

# THE COMPLEX DIELECTRIC PROPERTIES OF PETROLEUM AND THEIR ADMIXTURES

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The complex dielectric constant and the related properties of petroleum and their mixtures have been analyzed using Chelsea Dielectric Interface System, a microprocessor based Digital Dielectric Spectrometer. Frequency response curves have been drawn for the frequency range 0.1Hz-1MHz, at 303.5 °K. The real and imaginary part of dielectric constant  $\epsilon'$  and  $\epsilon''$ , and dissipation loss factor 'tan  $\delta$ ' have been plotted as a function of frequency. From the study of dielectric data, a general formalism is obtained for the permittivity of mixtures as a function of measurable parameters of its mixing components.

**Key words :** Dielectric constant, Capacitance, Loss factor, Conductance.

## Introduction

The physical and chemical properties of liquids and their admixtures is a subject of interest for many years. With respect of their electrical response for such systems, there does not exist a single formula and a reliable way of calculating even the dielectric permittivity and loss factor, despite these are the basic parameters. The more elemental definition for the effective permittivity of a system results from considering the response of the medium to an electrostatic field (Johnshere 1977; Peon Fernandez and Plglesias 1994).

Any possible procedure may define the complex permittivity in terms of some macroscopic property of the medium. For example, let us consider an ideal parallel plate capacitor with capacitance 'C' in vacuum. If the inner space is filled with a mixture of 'N' pure species and ' $\epsilon_i$ ' being the permittivity of the components, ( $i = 1.....2-N$ ), the capacitance increases as (Robert and Colin-Pickup 1985; McLachlan 1992).

$$C_m = \epsilon_e C \dots \dots \dots (1)$$

where ' $\epsilon_e$ ' is the effective permittivity of overall mixture, which depends upon the exact spatial distribution of  $i$ 'th components. As another approach (Peon Fernandez and Plglesias 1994), it is possible to define the effective permittivity by averaging over the whole volume of the mixture as:

$$\epsilon_e = 1/V \int \epsilon dV \simeq \sum \epsilon_i V_i \dots \dots \dots (2)$$

where 'V' is the volume of the mixture and ' $V_i$ ' is the fractional volume occupied by the  $i$ 'th components. Eq (2), is just an upper limit of the effective permittivity for any state with the distribution of phases, independent of the detailed distribution. This corresponds to a parallel distribution in separate phase of the same volume fraction of the components, and is widely known as the ideal permittivity of the mixture (Peon Fernandez and Plglesias 1994).

In harmonically varying field of frequency ' $\omega$ ', the measured capacitance is a complex quantity (Robert and Colin-Pickup 1985):

$$C^*(\omega) = C'(\omega) - i C''(\omega) \dots \dots \dots (3)$$

The real part,  $C'(\omega)$ , corresponds to the ordinary capacitance and the imaginary part,  $C''(\omega)$ , represents the dielectric loss, or 'tan  $\delta$ ', such that the a.c current,  $I(\omega)$ , component is (Hill 1975):

$$I(\omega) = I_w C^*(\omega) Y(\omega) \dots \dots \dots (4)$$

where 'w' is the distance between the plates.

Eq 3, can be rewritten in terms of admittance,  $Y(\omega)$ , being a complex quantity indicating phase shift ' $\phi$ '

$$C^*(\omega) = Y(\omega) / I(\omega) \dots \dots \dots (5)$$

Similarly, the capacitance can also be calculated in terms of real and imaginary part of dielectric constant,  $\epsilon'(\omega)$  and as  $\epsilon''(\omega)$  (Robert and Colin-Pickup 1985):

$$C^*(\omega) = A / w [ \epsilon'(\omega) - I \epsilon''(\omega) ] \dots \dots \dots (6)$$

where, 'A' is the area and 'w' is the distance between the plates.

The molecular study of polar liquids and their admixtures (Srivastava *et al* 1992; Amunbhari *et al* 1993), by dielectric methods, is one of the most active area of research, since the pioneering work of Debye (Onsager 1936; Bottcher and Bordeniji 1978), who developed a mathematical relation to calculate the dipole moment, ' $\mu$ ' and  $\epsilon$  the dielectric constant:

$$\mu = \frac{\sqrt{[9 M K T (\epsilon - n^2)(2 \epsilon + n^2)]}}{\sqrt{[4 \pi N p \epsilon (n^2 + 2)]}} \dots \dots \dots (7)$$

where 'M' is the molecular weight, 'K' the Boltzman constant, 'T' the absolute temperature, 'n' the refractive index, 'N' the Avagadro's number, and 'p' is the specific gravity. However, his earlier theory neglected the intermolecular interactions and gives satisfactory results only for the gases at low pressure.

