*Pak J Sci Ind Res 2003* ***46*** *(2) 88-94*

# DIELECTRIC RELAXATION STUDIES OF SOME PRIMARY ALCOHOLS AND THEIR MIXTURE WITH WATER

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(Received 29 September 2000; accepted 1st June 2002)

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The complex dielectric constant of ethyl alcohol, methyl alcohol and 1- propanol and their mixtures with water of different concentration, (0 to 100% by weight ) at the temperature of 303K has been evaluated ,within the frequency range of (100KHz- 100 MHz). Moreover, the viscosity η of each alcohol and its mixture with water have been measured at this temperature. The dielectric properties have been evaluated by Hartshorn and Ward apparatus. The purpose of this work is to study the influence of aliphatic group, size and shape on the extent of hydrogen bonding and also to obtain the thermodynamic data on hydrogen bond formation in the pure liquid state and its mixture. The width of the semicircle plot determines the distribution of average relaxation time. Dielectric relaxation time in pure alcohols and their water mixture has been calculated from the respected Cole-Cole plot and dielectric data. A single relaxation time of 117.16ps has been obtained for the molecules of pure methanol, whereas, the dielectric data of prophyl alcohol which indicates the viscosity η of each alcohol and its mixture with water have been measured at the temperature 303 K. The dielectric properties in distribution of relaxation time, which is in good agreement with the Davidson-Cole representation. The molecules in liquid mixture within frequency range, the mixture has more than one relaxation time, leading to the shortening of main relaxation time as compared with the pure alcohol and broadening of the complex permitivity spectra. The dependence of the dielectric relaxation on composition shows a remarkable behavior. Results are discussed in the light of H-bonded molecules.

***Key words:*** Relaxation time, Complex dielectric constant, Cole-Cole plots, Dielectric spectroscopy

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## Introduction

The dielectric relaxation have been used to investigate the molecular structures and the interaction of mixtures at various frequencies and temperatures (Walter *et al* 1963). The results obtained have been evaluated in terms of parameters such as relaxation time, the activation energy ‘ ΔE’ and ‘g’ the correlation factor and the free energy of transfer ΔG of a solute from a solvent and the dipole moment μ in this field (Kirkwood 1939).

In recent years, there has been a substantial range of studies on the molecular dynamics of hydrogen bonded liquids, (Lyaschchen and Zasetsky 1998) which has provided the finer details of the molecular re-orientation process. This is also showing some uniform aspects of dielectric relaxation mechanism. Petong and Pottle (1999), have presented the dielectric relaxation studies of binary mixture of ethanol and *n*-hexanol at different composition and temperatures. Within their frequency range of measurements the dielectric spectra has revealed two relaxation time ( Krishnaji *et al* 1972). The relaxation time $\tau_1$ and $\tau_2$ for the two processes, one is smaller than the other, which were in pico sec. Smith *et al* (1998) has measured the dielectric relaxation in aqueous alcohol solutions. His main object was to study the hydrogen bond formation of alcohol solution and their dipole relaxation by measuring the complex permitivity of alcohol-water mixture over the temperature range 297-363 K. The mixture had a negative excess permitivity. Megnassan *et al* (1994) have given a theoretical expression for the measurement of dielectric constant of density fluctuated liquid mixture that was skewed towards higher mole fraction of water. According to their theory the dielectric constant ‘ε ‘ at each point of the curve has been considered as a function of number of molecules ‘N’ per unit volume at a constant temperature and pressure. Garg and Smyth (1965) and many other research workers have explained several type of equations predicting the dielectric constant of a compound of different liquids. Jenkins and Hedgetts (1990) and Garg and Smyth (1965) and Krishnaji *et al* (1972) have presented the dielectric data of long chain alcohols at microwave frequencies and they calculated more than one relaxation time. They attributed the long relaxation time τ at high frequency is due to the breaking of hydrogen bonds in a molecule. A study of dielectric response of water over the temperature range 273-323 K using a resonant microwave cavity as a probe reported by Johri and Roberts (1990) and Gara badu and Swain (1993). They proposed a general form of equation for more than two relaxation time in long chain alcohols.

