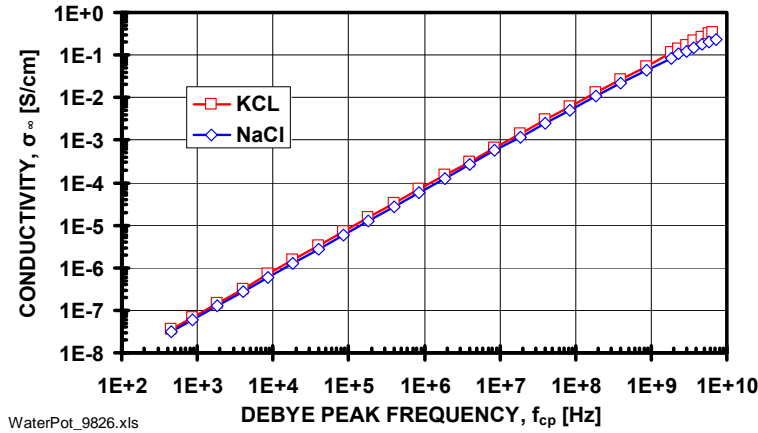

Fig. 9: Conductivity determined from the ion-dipole capacitance-peak frequency at 25 °C where the effect of the blocking capacitor has been removed. At low conductivity, $\sigma_\infty = 8.35 \times 10^{-11} \cdot f_{cp}$.

The second example shows how the dielectric constant shifts with frequency for fixed conductivity values. The dielectric constants derived above are inserted into the Debye equation [7]. The first Debye equation describes the real dielectric constant:

$$\varepsilon_r = \varepsilon_{OR\infty} + \frac{\varepsilon_{ORs} - \varepsilon_{OR\infty}}{1 + (\omega_{cp}\tau_{OR})^2} + \frac{\varepsilon_{IDs} - \varepsilon_{ID\infty}}{1 + (\omega_{cp}\tau_{ID})^2} \tag{12}$$

The second Debye equation describes the imaginary dielectric constant:

$$\varepsilon_i = \frac{(\varepsilon_{ORs} - \varepsilon_{OR\infty})\omega_{cp}\tau_{OR}}{1 + (\omega_{cp}\tau_{OR})^2} + \frac{(\varepsilon_{IDs} - \varepsilon_{ID\infty})\omega_{cp}\tau_{ID}}{1 + (\omega_{cp}\tau_{ID})^2} \tag{13}$$

The electrical conductivities (EC) in Figs. 10a-10d range from 10^{-4} to 0.1 S/cm (0.1 to 100 dS/m).
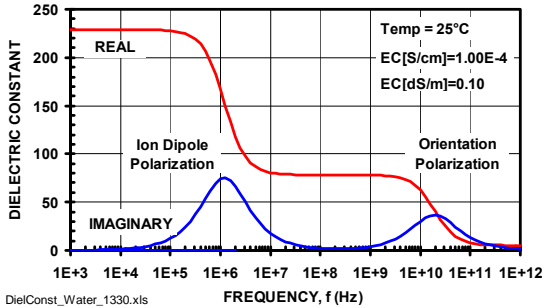

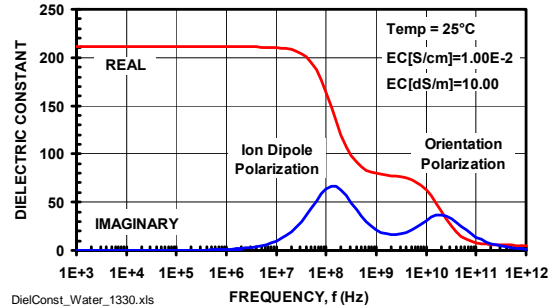*Fig. 10a: Dielectric constant of water with 0.1 dS/m KCl.*

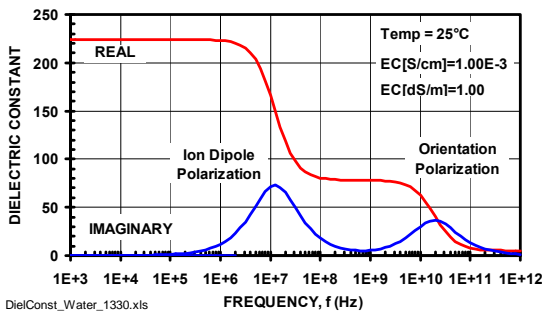*Fig. 10c: Dielectric constant of water with 10 dS/m KCl.*

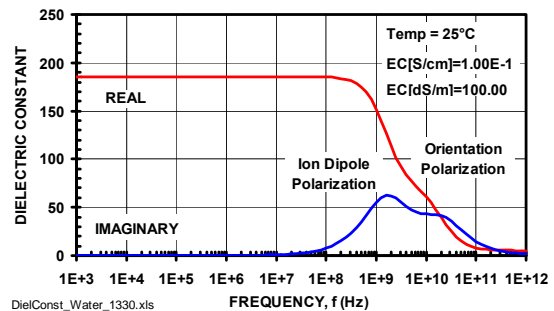*Fig. 10b: Dielectric constant of water with 1 dS/m KCl.*

Fig. 10d: Dielectric constant of water with 100 dS/m KCl.

The curves in Fig. 10 show that at a given frequency, ion-dipole polarization is more evident as the conductivity increases. Typically the frequency range for dielectric measurements is 50 MHz to 1 GHz. In this frequency range, salinity effects are not a factor if the conductivity is less than 10^{-3} S/cm. However, for salinities greater than 10^{-3} S/cm, salinity effects begin to manifest themselves due to an increase in the dielectric constant which is a result of the onset of ion-dipole polarization.