As an improvement over the Debye's theory, (Onsager 1936), treated the molecules of the dielectric substance as a polarizable point dipole at the center of spherical cavity of mole dimension in a continuous medium of static permittivity.

A better approximation was developed by (Bottcher and Bordeniji 1978):

$$\mu = \frac{0.0128 \sqrt{[MT (\epsilon - n^2) (2\epsilon + n^2)]}}{\sqrt{[p \epsilon (n^2 + 2)^2]}} \dots\dots\dots (8)$$

The above equation does not include the presence of ferroelectricity, because the effect of dielectric field due to polar molecules on their intermediate neighbours was not taken into account. It avoids one of the assumptions that the field due to a molecule in a spherical region is zero. Thus Eq 8 is only applicable to liquids without considering their density, as given by Debye's Eq 7.

But (Kirkwood 1939), obtained a mathematical expression for dielectric constant using the statistical methods by avoiding the force due to local field, including the short range intermolecular forces using statistical approach. The intermolecular interaction induces a hindrance to molecular rotation, that can be accounted by the introduction of the following equation:

$$\mu = \frac{0.0128 [M T (\epsilon - 2) (2\epsilon + 2)]}{g \quad 16 p \epsilon} - \frac{n^2 - 1}{n^2 + 2} \dots\dots\dots (9)$$

where, 'g' is a Kirkwood correlation factor, considered to be unity, 'T' the absolute temperature, 'n' the refractive index at optical frequencies.

This paper describes a general formalism to derive a theoretical approximation to calculate the effective permittivity of mixtures of petroleum, with kerosene in particular, which is complex in nature.

**Experimental**

*Measuring Instrument and Methodology:* The block diagram of Dielectric Spectrometer, used for this work, is adopted from the operating manual of the Chelsea Dielectric Spectromenta (Annon 1990), is presented in Fig. 1 and 2. The system consists of: Solatron 1255, Frequency Response Analyzer (FRA); a Chelsea Dielectric Interface (CDI) and a

personal computer. The system is capable of generating a.c. signal of frequency 10<sup>-2</sup> Hz to 10<sup>6</sup> Hz and a d.c. biasing of 0-15 V, is applied to an 3 V, a.c. signal. The FRA can analyze the dielectric properties such as: ε', ε'', tan δ, conductance G, and capacitance C\*(ω). The FRA generator can be set at a desired amplitude and frequency range. of the a.c output.

The measuring circuit, called the Frequency Domain Measurement (FDM), is also presented in Fig.2. The diagram comprises of an operational amplifier, and an I/V converter. The values of R<sub>m</sub> and C<sub>m</sub> are selected such that the voltage Vy lies in the range of 10mV to 1V. All other variables are controlled

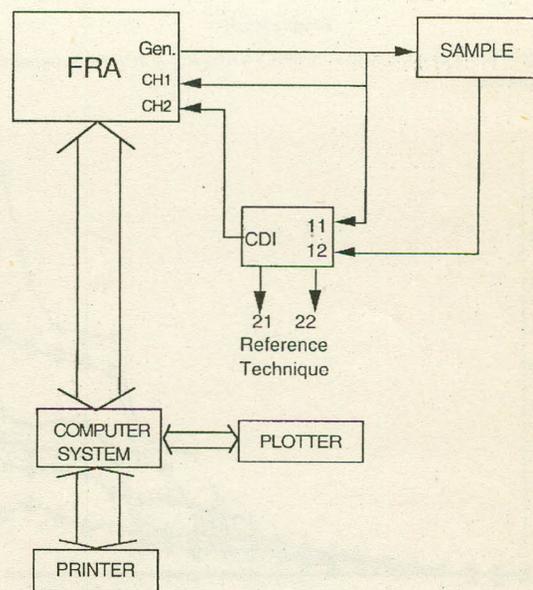


Fig. 1. Block diagram of dielectric spectrometer, (Chelsea Dielectric Interface and Frequency Response Analyser).

