# Dielectric properties of wet and fertilized soils at radio frequencies

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The dielectric constant  $\in'$  and dielectric loss  $\in''$  of moist soil and fertilized soil have been measured in the frequency range 10 kHz-2 MHz using a precision LCR meter. The values of  $\in'$  and  $\in''$  of the wet (Gandhinagar district sandy loam) soil are found to decrease with increase in frequency from 10 kHz to 2 MHz. The value of tan  $\delta$  is found to increase with increase in moisture content in the soil. The peak of tan $\delta$  is found to shift towards lower frequency side as the moisture content in the soil. The value of  $\sigma$  increases slowly with increase in conductivity  $\sigma^* = \sigma' + j\sigma''$  with increase in moisture content in the soil. The value of  $\sigma$  increases slowly with increase in frequency for wet soil. A dip is observed in the value of  $\sigma''$  spectra at electrode polarization frequency, which is also observed in complex impedance plane plot of the wet soils. To see the effect of fertilizer on the soil two fertilizers are selected, sulphet of potash (SOP) and zinc chelate. It has been observed that $\epsilon''$  and  $\epsilon'''$  of the wet fertilized soils decrease with increase in frequency from 10 kHz to 2 MHz. Further, the values of  $\epsilon'$  and  $\epsilon'''$  increase with increase in % concentration of fertilizer in the wet soil. The variation of tan  $\delta$  and conductivity with frequency and fertilizer in the soils has also been studied.

Keywords: Dielectric properties, Soil, Moisture content, Fertilizer content, Precision LCR meter

# **1** Introduction

The permittivity of a material represents the extent of distortion of its electric charge distribution in response to an applied electric field<sup>1</sup>. At low frequencies (Hz-MHz), the perturbation of charges at the solution-solid interface is responsible for permittivity or impedance variation. The large enhancement in permittivity at low frequency end result from two mechanisms, namely (i) polarization of the counter ions in the diffuse double layer (DDL) called DDL polarization, and (ii) polarization of the charge imbalance created at the contact of two phases with different permittivity, called Maxwell-Wagner (MW) polarization.

The application of an electric field causes the counter ions in the DDL to move along the surface in response to the electric gradient<sup>1</sup>. When electric field is applied, the electric charges accumulate at the particle interfaces such as particle-air, particle-water, and water-air interfaces. When the field is removed, the charges relax back to their original distribution by diffusion. The second mechanism results from the polarization of charge created by contact of two phases with different permittivity (MW polarization).

Complex systems consisting of materials of different permittivity values such as soil, water, air, rocks, and solutions containing macromolecules or alumino-silicate colloids exhibit extremely large changes in their electric properties like permittivity and impedance, with change in frequency of the applied electromagnetic field<sup>1</sup>. These large changes in permittivity or impedance are very much useful to study the electrochemical properties of porous media in geophysics, and could be useful for the determination of geometric as well as electrochemical properties of solids.

Porosity of soil is helpful to judge the moisture content and moisture movement in the soil. Any operation that reduces aggregation and decreases the amount of organic matter in the soil decreases pore space. Yadav *et al*<sup>2</sup>. measured the dielectric properties of fertilized sand for various concentrations of urea, Shree Ram-33, Shree Ram-50P, DAP (diammonium phosphate), and mosaic at X-band microwave frequency using two-point method. The dielectric constant and dielectric loss of the soil are found to increase with increase in fertilizer content in the soil. Further, the dielectric constant was found to increase slowly with increase in DAP content in the soil, whereas it increased rapidly with increase in Shree Ram-33 content in the soil.

Shaikh and Navar Khele<sup>3</sup> measured the dielectric properties of black soil with organic and inorganic matters at microwave frequency. It has been observed

that the dielectric constant decreases with increase in frequency and increases linearly with increase in fertilizer content in the soil. It has been explained that with the addition of organic matter in the soil, the water holding capacity of the soil increases. The dielectric loss is found to increase with increase in inorganic and organic matter content in the soil equally. To gain more information in this area, the dielectric properties of soils with moisture and fertilizer content are measured in the frequency range 10 kHz-2 MHz, at room temperature and the results are presented in this paper.