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A major goal of complex permitivity measurements in a liquid is to obtain an understanding of rotational dynamics through analysis of both the absorption and dispersion spectra. By the relevant correlation function of molecular motion and the level of impurity detection through this technique.

*Theory of complex dielectric spectrum.* Spectra are analysed with respect to their frequency response curves, which may follow either a resonant law or relaxational law (Garg and Smyth 1965) indicating the nature of underlying physical process. For a relaxational process the dielectric susceptibilities obey the Debye equations.

The Debye equations are

$$\varepsilon' = \varepsilon_\alpha + \frac{\varepsilon_s + \varepsilon_\alpha}{1+\omega^2\tau^2} \ldots\ldots(1)$$

$$\varepsilon'' = \frac{(\varepsilon_s - \varepsilon_\alpha)\omega\tau}{1+\omega^2\tau} \ldots\ldots(2)$$

and

$$\tan\delta = \varepsilon''/\varepsilon' \ldots\ldots(3)$$

and the relaxation time is calculated by

$$\tau = 4\,\pi\eta N a^3 / RT \ldots\ldots(4)$$

Eqn. (4) was given by Debye where $\varepsilon_s$ and $\varepsilon_\alpha$ are the low frequency (static) and high frequency dielectric loss, the transition from high to low occurs at $\omega_0 = t^{-1}$, it tends to be broader than for resonance absorption. $\omega$ is the frequency, $\eta$, is the viscosity in centipoise, N is the avagadro number, R is the gas constant, a is the radius of the molecule and T is the absolute temperature. Also $\varepsilon'$ and $\varepsilon''$ are the real and imaginary parts of complex permitivity.

According to Debye and Hill (1954) the dielectric relaxation time is calculated from eq (4).

or

$$\tau = 4\pi\eta a^3 / k\,T \ldots\ldots(5)$$

Where, k is the Boltzman constant and is equal to $R_o/N_o$, and T is the absolute temperature in Kelvin. $N_o$ is avagadro number and $R_o$ is the gas constant. The lower aliphatic alcohols provide an ideal series of test compounds for such investigations. It is the purpose of this work to determine the dielectric constant $\varepsilon'$ and $\varepsilon''$ (loss) and to compare the relaxation time of the molecule also to study the influence of aliphatic group, size and shape on the extent of hydrogen bonding. Cole and Cole (1966) with the help of thermodynamic data, we can get information on hydrogen bond formation in the pure state and in water mixtures at temperature of 303 K within the frequency range 100kHz-100MHz, by using Hartshorn and Ward Bridge. Because of the probability of strong hydrogen bond formation between adjacent molecules, in alcohol, they present a complex and interesting picture in the liquid structure which have been extensively studied by a variety of methods.

## Experimental

The dielectric properties such as complex dielectric constant, $\varepsilon^* = \varepsilon' - \varepsilon''$ and the relaxation time $\tau$ for the three alcohols and their mixtures with water at a temperature 303°K have been evaluated within the frequency range 0.1MHz-100MHz. In this work the apparatus Hartshorn Ward with cylinderical dielectric cell was used. It consists of a pair of concave and convex plates. The instrument is based on a.c bridge principle, in which the output of a low impedance a.c signal generator is coupled through a small capacitor Cs with a parallel resonant circuit, which consists of tunning coils of different inductance L and at resonant frequency (Shakil and Yaqub 2000). A 50 $\Omega$ coaxial line with adapter was used to connect the Leader Sinosoidal Waves Generator at a frequency of 100KHz-1MHz with dielectric cell to the bridge terminals. Figure 1a & b are the block diagrams of this instrument used for the high and low frequency measurements. For frequencies range, above 10MHz , three sets of resonant coils were used. Frequency was measured with a frequency counter TRIO Japan Model FC-754A, within an accuracy of ±1%. The width of the resonance curves determines the change in the capacitance of the sample. The general characteristics and the limits of accuracy of the measurements obtained by this instrument is ±5% for the loss and ±1% for the dielectric constant. Highly purified and doubly distilled water were used in this work.The viscosity at different water concentration were measured by Happlier Falling Ball Viscometer.It is determined from the rate of fall of a sphere by employing this equation(6)