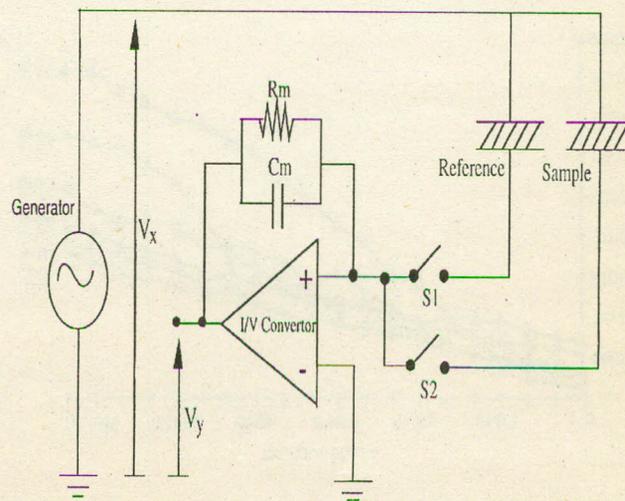


Fig. 2. Circuit diagram for the frequency domain measurements.

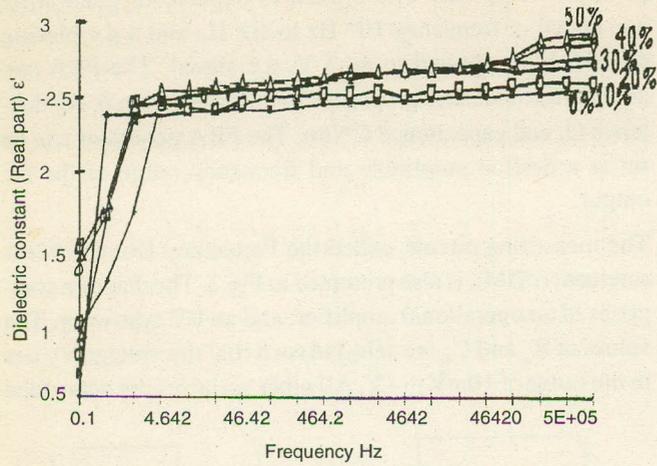


Fig 3. Plots of dielectric constant Vs frequency at various percentage of concentration.

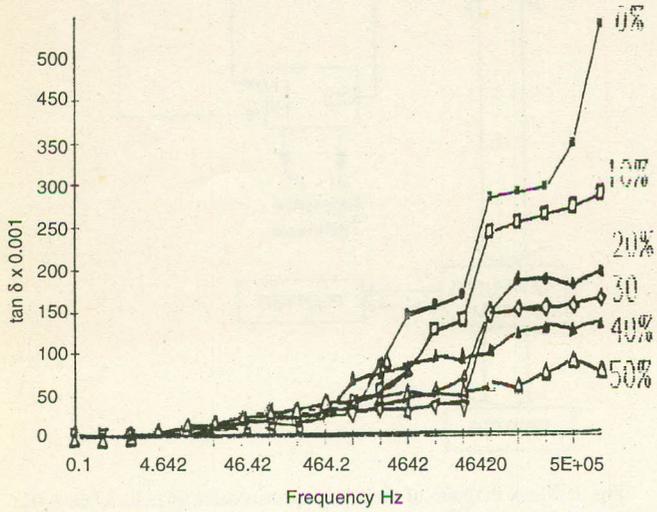


Fig 4. Plots of  $\tan \delta$  Vs frequency at various percentage of concentration.

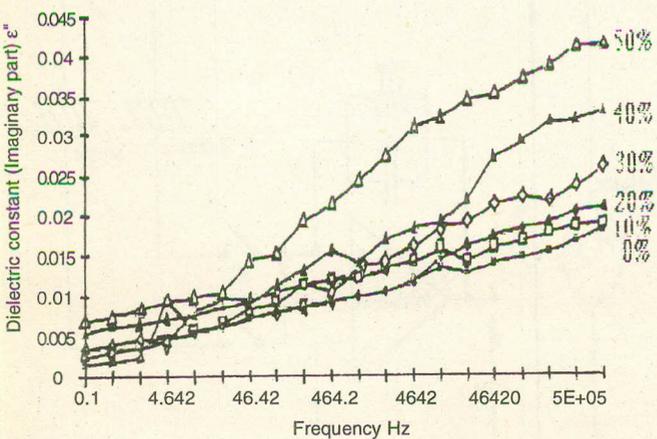


Fig 5. Plots of dielectric constant (IP) Vs frequency at various percentage of concentration.