# **2** Sample Preparation

The soil samples were collected from the fields of Gandhinagar and Palanpur districts. Stones and gravels were removed from the soil samples and then the soil samples were oven dried. The distilled water was added in the oven dried soil samples and allowed to saturate for 24 h. As the days went on, the moisture content in the soil decreased and the measurements of dielectric constant of the soil sample for various moisture contents were carried out. Volumetric moisture content of the wet soil<sup>4</sup> was found as :

$$W_{\nu} = \rho_{dry} \times \frac{\text{Weight of wet soil} - \text{Weight of dry soil}}{\text{Weight of dry soil}}$$

where  $\rho_{dry}$  = the dry density of the soil. The texture structure of the soil samples was obtained from the KBM Engineering Company, Ahmedabad as shown in Table 1.

The wilting point (WP) and transition moisture (Wt) of soil in terms of volumetric water content  $(cm^{3}/cm^{3})$  have been calculated<sup>5</sup> as :

WP = 0.06774-0.00064 x Sand + 0.00478 x Clay Wt = 0.49 WP + 0.165.

where sand and clay are the sand and clay contents in per cent of dry weight of the soil.

To observe the effect of fertilizer on the dielectric properties of soils two fertilizers (i) sulphate of potash (SOP) also called potassium sulphate, and (ii) zinc

chelate have been selected. The SOP contains potash  $(K_2O)$  per cent by weight minimum-50.0, sulphur (S)per cent by weight minimum-17.5. SOP was imported from Finland. It is prescribed to prepare 0.2% to 0.5%solution of SOP (by dissolving 200 to 500 g / 100 liters of water). It is 100% water soluble fertilizer for folier spray. It is recommended for use on cotton and vegetables. The microgranual formulation of zinc chelate contains water soluble zinc (Zn) minimum = 12.0%, zinc (Zn) chelated by EDTA minimum = 12.0%, and pH stability range was 4.9 in aqueous solution. It is recommended for use on paddy, cotton, chillies, vegetables, sugarcane, groundnut and horticultural crops. It has been prescribed to dissolve 100-150 g of librel zinc chelate in 150-200 l of water and to be sprayed over one acre of standing crop or if required the dose can be increased. Zinc chelate fertilizer is manufactured by Ciba UK Plc, Bradford, West Yorkshire, UK. The % solutions of fertilizers by weight in the soil samples were prepared as shown in Table 2.

Taking the dry soil sample of 100 g, the fertilizer dissolved water of 6 ml with different concentration, was mixed in the soil. The corresponding moisture content in the Gandhinagar district sandy loam was

Table 2 — % solution content of fertilizer in the soil samples					
Soil Type	Fertilizer Type	Weight of Fertilizer in 50 ml double distilled water	% solution of fertilizer		
Gandhinagar district Sandy Loam Palanpur district Sand	Sulphate of Potash (SOP) Zinc Chelate (Librel) Sulphate of Potash (SOP) Zinc Chelate (Librel)	110 mg 160 mg 200 mg 250 mg 40 mg 60 mg 80 mg 100 mg 120 mg 170 mg 250 mg 310 mg 40 mg 50 mg 60 mg 90 mg	$\begin{array}{c} 0.22 \ \% \\ 0.32 \ \% \\ 0.40 \ \% \\ 0.50 \ \% \\ 0.12 \ \% \\ 0.12 \ \% \\ 0.20 \ \% \\ 0.24 \ \% \\ 0.24 \ \% \\ 0.34 \ \% \\ 0.50 \ \% \\ 0.62 \ \% \\ 0.62 \ \% \\ 0.08 \ \% \\ 0.10 \ \% \\ 0.12 \ \% \\ 0.18 \ \% \end{array}$		

Location	Soil texture (%)		Soil type	Wilting point	Transition	Dry density		
(Region)	Sand	Silt	Clay		$(WP) cm^3/ cm^3$	moisture (Wt) cm <sup>3</sup> / cm <sup>3</sup>	g/cm <sup>3</sup>	
Gandhinagar district	65	31	4	Sandy loam	0.045	0.1872	1.389	
Palanpur district	82	16	1	Sand	0.02114	0.1698	1.59	

# Table1 — Texture structure of soil samples

found to remain fixed to be  $0.083 \text{ cm}^3/\text{cm}^3$ , whereas that of Palanpur district sand remained fixed as  $0.0954 \text{ cm}^3/\text{cm}^3$ .

# **3** Experimental Set-up

A precision LCR meter Agilent make E-4980A operating in the frequency range 20 Hz-2 MHz was used for the measurements of capacitance and resistance offered by the coaxial capacitor. The LCR meter can take simultaneous measurements during one trigger in the frequency range 20 Hz-2 MHz in 201 linear steps (or logarithmic steps if required).