$$\eta = KT\,(ds - dl)/dt \ldots\ldots(6)$$

where K is a constant,ds is the distance covered by falling ball, dl is the length of the liquid column and dt change in time, within an accuracy of ±1% and the apparatus is calibrated for each time, against the viscosity of distilled water (standard). From the eqs (4) and (5) the relaxation time of a molecule in a liquid is determined. The dielectric cell used for this purpose was calibrated by using a standard liquid of known permitivity (distilled water).

*Purification of the chemicals.* All the chemicals (three alcohols ) were obtained from Merck Schuchardt of Analar grade

*Calcuation.* Relaxation time is calculated for eq (5) (Hill 1970).

where

$$\tau = 4\pi\eta N a^3 / RT$$

'$\eta$' is the viscosity in centipoise and 'a ' is the radius of the molecule =4.73136x$10^{-9}$meter, 'R' is equal to 8.3145 x$10^{9}$J mole$^{-1}$K$^{-1}$, N is the avagadro number=6.022x$10^{23}$ and T is the absolute temperature in Kelvin (Kaplan 1979).

*Experimental results*. For each of three samples of pure alcohols we have evaluated the dielectric constant $\varepsilon'$ with different frequencies (0.1MHz-100MHz), methanol (pure), ethanol (pure) and 1-propanol (A R Grade) are, in Fig. 2 of three primary alcohols. In these graph it is seen that the dielectric constant ($\varepsilon'$ ) of ethanol and 1- propanol decreases very slowly and showing a dispersive behavior over a wide range of frequency. Within a frequency range of 10-100MHz. These curves behave as constant over high frequency range. The calculated value of dielectric relaxation time for methanol (pure) is117.l6x$10^{-12}$sec. which is the lowest value. Figure. 3 shows the Cole-Cole plot for pure methyl alcohol and is asymmetrical distribution of relaxation time. As the frequency decreases, the corresponding values of dielectric loss approaches a maximum and than drops at the listed values of frequencies making a locus of semicircle plot. The Cole-Cole plot in Fig 4 ethanol (A.R Grade) and Fig. 5 is the loci of Cole-Cole plot for 1-propanol (pure) at 303 K. In both plots the dielectric constant increases with increase in imaginary parts. The calculated value of the relaxation time for this liquid is 232.07 ps.The $\varepsilon'$ was measured to ± 1% and $\varepsilon''$ (loss) were measured to within ± 5%. By evaluating the apparent value of viscosity which we have measured within ± 2.5 %. The Cole-Cole plot for the propanol + water mixture of each concentration between 0 to 100% (within a step of 10%) given in Table 3 and showing in Fig 6. Within the frequency range 0.1MHz 100MHz and at a specific temperature for each sample, we have tabulated, viscosity at 303K. The Cole-Cole plot, a complex dielectric loci for the pure sample of 1-propanol is showing in Fig 5. The calculated value of relaxation time for this liquid in pico second.

**Table 1**

Dispersion parameters for methanol+water mixture

| wt%methanol in$H_2O$ | $\varepsilon'$ | $\varepsilon''$ | Viscosity cp | Relax time $\tau$ sec |
|---|---|---|---|---|
| 0 | 78.410 | 0.350 | 0.862 | 103.44x$10^{-12}$ |
| 10 | 75.220 | 0.940 | 0.873 | 105.45x$10^{-12}$ |
| 20 | 71.350 | 1.150 | 0.877 | |
| 30 | 69.330 | 1.220 | 0.889 | |
| 40 | 62.110 | 1.410 | 0.899 | 123 .75x$10^{-12}$ |
| 50 | 55.250 | 1.499 | 0.912 | |
| 60 | 52.410 | 1.499 | 0.927 | |
| 70 | 46.220 | 1.405 | 0.945 | 144.76x$10^{-12}$ |
| 80 | 43.400 | 1.311 | 0.955 | |
| 90 | 39.330 | 0.955 | 0.975 | |
| 100 | 33.120 | 0.100 | 0.995 | 166.73x$10^{-12}$ |

Measured values of dielectric constant and (Real and imaginary parts) and their relaxation time and apparent values of viscosity for methonal + water mixture at 303 K and 100KHz (frequency).