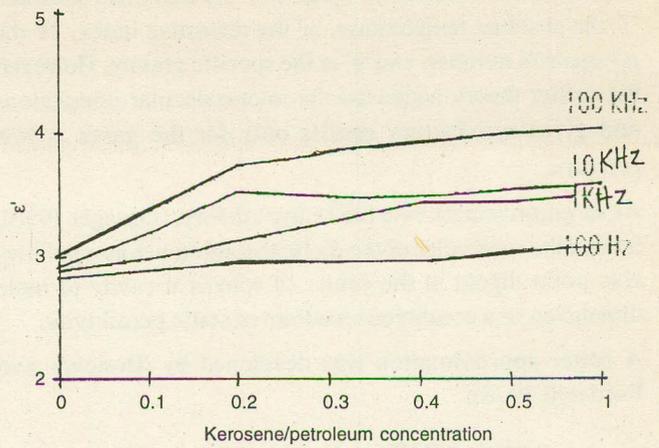


Fig 6. Plots of dielectric constant Vs concentration at various frequencies.

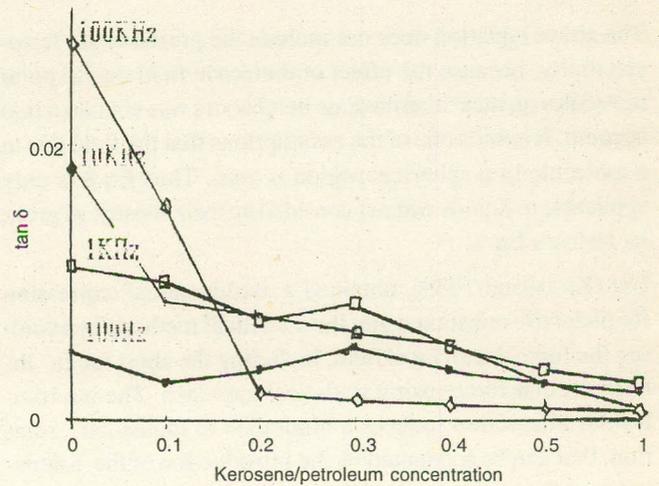


Fig 7. Plot of  $\tan \delta$  Vs concentration at different fixed frequency.

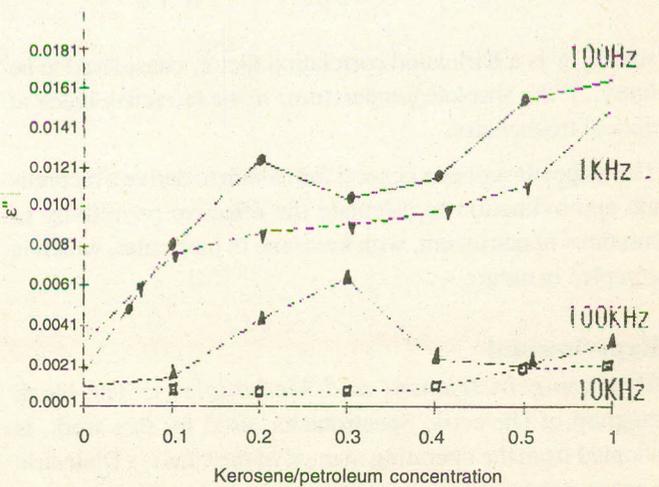


Fig 8. Plots of dielectric constant (Imaginary part) Vs concentration at different fixed frequencies.

by the interface unit. The switches  $S_1$  and  $S_2$  are set for the selection of other parameters.

Six samples were taken for the work described in this paper: the pure gasoline, and the gasoline mixed with 10%, 20%, 30%, 40%, and 50% kerosene. Each sample was subjected to measurement into a teflon cylinder of 1.2 cm dia, surrounded by two stainless steel hollow cylinders with metallic gauge on one end and a BNC socket soldered to the other end. The BNC output is connected to the liquid sample holder and to the Frequency Response Analyzer via a coaxial cable. The separation between the electrodes was kept at 0.6 cm. The observations were recorded up to four decimal points, with the accuracy of  $\pm 0.5\%$ , and the data was stored in the computer memory. The readings were taken with 50% relative humidity at 303.5 °K.