A standard four point probe Agilent 16089A with Kelvin clip leads was connected to the LCR meter. The coaxial capacitor was connected at the end of the probe and fixed pointing downward, in a stand.

#### 3.1 Design of Coaxial Capacitor

For the frequency range below 5 MHz, even a relatively large sample has dimensions less than the wavelength and the time of wave propagation remains short in comparison with the wave period<sup>6</sup>. Methods of measuring lumped parameters can be used at frequencies up to 100 MHz, provided the dimensions of the sample are made substantially smaller than the wavelength. A parallel plate capacitor with disk electrodes is most commonly used as a sample holder in this frequency range. Levitskaya and Sternberg<sup>6</sup> determined the complex permittivity of the material by measuring the magnitude Z and phase  $\phi$  of the sample impedance by using an impedance analyzer. The measurements were carried out in the frequency range 1 kHz-100 MHz using disk electrodes and in the frequency range 1 kHz-1 GHz using coaxial sample holder.

Even though a parallel plate capacitor with disk electrodes is most commonly used as a sample holder<sup>6</sup>

in the frequency range up to 100 MHz, the limitation of the parallel plate capacitor is that when we put the soil sample between parallel plates, the soil sample gets disturbed. Further, it is difficult to verify about how much pressure is to be applied between the two plates of the parallel plate capacitor, since increasing the pressure between plates means to increase the density of the soil sample and the complex permittivity of the soil is dependent on the density, too.

To avoid these difficulties, a coaxial capacitor with vertical cuts on the outer cylinder (Fig. 1) was designed which gives almost *in-situ* dielectric properties of the soil sample. The inner conducting rod of diameter 2 mm was surrounded by a conducting outer cylinder with inner diameter 6.65 mm and outer diameter 7.93 mm. The central conductor and surrounding outer cylinder were separated by teflon ring of thickness 4.66 mm. Four vertical cuts of length 10.26 mm and 1 mm wide spacing were made on the outer cylinder reaching up to the teflon ring. The cuts on the outer cylinder help in removing the air inside the coaxial capacitor as it was dipped in the MUT. The total length of the capacitor was 14.92 mm.

While measuring the capacitance and resistance of the coaxial capacitor filled with the liquid or soil sample, the capacitance and resistance of the teflon spacer used between the two coaxial cylinders and the connecting terminals, were taken into account during calibration. Further, for the coaxial capacitor the limiting wavelength related with the complex permittivity  $\in$ \* of the soil samples was taken into consideration according to Levistkya<sup>6</sup> and Brandt<sup>7</sup> as  $\lambda_{\text{lim}} > \pi \sqrt{\in (b+a)}$ , where *a* and *b* are the radii of the inner and outer cylinders of the coaxial capacitor, respectively.



Fig. 1 — Design of coaxial capacitor,(a) Vertical cuts, (b) Outer cylinder, (c) Connector of central conductor, (d) Connecting wire for outer cylinder, (e) Central conductor

The compensation of the LCR meter and coaxial capacitor was done in following steps:

- (i) Open: The LCR meter was compensated for open circuit coaxial capacitor with air as dielectric medium.
- (ii) Short: A vessel containing mercury was raised from the lower side of the capacitor till it fills the capacitor completely and then LCR meter was compensated for short.

The LCR meter is said to be compensated up to the end of the coaxial capacitor.

#### 3.2 Standardization of Capacitor

The coaxial capacitor was standardized using the liquids of known dielectric constant as follows:

- (1) The capacitance  $C_0$  and resistance  $R_0$  of the coaxial capacitor were measured using LCR meter for open circuit condition with air as dielectric for the frequency in the range 20 Hz-2 MHz.
- (2) Now a small vessel containing carbon tetra chloride (CCl<sub>4</sub> of AR grade) was kept below the coaxial capacitor. Then raising the vessel until the CCl<sub>4</sub> level completely fills the capacitor, the capacitance  $C_p$  and resistance  $R_p$  were measured for the frequency in the range 20 Hz-2 MHz.
- (3) Now the step (2) was repeated for other standard liquids like benzene and chloro-benzene of known dielectric constant.

For each capacitance value of standard liquid, the difference capacitance  $C_p-C_0$  was calculated. A graph was drawn for the dielectric constant against  $C_p-C_0$  for the known standard liquids as shown in Fig. 2.

The equation for the straight trend line connecting all points was obtained from the graph as:

$$y = 2.0139 x + 0.98 \qquad \dots (1)$$

where,  $x = C_p - C_0$  in pF

y = Dielectric constant  $\in$  ',

2.0139 = slope of the straight line from the graph of Fig. 2 and

0.98 = intercept of the straight line from the graph of Fig. 2.