## Results and Discussion

As shown in the Figs 3-6 from the measured values of the complex dielectric constant $\varepsilon^*$ of three primary alcohols (pure 99.99% AR Grade). We have measured only the values of real and imaginar parts ($\varepsilon'$ and $\varepsilon''$) at frequency of 100KHz to 100MHz.

**Table 2**

Viscosity of pure ethanol=0.9851cp

Dispersion parameters of ethanol+water mixture

| wt% ethanol in $H_2O$ | $\varepsilon'$ | $\varepsilon''$ | Viscosity cp | Relax time $\tau$ sec |
|---|---|---|---|---|
| 0 | 78.410 | 0.411 | 0.863 | 101.76x$10^{-12}$ |
| 10 | 67.220 | 1.352 | 0.871 | |
| 20 | 55.220 | 1.771 | 0.871 | |
| 30 | 51.330 | 1.822 | 0.782 | 102.45x$10^{-12}$ |
| 40 | 45.150 | 1.772 | 0.771 | 102.35x$10^{-12}$ |
| 50 | 41.420 | 1.712 | 0.734 | 103.76x$10^{-12}$ |
| 60 | 36.620 | 1.355 | 0.677 | |
| 70 | 32.490 | 1.000 | 0.633 | 104.450x$10^{-12}$ |
| 80 | 28.690 | 1.650 | 0.955 | 108.765x$10^{-12}$ |
| 90 | 26.110 | 0.351 | 0.975 | 112.750x$10^{-12}$ |
| 100 | 24.410 | 0.050 | 0.992 | 166.730x$10^{-12}$ |

Measured values of the dielectric constant (Real and imaginary parts) and their relaxation time and apparent values of viscosity for ethanol+water mixture at 303K and 100KHz (frequency)

**Table 3**

Viscosity of pure I-propanol=1.755cp. Dispersion parameters of 1-propanol+water mixture at 303K

| wt % propanol in $H_2O$ | $\varepsilon'$ | $\varepsilon''$ | Viscosity cp | Relax time $\tau$ sec |
|---|---|---|---|---|
| 0 | 78.410 | 0.352 | 0.896 | |
| 10 | 70.220 | 1.222 | 0.987 | |
| 20 | 64.440 | 1.455 | 1.118 | |
| 30 | 59.130 | 1.701 | 1.201 | |
| 40 | 55.230 | 1.720 | 1.211 | |
| 50 | 50.110 | 1.750 | 1.254 | 175.76x$10^{-12}$ |
| 60 | 46.270 | 1.760 | 1.333 | 187.77x$10^{-12}$ |
| 70 | 42.550 | 1.650 | 1.453 | |
| 80 | 36.170 | 1.350 | 1.666 | 232.07x$10^{-12}$ |
| 90 | 32.290 | 0.100 | 1.685 | 215.10x$10^{-12}$ |
| 100 | 26.550 | 0.250 | 1.703 | 217.75x$10^{-12}$ |

Measured values of dielectric constant (Real and imaginary parts) and their relaxation time and apparent values of viscosity for propanol+water mixture at 303K and 100 KHz (frequency).