### Results and Discussion

The graph of Fig. 3, presents the real part of permittivity,  $\epsilon'$  at 0%, 10%, 20%, 30% 40% and 50% kerosene concentration in petroleum. It is observed that for each sample the permittivity increases almost linearly between 0.1 Hz to 4.642 Hz. At higher frequencies the permittivity remains constant upto 4642 Hz. This is because of the inherent behaviour of the sample at constant temperature. At higher frequencies, however, the permittivity shifts towards the higher values with the increase in concentration. The plots of imaginary part,  $\epsilon''$  Fig 5 are analogous to the curves of loss factor,  $\tan \delta$  Fig 4, since it is a ratio of  $\epsilon''/\epsilon'$ . Both curves show the least value of  $\tan \delta$ , between 0.1 to 10Hz which is negligible. With increase in impurity,  $\tan \delta$  also increases at higher frequencies. Like imaginary part,  $\tan \delta$  also shows various peaks, particularly at 4642Hz and 46420Hz, which may be due to the evaporation of samples at room temperature.

The curves have been plotted at four fixed frequencies, 100Hz, 1kHz, 10kHz, and 100kHz Fig 6-8. Fig 6 shows that with the increase in the concentration ratio, the  $\epsilon'$  slowly increases and becomes constant at a particular frequency. However,  $\epsilon'$  shift towards higher values with the increase in frequency. As the concentration ratio of kerosene/petroleum increases, the value of ' $\tan \delta$ ' decreases for pure kerosene, and approaches parallel to the X-axis Fig 7. This is due to the least evaporation nature of kerosene at a particular frequency. Fig 8 shows the imaginary part variation with increasing concentration, showing various peaks at different frequencies. The peaks are more prominent at 20% and 30% kerosene/petroleum mixture at particular frequencies.

The dielectric constants  $\epsilon'$  vs frequency Fig 9 for pure kerosene have also been drawn and analysed. The values are unstable between 0.1Hz and 4.642 Hz but become stable

at 50 Hz. In the plot of Fig.10,  $\epsilon''$  varies linearly. The graph of Fig.11 for ' $\tan \delta$ ' shows some peaks in pure kerosene due to evaporating nature and increases with the increase in frequencies.

The observed number of peaks are more in pure kerosene, as compared with the petroleum mixture. This is because of the dispersive nature of the sample. In case of the pure sample, the dipole moment  $\mu$ , can be calculated, using Eq. 9, by substituting the values for M, T, n and p.

The recorded data have been analyzed on the basis of existing model of the dielectric response of both ideal and real curves (Johnshere 1977) i e for commercial and pure petroleum and kerosene. In addition, the complex capacitance ' $C^*$ ' plots have been analyzed in (McLachlan 1992), most extensively due to their greater sensitivity in the variation of dif-

**Table 1**  
Permittivity of the liquids/solids, measured at two different frequencies (Robert and Colin-Pickup 1985)

S. No.	Liquids/Solids	Permittivity at 50 Hz	Permittivity at 1 MHz
1.	Petroleum (pure)	1.90	2.21
2.	Kerosene (commercial)	2.15	2.27
3.	Kerosene (Pure)	2.20	2.42
4.	Kerosene (Commercial)	2.45	2.55
5.	Transformer oil	2.25	2.47
6.	Lubricating oil	2.37	2.55
7.	Paraffin oil	2.25	2.35
8.	Vaseline oil	2.25	2.45
9.	Wax	2.37	2.60
10.	Grease	2.48	2.68

ferent dielectric parameters with frequency. The dispersive nature of the curves is more easily deduced from the study of the complex capacitance ' $C^*$ '.

The results described in this work, agree well with the results of earlier researchers (Sommerman 1964; Robert and Colin-Pickup 1985). Some of the typical results for the permittivity at 50 Hz and 1 MHz are also tabulate by Sommerman (Table 1) for comparison with the observed results.

### Conclusion

A general formalism may be obtained from the obereved data discussed above. It is possible to derive a theoretical approximation for the calculation of the effective permittivity of the

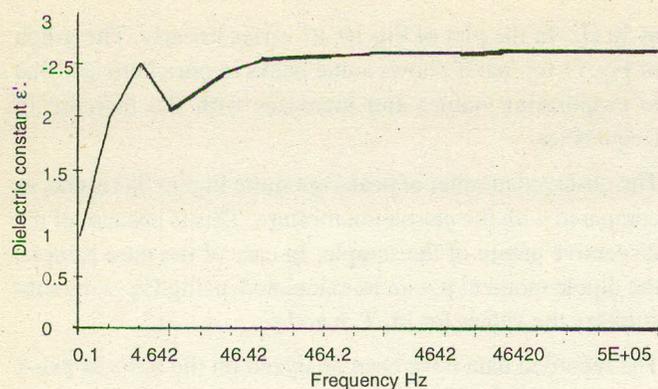


Fig. 9. Plot of dielectric constant (Real) Vs frequency for pur kerosene.