The correlation coefficient of difference capacitance values and the dielectric constant for the linear trend line was observed to be 0.9999.

The variation of  $C_0$ ,  $C_p$  and  $C_p - C_0$  for CCl<sub>4</sub> and chloro-benzene with frequency is shown in Fig. 3. The values of  $C_0$ ,  $C_p$  and  $C_p - C_0$  for CCl<sub>4</sub> and chlorobenzene remain constant over the frequency range from 10 kHz to 2 MHz. Thus, the designed capacitor has linear behaviour over the given frequency range. Hence, Eq. (1) can be applied equally to the data obtained for carbon tetra chloride, benzene and chloro-benzene over the given frequency range 10 kHz-2 MHz.

The dielectric constant for each sample was calculated using Eq. (1) as:



Fig. 3 — Variation of  $C_0$ ,  $C_p$  and  $C_p - C_0$  for (a) CCl<sub>4</sub> and (b) chloro-benzene with frequency

The dielectric loss of the sample was calculated using equation

$$\in$$
 "= $\in$  '<sub>meas</sub>/*CR* $\omega$  ...(3)

where  $C = C_P - C_0$ ,  $R = R_p$  and  $\omega = 2\pi f$ 

The conductivity  $\sigma'$  of the samples was calculated using the equation

$$\sigma' = \omega \in " \in_0 \qquad \dots (4)$$

where  $\epsilon_0$  = dielectric permittivity of vacuum =  $8.854 \times 10^{-12}$  F/m.

A graph of  $\sigma'$  against frequency was drawn for each sample. Extending the linear fitting line towards lower frequency end, the value of dc conductivity  $\sigma_{dc}$  was obtained. Subtracting the dc conductivity  $loss \in_{dc} = \sigma_{dc} / \omega \in_0$  from the measured value of dielectric loss  $\in''$ , we get the actual dielectric<sup>8</sup> loss  $\in''_{actual}$  as:

$$\in "_{\text{actual}} = \in "-\frac{\sigma_{dc}}{\omega \epsilon_0} \qquad \dots (5)$$

To check the validity of the results obtained using the designed dielectric capacitor, the measurements were carried out for the other liquids like 1-propanol and acetone (AR Grade) as explained in step (2) in measurement procedure.

Figure 4 shows the variation of dielectric constant, dielectric loss and  $\tan \delta = \epsilon''/\epsilon'$  of acetone over the frequency range from 20 Hz to 2 MHz. It can be observed that over the frequency range from 10 kHz to 2 MHz, the dielectric constant of acetone remains



Fig. 4 — Measured values of dielectric constant, dielectric loss and tan $\delta$  for acetone with frequency

constant and there is no effect of polarization above 10 kHz in this case. The determined values of dielectric constant were compared with the literature values as presented in Table 3, and are found to be in good agreement with error less than 1%. This shows that the probe design, for the estimation of complex permittivity, is equally applicable over the frequency range from 10 kHz to 2 MHz.

The measurements were carried out for the estimation of dielectric constant and dielectric loss of Gandhinagar district sandy loam soil, for various moisture contents over the frequency range from 10 kHz to 2 MHz using the LCR meter. The dc conductivity of the soil for all moisture contents was also calculated using the method explained by Sengwa *et al*<sup>10</sup>. The value of dielectric loss is obtained by subtracting the dc conductivity from the measured value of dielectric loss. The measurements for fertilized wet soil samples of Gandhinagar district sand were also carried out in the same manner.

### 4 Results and Discussion

#### 4.1 Gandhinagar district Sandy Loam Soil

Figure 5 shows the variation of dielectric constant and dielectric loss of Gandhinagar district sandy loam soil with frequency for various moisture contents in the soil. A very large enhancement in the values of  $\in$ and  $\in$  " is observed with decrease in frequency from 2 MHz to 10 kHz for wet soil. This very large enhancement in the permittivity value of wet soil is due to electro chemical polarization<sup>11</sup> which arises due to increase in surface charge carrier density in the presence of water molecules in the pore spaces of the soil. Sengwa *et al*<sup>12</sup>. measured the dielectric permittivity of dry and water saturated shale, sandy sandstone and calcareous sandy stone of Jodhpur region at room temperature in the frequency range from 100 Hz to 100 kHz, and also at 10.1 GHz microwave frequency. It has been observed that the