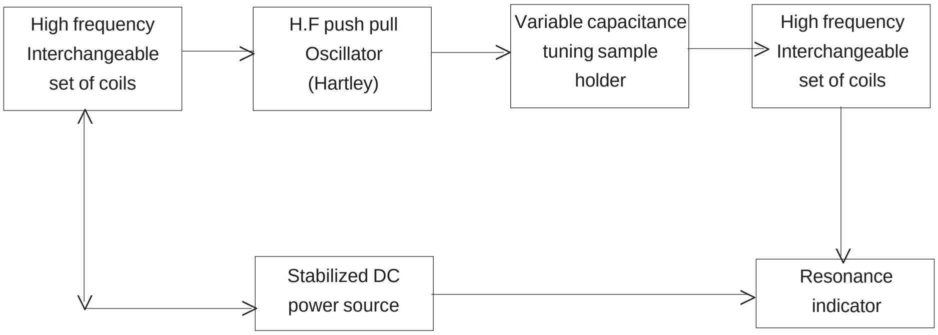

**Fig 1 (a).** Block diagram for the high frequency dielectric test jig 20-100 MHz.

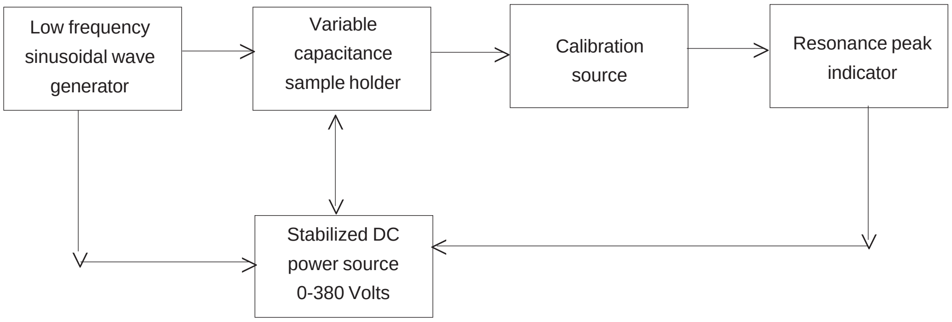

**Fig 1 (b).** Block diagram for the low frequency dielectric test jig 10 KHz to 20 MHz.

From Table 1-3, the viscosity data and their calculated value of relaxation time is calculated at the temperature of 303 K, it has been compared with their data from Merck(pure). The values of $\varepsilon'$ and $\varepsilon''$ for mixtures have been obtained from 0 to 100% alcohol by weight in water.

The study is based on Debye (1936) and Cole (1951) model and from their corresponding arc plot. The width of the Cole-Cole plot determines the symmetry in distribution of relaxation time. The following points are observed in the values of permitivity of the mixture shown Table 1-3.