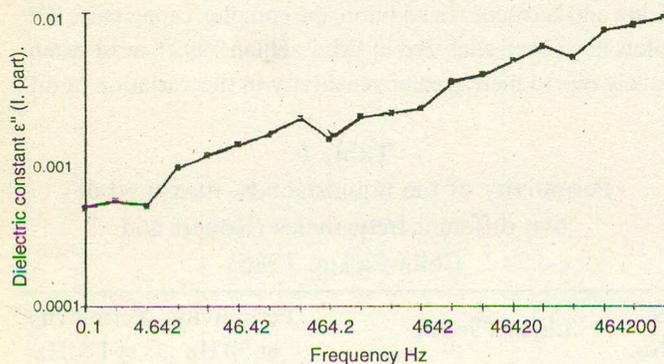


Fig. 10. Plot of dielectric constant (Imaginary part) Vs frequency for pure kerosene.

nonpolarizable liquid mixtures, petroleum in particular. It can be estimated that the curves of dielectric constant vs frequency shift towards higher ' $\epsilon'$ ' values with the addition of kerosene impurities.

The dielectric response obtained from this experiment shows that as the concentration ratio of the mixture increases the dielectric constant ' $\epsilon'$ ' also increases in addition, when the concentration ratio of the sample is increased, it becomes anisotropic in phase, which gives a decrease in loss factor. This experimental technique gives good resolution at high frequencies. At very low frequencies i.e. 0.01 Hz to 0.462 Hz the results become unstable. It is sufficient to use the difference between the dielectric constant and the square of the refractive index ' $n^2$ ', obtained at standard temperature, as a measure of permittivity, when the material of wide range of density mixtures are being compared. It is suggested that for highly polar liquids, as obvious from the calculated values of permittivity, the principal value of dipole moment ' $\mu$ ' can also be calculated. Furthermore, other data of the samples such as conductance  $G$ , refractive index ' $n$ ' molecular weight  $M$ , etc. can be used as an analytical tool, to analyze the measured amount of polar compounds present in the sample. Also, the presence of unsaturated resins, oxidized compounds and

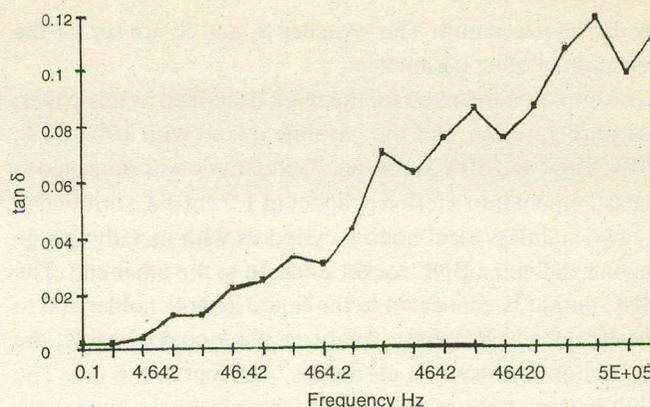


Fig. 11. Plot of tan d Vs frequency for pure kerosene.

kerosene impurities which may be present in fairly quantity, can be detected from such measurements.

It is sufficient to use the difference between dielectric constant ' $\epsilon'$ ' and the square of the refractive index ' $n$ ', obtained at the standard temperature as a measure  $\epsilon_p = \epsilon_i - n^2$ . When the material of wide range of density mixtures are being compared, it is better to compare the difference between the specific polarization and the refractive index ' $n$ ' of the material.

Finally, it can be summarised that, the study of dielectric properties of petroleum is important for two main reasons. Firstly, the accurate and precisely measured dielectric data is useful to detect the presence of impurity in gasoline mixture, and other constituents. Secondly, the dielectric constant of the petroleum and their products like kerosene mixture is utilized in components such as oil impregnated paper condensers and high voltage cables, which affects the electrical characteristics of the equipments. Since the petroleum is a mixture of long chain Hydrocarbon  $C_9-C_{11}$ , therefore, the properties may vary from sample to sample. Usually due to the difference in their prices the adulteration is locally made. Also the presence of unsaturated resins, oxidized compounds and kerosene impurities which may be present in fairly large quantity can be detected from such measurements.

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