Table 3 — Comparison of measured values and literature						
values' of dielectric constant						
Material	$\in$ ' known at	$\in$ ' measured	$\Delta \in \mathcal{A} \in \mathcal{A}$ in			
	given temperature	at 2 MHz	per cent			
Air	1	0.98	2 %			
CCl4	2.238 <sup>9</sup> (20°C)	2.225	0.581 %			
Benzene	2.2836 <sup>9</sup> (20°C)	2.294	0.455 %			
Chloro-benzene	5.708 <sup>9</sup> (20°C)	5.491	0.396 %			
1-Propanol	19.5 <sup>9</sup> (20°C)	19.558	0.297 %			
Acetone	20.7 <sup>9</sup> (25°C)	20.760	0.289 %			

dielectric constant of these samples decrease with increase in frequency. Further, it has been observed that there is a large enhancement in the  $\in'$  values of water saturated samples in comparison to the  $\in'$ values of the dry samples. Sengwa and Soni<sup>13</sup> also measured the dielectric constant  $\in$  ' and dielectric loss  $\in$  " of dry samples of clay, siliceous earth, fuller's earth, gypsum, lignite, calcite, tourmaline and magnesium rock of opencast mines of western Rajasthan, India, in the frequency range 100 Hz to 100 kHz and also at X-band microwave frequencies. It has been reported that the dielectric constant  $\in$ decrease with increase in frequency in the lower frequency region. The increase in  $\in'$  with decrease in frequency range from 100 kHz to 100 Hz is the common characteristic of the geological materials<sup>11</sup>. Further, it is observed that in this frequency range the dielectric constant  $\in$  ' and dielectric loss  $\in$  " of the soil increases vary rapidly with increase in moisture content in the soil. The dielectric constant and dielectric loss of wet soil are function of the water volume fraction in the soil-water mixture.

The formation of electric double layer (EDL) capacitances by the free charges build up at the



Fig. 5 — Measured values of (a) dielectric constant and(b) dielectric loss of Gandhinagar district wet sandy loam soil for various moisture contents with frequency

interface between the electrode surface and wet soil mixture is responsible for electrode polarization<sup>14</sup>. The Maxwell-Wagner phenomena occur due to the free charge build-up at the interfacing boundaries of soil-water-air, in wet soil medium, having different values of dielectric constant that results in nano capacitors. The logarithmic slope of frequency dependent  $\in'$  value of wet soils is close to-1 for the frequency below ~100 kHz, which indicates the leakiness of the EDL capacitances (blocking layers) to moving charges. Above 100 kHz, the slope decreases from-1 towards 0, but does not approach 0. the decrease in the slope of frequency dependent  $\in'$ values for wet soil, above 100 kHz (Fig. 5), suggests decrease in charge movement through the layers. Further, the value of  $\in'$  increases with increase in moisture content in the soil, which suggests the increase in the amount of dissolved salts and their mobility in the wet soil medium.

The variation of loss tan  $\delta$  of the Gandhinagar district sandy loam soil for various moisture contents in the frequency range from 10 kHz to 2 MHz is shown in Fig. 6. It is observed that at very low moisture content of  $Wv = 0.005 \text{ cm}^3/\text{cm}^3$ , a very small peak is observed at 1.262 MHz. As moisture content in the soil increases the value of tan  $\delta$  increases, which also show shift of  $tan\delta$  peak towards lower frequency side. Analogous behaviour has been reported in literature<sup>12</sup>. The shifting of loss peak towards lower frequency with increase in moisture content in the soil suggests the change in size of the orienting ions in the presence of pure water in the samples<sup>11</sup>. The peaks in the frequency dependent tan $\delta$ values of the soil for various moisture contents correspond to the electrode polarization (EP)



Fig. 6 — Calculated values of loss  $\tan \delta$  of Gandhinagar district wet sandy loam soil for various moisture contents with frequency

relaxation<sup>15</sup> frequency  $f_{EP}$ . The bulk material and the electrode surface polarization phenomena are separated by the relaxation frequency. When water is mixed with soil, the initially adsorbed cations with the soil particles defuse into soil water mixture adjacent to the soil particle surfaces and form electric double layers (EDL). The electrode polarization relaxation time  $\tau_{EP}$  for each soil sample can be obtained from the relaxation frequency  $f_{EP}$  for each peak in tan $\delta$  value as  $\tau_{EP} = (2\pi f_{EP})^{-1}$ . The  $\tau_{EP}$  is related with the charging and discharging time of EDL capacitance which represents the overall dynamics of the adsorbed ions on the electrode surfaces in the alternating electric field<sup>14,15</sup>, and are associated with the overall dynamics of the micro-aggregates. The calculated values of  $\tau_{EP}$ for each soil sample are presented in Table 4. The peaks in tan  $\delta$  spectra of wet soil (Fig. 6), correspond to the electrode polarization relaxation frequency  $(f_{\rm EP})$ , which separates the bulk material and EP phenomena. In the dielectric spectra of wet soil, the electrode polarization dominates the MW polarization<sup>14</sup> in the frequency range below  $f_{\rm EP}$ .