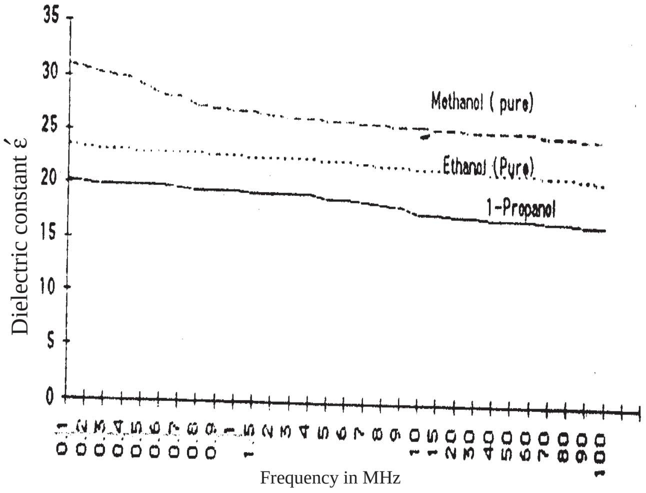

**Fig 2.** Diagram showing the variation of dielectric constant Vs frequency of alcohal samples.

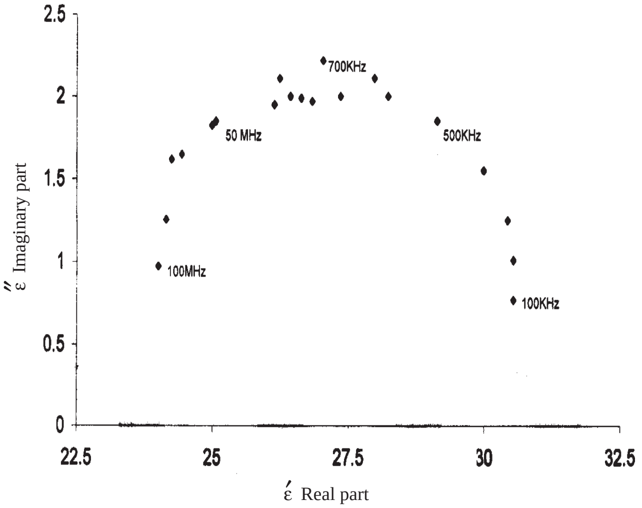

**Fig 3.** Cole-Cole plot pure methanol in the complex plane.

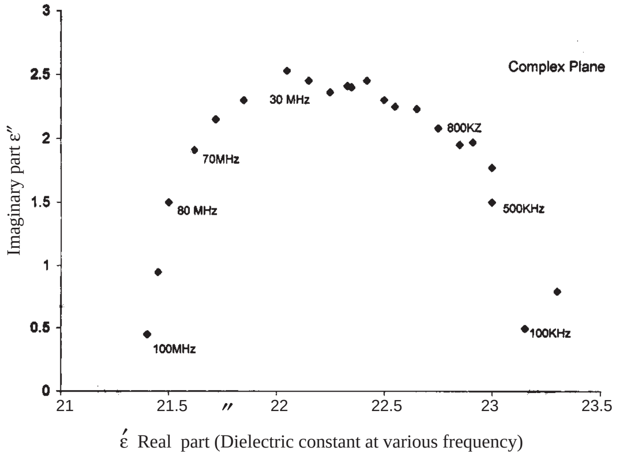

**Fig 4.** Cole-Cole plot for pure ethyl alcohal at 303K.

1. The dielectric constant $\varepsilon'$ decreases with increase in alcohol concentration in all three alcohol mixtures also viscosity increases at 303K and at a frequency of 100KHz. From Fig. 3 $\varepsilon''$ increases with the increase in frequency of measurement and than drops making a symmetrical (normal distribution) of the loss for the diluted sample.

2. Dielectric relaxation time increases with an increase in concentration in water showing wider molecular chain as in Table 3 for 1- propanol because of the aggregates of long chain molecules.

3. As it is seen that all alcohol molecules are arranged by means of hydrogen bond and each alcohol is connected with a member of an infinite chain, molecules are correlated in orientation only with member of its own chain.The solute and surrounding solvent molecules exert a mutual net attraction . Directed hydrogen bonds of the type existing in water mixture are assumed to link with each alcohol molecule.

4. Within the experimental errors, the relaxation time of the molecules in each three solvent increases with increasing alcohol concentration.

5. The static permitivity $\varepsilon_0$ of pure alcohol and their mixtures with water shows that there is a noticeable effect of permanent electric dipoles in orientation correlation.

*Analysis of the results from dielectric spectra.* The measurements of the dielectric relaxation time provides a means of investigating molecular motion and the intermolecular forces in liquids (Suryannarayana and Somasundaram 1960). In Debye model the microscopic relaxation time is directly proportional to viscosity of the surrounding medium, provided the orientation of molecules describe a sphere in the continuous medium. For a dilute aqueous solution, the dielectric constant is a linear function of concentration, the slope of Fig. 6 is $\delta$, being the characteristic of the solute and is independent of concentration at low temperatures (Johri and Roberts 1990).