In the third example, the dielectric constants are determined at a fixed frequency as the conductivity is varied to better understand when salinity effects become important. The results, shown in Fig. 11, indicate that salinity effects become important when the curves begin to increase above the traditionally assumed value of 78.36 for the dielectric constant of water. For example, at 50 MHz the 78.36 value for the dielectric constant of water can be used up to a conductivity of 10^{-3} S/cm. For conductivities greater than 10^{-3} S/cm, the increase in the dielectric constant must be accounted for. This suggests these curves might be used to correct water-content calibrations curves and extend their usefulness to higher salinity cases.

The curves in Fig. 11 can be understood as follows. The lower bound of these curves is controlled by orientation polarization at low conductivity; see the lower curve in Fig. 8. The upper bound is controlled by ion-dipole polarization at high conductivity; see the upper curve in Fig. 8.
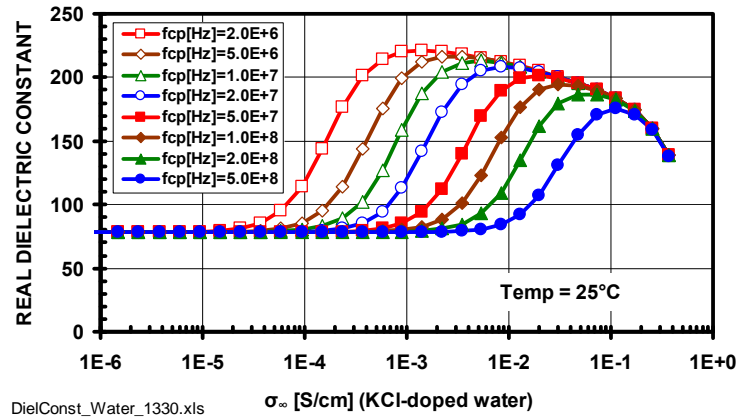

Fig. 11: The increase in the dielectric constant of saline water above the traditional 78.36 value depends on the solution's electrical conductivity and measurement frequency.

The forth example involves demonstrating that the capacitance-peak frequency (or conductivity) is linearly related to the osmotic potential, ψ_0. Combining several equations from [5, Chapter 2] leads to:

$$\psi_o = -\frac{RT\varphi\nu}{\Lambda}\sigma_\infty \qquad (14)$$

where R is the Gas constant, T is temperature, ν is the number of types of ions in solution (for KCl $\nu = 2$), φ is the osmotic coefficient, and Λ is the equivalent ionic mobility. The osmotic coefficients for KCl were taken from [5, Appendix 8.3] and fitted with the following forth-order polynomial:

$$\varphi = 1 - 0.3657 C*^{0.5} + 0.5320 C* - 0.3969 C*^{1.5} + 0.1284 C*^2 \qquad (15)$$

The correlation coefficient is 0.9997. A plot of (14) appears in Fig. 12. Also shown in Fig. 12 are values obtained from water activity, a_w, for KCl obtained from [5, Appendix 8.3]. The a_w data were converted to osmotic potential [5, p. 205] using $\psi_o = (RT/V_A)\ln a_w$ where $V_A = 18.068$ cm^3/mol is the partial molar volume for water at 25 °C. Notice that the data [5] is limited to osmotic potentials having more suction than -0.03 MPa; whereas, conductivity measurements or capacitance-peak frequency measurements can be used to obtain values over the entire range. Over this range, the osmotic potential varies by more than seven orders of magnitude from -10^{-6} MPa or -1 Pa for pure water to -2 MPa for saturated KCl solutions.
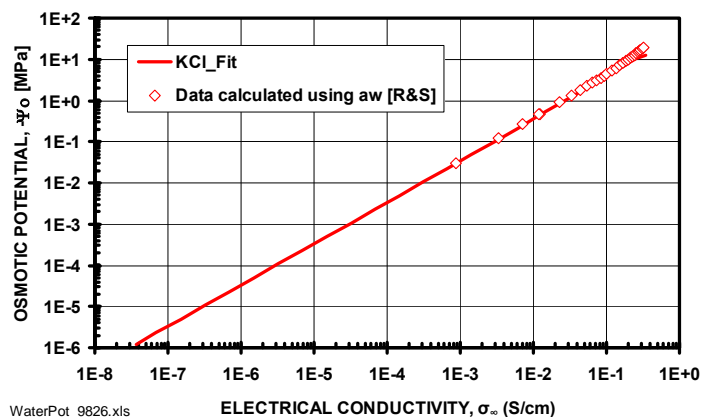
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WaterPot_9826.xls

Fig. 12: Osmotic potential is proportional to conductivity and hence to capacitance-peak frequency.

DISCUSSION: This effort quantified how salinity increases the dielectric constant of water by the onset of ion-dipole polarization allowing the water's dielectric constant to increases from 78 to 228 at 25 °C and at low ionic concentrations. The dielectric constant for ion-dipole polarization were determined at low concentrations and were extended to higher concentrations using published data for equivalent ionic mobilities for KCl and NaCl. All measurement data were acquired at room temperature where the temperature coefficient for orientation polarization is -0.4575 %/°C [4]. Preliminary data indicate that ion-dipole also has a negative temperature coefficient but its magnitude is larger. The conductivity-frequency data shown in Fig. 9 indicates that ion-dipole effects vary over seven orders of magnitude. To the author's knowledge there is no single impedance spectrometer that can measure over this range. The development of such an instrument represents a challenge. This work used simple 1:1 electrolytes. Additional efforts should include measurements of ion-dipole dielectric constants of more complex ions to get greater insight into soil water content measurements.

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