Figure 7 shows the variation of real and imaginary values of conductivity with variation in frequency for various moisture contents in the Gandhinagar district soil. It can be observed from Fig. 7 that for dryer soil  $(Wv = 0.005 \text{ cm}^3/\text{cm}^3)$  the frequency dependent real part of conductivity  $\sigma$  of the soil is very small at lower frequency ( $\sigma' \sim 1.74 \times 10^{-6}$  S/m at 10 kHz) and increases with increase in frequency ( $\sigma \sim 1.6 \times 10^{-4}$  S/m at 2 MHz). At higher moisture contents in the soil  $\sigma'$ increases slowly with increase in frequency. Analogous behaviour was observed by Sternberg and Levitskaya<sup>8</sup>, Sangwa *et al*<sup>12,13</sup>. The increase in the value of conductivity  $\sigma'$  of wet soil samples shows that the conductivity of soil-water matrix increases with increase in moisture content in the soil<sup>6</sup>. The imaginary conductivity  $\sigma''$  of the dryer soil ( $Wv = 0.005 \text{ cm}^3/\text{cm}^3$ ) is very small at lower frequency ( $\sigma'' \sim 5 \times 10^{-6}$  S/m at 10 kHz) and increases with increase in frequency ( $\sigma'' \sim 0.00045$  S/m at

Table 4 — Values of *dc* resistance  $R_{dc} = Z''_{mini}$ , corresponding Z', relaxation frequency  $f_{EP}$ , and electrode polarization relaxation time  $\tau_{EP}$ , for soil samples

Soil moisture cm <sup>3</sup> /cm <sup>3</sup>	$R_{dc} = Z''_{\min}$ ohm	Z' ohm corresponding to R <sub>dc</sub>	<i>f<sub>EP</sub></i> kHz	$ au_{EP}$ $\mu s$
0.097	99.49	1654	211.8	0.75
0.177	29.19	772	158.8	1
0.219	11.20	436	149.9	1.06

2 MHz). At given higher moisture content in the soil, the conductivity  $\sigma''$  decreases with increase in frequency up to certain minimum value after which it increases. It has been observed that the minimum value of  $\sigma''$  shifts towards lower frequency side as moisture content in the soil increases ( $\sigma'' \sim 0.0014$  S/m at 178.25 kHz for Wv = 0.097 cm<sup>3</sup>/cm<sup>3</sup>;  $\sigma'' \sim 0.00187$  S/m at 158.865 kHz for Wv = 0.178 cm<sup>3</sup>/cm<sup>3</sup>;  $\sigma'' \sim 0.0021$  S/m at 149.987 kHz for Wv = 0.219cm<sup>3</sup>/cm<sup>3</sup>). Further, it has been observed that the value of  $\sigma''_{min}$  increases with increase in moisture content in the soil. The effective conductivity in the wet soil is due to the presence of salts composed primarily of calcium <sup>16</sup> in the wet soil medium.

Figure 8 shows the variation of dc (ohmic) conductivity with moisture content in the soil. It has been observed that for the soil with moisture content of 0.005 cm<sup>3</sup>/cm<sup>3</sup> the dc conductivity is of the order of  $4\times10^{-7}$  S/m, which increases with increase in moisture content in the soil approaching saturation value of 0.0214 S/m at moisture content of 0.219 cm<sup>3</sup>/cm<sup>3</sup>. The relation between water content and dc conductivity is a strong function of soil type<sup>17</sup>. The charge carrier



Fig. 7 — (a) Real and (b) imaginary values of conductivity for variation with frequency for various moisture contents in the soil

density and the mobility of charges determine the ionic conductivity<sup>15</sup> ( $\sigma_{dc}$ ). The increase in ionic conductivity of wet soil medium represents the increase in number of mobile charge carriers introduced/produced with increase in moisture content in the soil. As explained by Dobson *et al*<sup>18</sup>, the adsorbed cations are tightly held with negatively charged dry soil particles, mainly clay. The excess amount of cations above the required value to satisfy the surface charge density  $\sigma$  of the soil particles is present in the dry soil as the salt precipitates. When water is mixed with soil, the salt precipitates dissolve in the water and increase the conductivity of the soil. Further, the adsorbed cations with the soil particles also diffuse into soil-water mixture adjacent to the soil particle surfaces, which also increases the conductivity of wet soil.