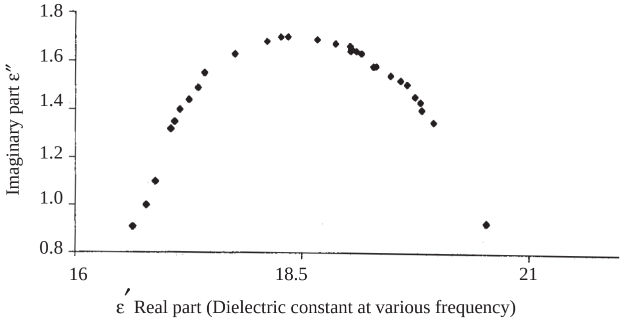

**Fig 5.** Cole-Cole plot for 1-propanol (pure) at 303 K, a complex dielectric locii.

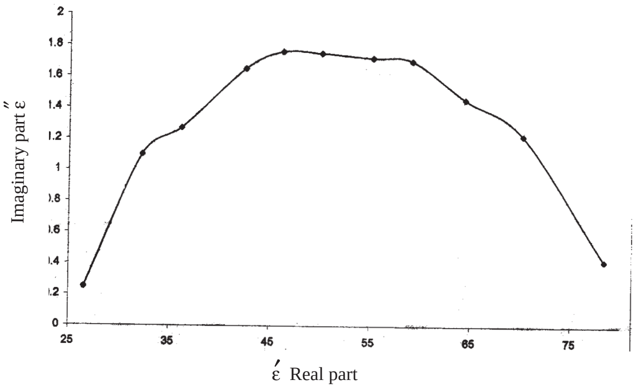

**Fig 6.** Cole-Cole plot for 1-propanol +water mixture in the complex plane at 303K.

According to Sciortino and Fornile (1989), in many liquids, the high frequency permitivity $\varepsilon_\alpha$ is quite sensitive to small impurities with free molecules like water. These impurities have very short relaxation time and relatively high specific permitivities. Alcohols can be thought of as organic derivative of water in which one of the hydrogen has been replaced by an organic group. As such, alcohol has nearly the same geometry as the water H-OH with bond a angle of $109^0$ (tetrahedral values) and the hydrogen in methanol is $sp_3$ hybridized, but alcohols are quite different from hydrocarbons. Also it is concluded that the molecules affect one another more strongly, on the application of a.c field which are depending upon their dipole moment.

According to Petong and Pottle (1999) and Jekko and Prasad (1970) the mechanism underlying the dielectric relaxation process occurs in this region involves the breaking and re-forming of hydrogen bonds with the re-orientation of dipole moment.

The real and imaginary parts of dielectric constant and the spectra of binary mixtures of different compositions of

1-propanol+water mixture at different concentration are showing in Fig 6.

## Conclusion

From the above dielectric spectroscopy of (pure) aliphatic alcohols and their mixtures with water. They have been observed that the relaxation time for the major dispersion region increases with the length of the carbon chains as mentioned by Hill (1954). As a result of measurements, it is obvious that the effect of polar molecules upon one another in dilute solution varies with its concentration and temperature. It is also clear from this work that the accurate determination of dielectric data, permitivity loss, viscosity and density over a wide range of temperature or frequency is necessary for such studies. These points are additive in conclusion.

1. Our results without adding any new information about orientation polarization are in good agreement with the previous workers (Jenkins and Hedgetts 1990).

2. If two polar mixtures ( water and alcohol ) their ‘g‘ called the Kirkwood –Correlation factor (Kirkwood 1939) which is a parameter and is a direct measure of the extent of molecular association. As the mixture is made diluted, the dilectric constant becomes higher, since the dipoles become free of each other.

3. The observed skewness in the complex plane (Fig.5, for the propanol + water mixture is probably caused by the uneven distribution of relaxation time between the limiting values. The relaxation time for pure liquids are more evenly distributed than in their mixtures. This occurs in a pure liquid which donot form a complex association with water.

4. As a result of measurements, it is obvious that the effect of polar molecules upon one another in dilute solution varies with its concentration and temperature.

5. It may be noted that the reported values of relaxation time vary considerably among different workers. If we plot $\tau$ against different temperatures of observations we will get a set of linear curves (Hugo 1969).