Figure 9 shows the complex impedance plane plot (Z'' against Z'') for various moisture contents in the soil. The frequency of the experimental points decreases while looking from right to left side on the arcs of the complex impedance plane plot. At lower moisture content of 0.005, the linear trend of Z''against Z' towards right results from the diffusioncontrolled impedance, also called Warburg impedance<sup>1</sup>. A diffused double layer polarization exists at soil-water interface, as well as at the electrode interface, that result in Warburg impedance. For higher moisture contents in the soil, the complex impedance plane plot has two arcs, separated by some minimum value of Z". The frequency corresponding to minimum value of Z'' in the plot for various moisture contents in the soil is exactly equal to the tan $\delta$  peak frequency  $f_{EP}$ . The arc on the right side of  $Z''_{min}$  (the lower frequency arc) for each soil sample corresponds to the electrode surface polarization effect and the arc on the left side of  $Z''_{min}$  (the upper



Fig. 8 — dc conductivity for various moisture contents (cm<sup>3</sup>/cm<sup>3</sup>) in the soil

frequency arc) for each soil sample corresponds to the bulk material effect. In complex impedance plane plots, the extrapolated intercept on the Z' axis corresponding to  $Z''_{min}$  is useful for the estimation of the dc bulk resistance  $R_{dc}$ , which is also denoted by  $R_b$ of the dielectric material  $^{16}$ , as represented in Table 4. In impedance spectroscopy, the  $R_b$  values are useful for the estimation of conductivity of the material of thickness l and surface area A, according to the relation  $\sigma_{dc} = l/(R_b A)$ . It can be observed from the graph that for the wet soil, the  $R_{dc}$  values decrease rapidly with increase in moisture content in the soil. The decrease in  $R_{dc}$  values represent decrease in the time taken by EDL for its charging and discharging, as observed by decrease in  $\tau_{EP}$  values with increase in moisture content in the soil (Table 4).

#### 4.2 Fertilized soils of Gandhinagar and Palanpur districts

Figure 10 shows the variation of complex permittivity ( $\in', \in''$ ) of the wet fertilized soils (Sandy loam soil of Gandhinagar district, and Sandy soil of Palanpur district) for various concentrations of different fertilizers [sulphate of potash (SOP) and zinc chelate] in the frequency range 10 kHz-2 MHz. It has been observed that the dielectric constant  $\in'$  and dielectric loss  $\in$  " of the wet fertilized soils decrease with increase in frequency from 10 kHz to 2 MHz. The dielectric constant  $\in'$  and dielectric loss  $\in''$ increases with increase in % concentration of fertilizer content in the wet soil. This behaviour is mainly dependent on the moisture content in the soil. There is approximately linear increase in  $\in'$  with percentage volume of organic and inorganic matter. This may be due to the fact that the added organic and inorganic



Fig. 9 — Plot of Z" against Z' for various moisture contents in the Gandhinagar district Sandy loam soil



Fig. 10 — Variation of dielectric constant and dielectric loss of the wet fertilized soils for various concentrations of different fertilizers

matter forms a chemical composition of low concentration along with the chemicals present in the soil. According to the theory of electrolyte, in the limit of low concentration the dependence of  $\in$  ' is approximately linear<sup>3</sup>. By adding fertilizer in the soil, the water holding capacity of soil improves. The dielectric permittivity of soil directly depends on the amount of moisture content present in the soil. The higher moisture content increases the dielectric constant of the soil. The dielectric loss  $\in$  " of soil increases with increase in % volume of fertilizer. The reason may be that  $\in$  " is a parameter which describes the motion of electric charge i.e. is a conduction phenomenon<sup>3</sup>. Certain dielectrics display conduction which arises from the actual charge transport (ionic conduction in electrolytes) rather than due to the displacement current. Such conduction is described by

volume conductivity which adds an additional term to the dielectric  $loss \in$  ". Due to this additional term, the dielectric loss increases with increase in fertilizer content in the soil.