6. In many materials, the high frequency permitivity $\varepsilon_\alpha$ is quite sensitive to impurities of small, free molecules like water. These impurities have very short relaxation time and relatively high specific permitivities. In this sense the detection of impurity by such measurements can be helpful. This paper describes an analysis and interpreptation of some experimental results by the use of function for the distribution of relaxation time in mixture.

It is concluded, from the above studies that molecules in primary are arranged in chain by means of hydrogen bonds and each molecule is a member of an infinite chain and the relaxation is affected.

## References

Ahmad S S, Yaqub M 2001 Dielectric relaxation studies of some aromatic hydrocarbons and their naphthene mixture. *Pak J Sci & Ind Res* **44** (1) 5-11.

Cole R H, Cole K S 1941 Dielectric relaxation in water. *J Chem Phy* **9** 341-344.

Debye P 1936 *Polar Molecules,* Chemical Catalog. Co Inc. N.Y pp 97-110.

Garg S K, Smyth C P 1965 Microwave absorption and molecular structure in liquids *LXII.* The three dielectric dispersion regions of the normal primary alcohols. *J Phy Chem* **69** 1294-1301.

Garabadu K, Swain B B 1993 Dielectric response of some long chain alcohols in non polar solvent. *Indian J Pure and App Phy* **10** (31) 741-743.

Hill N E 1970 The temperature dependence of the dielectric properties of water. *J Phy Chem Solid State* **3** (10-12) 238-240.

Hill N V 1954 Relaxation phenomenon in liquids. *Nature* **67B** 149-154.

Hugo F F 1969 The measurement of dielectric in the time domain. *J Phy Chem* **73** (3) 616-631.

Jakkeo K E, Prasad K K 1970 Dielectric relaxation in some mixture of nitriles. *Transaction of Faraday Society* (23) 817-823.

Jenkins S, Hedgetts T E, Clarke R N1990 Dielectric measurements on reference liquids using automatic network analyzer and calculable geometries. *Measurement Science and Technology Pak* (1) 691-99.

Johri G K, Roberts JA 1990 Study of the dielectric response of using a resonant microwave cavity as a probe. *J Phy Chem* **94** 7386-7399.

Kaplan I 1979 *Nuclear Physics.* Addison-Wesley Publishing Co, Inc.Massachusetts, pp-212-213.

Kirkwood F 1939 Dielectric polarization in liquids. *J Chem Phy* **7** 77-80.

Krishnaji, Vinod K, Agarwal, Pardeep K 1972 Dielectric relaxation mechanism in some alkane thiols. *J Chem Phy* **56** (10) 5034-39.

Lyaschchen A K, Zasetsky A Yu 1998 Complex dielectric permitivity dibenzothiophene, triphenylphosphine and triphenylarsine. *J Am Chem Soc* **62** 773-777.

Magnessan E D, Goff L E, Proutiere A 1994 Dielectric constant and density variations in pure liquids and their theoretical relation comparison with experiments. *Journal of Molecular Liquids* **50**, pp37-50.

Petong P, Pottle R 1999 Dielectric relaxation of H-bond liquid mixture of ethanol and *n*-hexanol at different composition and temperatures. *J Phy Chem A* **31** (103) , 6114-6121.

Sciortino J, Fornile S L 1989 Hydrogen bonds cooperativity in simulated water, time dependence of pair interaction. *J Phy Chem* **90** (5) (2786-90).

Smith R L Jr, Lee SB, Kumari H, Arai K 1998 Relative permitivity and dielectric relaxation in aqueous alcohol solution. *Fluid Phase Equilibrium* **1-2**, 315-322.

Sugget A, Amackness R, Tait MJ 1970 Dielectric relaxation studies by time domain spectroscopy. *Nature* **228** 456-457.

Suryannarayana C V, Somasundaram K M 1960 Dielectric behavior at the miscibility point in methanol-water-benzene system. *Ind J Sc Ind Res* **19B** 375-377.

Walter D, Lowell W B 1963 Dielectric constant of hydrogen bonded liquids IV. Studies of Homologous Neo-Alcohol. *J Chem Phy* **43** (10) 257-266.