Figure 11 shows the variation of complex permittivity ( $\in'$ ,  $\in''$ ) of the soils for various % concentrations of fertilizers [sulphate of potash and zinc chelate] at spot frequency of 2 MHz. It can be observed from Fig. (11a) that, for the variation of fertilizer SOP from 0.22% to 0.50% in the soil, the dielectric constant $\in$  increases from 6.12 to 8.99 and dielectric loss $\in$  increases from 60.4 to 90.4. For the variation of fertilizer (zinc chelate) from 0.28% to 0.20% in the soil, Fig. (11b) the dielectric constant  $\in'$  increases from 9.99 to 12.64 and dielectric loss  $\in''$  increases from 82 to 134.5. The variation of dielectric constant and dielectric loss of Palanpur district sandy



Fig.11 — Variation of dielectric constant and dielectric loss of the wet fertilized soils for various concentrations of different fertilizers at spot frequency of 2 MHz

soil for various % concentrations of sulphate of potash (SOP) in the soil at 2 MHz is shown in Fig. (11c). It can be observed that for the variation of fertilizer SOP from 0.24% to 0.62% in the soil, the dielectric constant  $\in'$  increases from 8.12 to 11.25 and dielectric loss  $\in$  " increases from 68.9 to 115.4. From Fig. (11d) it can be observed that for the variation of fertilizer zinc chelate from 0.08% to 0.18% in the soil, the dielectric constant  $\in$  ' increases from 8.10 to 9.94 and dielectric loss  $\in$  " increases from 63.2 to 98.65. The reason for large increase in  $\in$  " may be due to the fact that  $\in$  " describes the motion of electric charge i.e. is a conduction phenomenon<sup>3</sup>, which arises from the actual charge transport (ionic conduction in electrolytes), described by volume conductivity that adds an additional term to the dielectric loss  $\in$  ".

Figure 12 shows the variation of loss tan  $\delta$  of the wet fertilized soils for various concentrations of different fertilizers in the frequency range 10 kHz-2 MHz. It has been observed that a loss peak appears

near  $10^5$  Hz for the wet soils for all the % concentrations of fertilizers in the soils. In general, the loss peak is observed to shift towards lower frequency end with increase in fertilizer content in the soils.

The variation of real and imaginary conductivity of the wet fertilized soils (Sandy loam soil of Gandhinagar district, and Sandy soil of Palanpur district) for various concentrations of different fertilizers [sulphate of potash (SOP), and zinc chelate] in the frequency range 10 kHz-2 MHz is shown in Fig. 13. It has been observed that the real conductivity  $\sigma'$  of the soils increases slowly with increase in frequency. The real conductivity  $\sigma$ ' of the soils also increase with increase in % concentration of fertilizer in the soil. The imaginary conductivity  $\sigma$ " of the soils decreases with increase in frequency up to certain value of  $\sigma''_{min}$  after which it increases with increase in frequency. The value of  $\sigma''_{min}$  is observed to shift towards higher frequency end with increase in % concentration of fertilizer in the soils except that for



Fig. 12 — Variation of loss tan  $\delta$  of the wet fertilized soils for various concentrations of different fertilizers with frequency



Fig. 13 — Variation of real and imaginary conductivity of the wet fertilized soils for various concentrations of different fertilizers with frequency



Fig. 14 — Variation of *dc* conductivity of the wet fertilized soils for various concentrations of different fertilizers

SOP in Gandhinagar district sandy loam soil in which the value of  $\sigma''_{min}$  is observed to shift towards lower frequency end with increase in % concentration of SOP in the soil.

Figure 14 shows the variation of dc conductivity of the wet fertilized soils for various concentrations of fertilizers. It has been observed that the dc conductivity of Gandhinagar district sandy loam soil increases from  $\sigma_{dc}$  = 0.0035 to 0.0057 S/m for % solution variation of SOP from 0.22% to 0.50%. The dc conductivity of Gandhinagar district sandy loam soil increases from  $\sigma_{\rm dc}$  = 0.0052 to 0.009 S/m for % solution variation of zinc chelate from 0.08% to 0.20%. Further, it can be observed from Fig. 14 that the dc conductivity of Palanpur district sandy soil increases from  $\sigma_{dc} = 0.0045$  to 0.0099 S/m for % solution variation of SOP from 0.24% to 0.62%. The dc conductivity of Palanpur district sandy soil increases from  $\sigma_{dc} = 0.0034$  to 0.0067 S/m for % solution variation of zinc chelate from 0.08% to 0.18%. This represents that zinc chelate increases the dc conductivity of the soil more rapidly in comparison with SOP.

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