



HIGH FREQUENCY DIELECTRIC RELAXATION STUDY OF DIHYDRIC ALCOHOLS USING A TDR TECHNIQUE

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Abstract -The time domain reflectometry (TDR) technique was used to measure the complex dielectric permittivity spectra of dihydric alcohols at various temperatures in the frequency range from 10 MHz to 30 GHz. The complex permittivity spectra of dihydric alcohol show the Cole-Davidson type of relaxation. The dielectric parameters such as static dielectric constant and relaxation time are determined from the complex permittivity spectra using the nonlinear least squares fit method. The orientation of electric dipoles in diols was studied using the Kirkwood correlation factor.

Keywords -Complex permittivity spectra, Dielectric constant, Relaxation Time, Time domain reflectometry, Kirkwood correlation factor.

I. INTRODUCTION

In recent years, dielectric spectroscopy has become a crucial tool for studying the interactions in systems with hydrogen bonds, such as alcohols. In order to learn more about molecular reorientation, dipole arrangements, hydrogen bonding, polarization strength, network formation, and kinetic depolarization characteristics of liquids across a wide frequency range the dielectric spectroscopy technique is useful [1-2]. There's a lot of curiosity on investigating the dielectric relaxation properties of diols [3-5] because they play a significant role in various chemical and biological processes and resemble water in their dielectric behavior [5-7]. Diols are organic compounds in which two hydroxyl groups are present as a result; Intermolecular hydrogen bonding can be significantly affect how these chemicals dissolve

in liquids. Furthermore, it has a substantial effect on the physical properties of molecules.

The present investigation is carried out on the dielectric relaxation studies on dihydric alcohols at various temperatures using a TDR method in high frequency range (10 MHz to 30 GHz). The dielectric parameters and Kirkwood correlation factors have been calculated.

II. EXPERIMENTAL DETAILS

Chemicals

The chemicals under study (1,5-pentanediol, 1,4-butanediol and 1,3-propanediol) are purchased from Merck specialties private Ltd. with 99% purity.

Experimental

The complex permittivity spectra (CPS) of all three diols were measured at various temperatures using the TDR method with frequencies ranging from 10 MHz to 30 GHz. The oscilloscope, a two-channel sampling module 80E10B equipped with a Tektronix DSA 8300 digital serial analyzer, was used. The experimental setup is shown in Fig.1 and done accordingly as mentioned in reference [8]. The temperature bath is used along with digital thermometer to maintain the constant temperature.

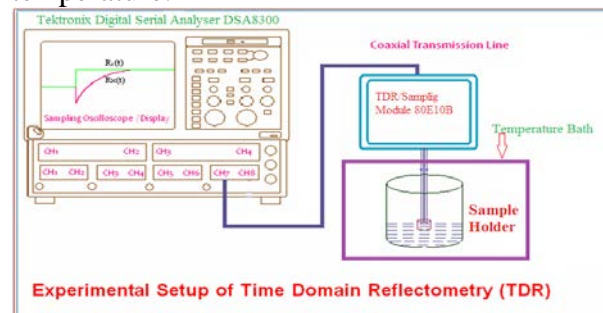


Fig. 1 The Time Domain Reflectometry experimental setup.

III. RESULT AND DISCUSSION

High frequency CPS for all three diols are shown in Fig.2 at 25°C which shows how dielectric permittivity and dielectric losses are systematically varies with respect to frequency ranging from 10 MHz to 30 GHz. From Fig.2 It is noted that the dielectric permittivity (ϵ') value decreases as the frequency increases this is due to the dielectric dispersion phenomenon whereas, the dielectric loss (ϵ'') shifted towards lower frequency as the number of carbon atoms increases this suggest the increase in relaxation time with increase of number of carbon atoms and the dielectric loss approaches maximum in the frequency range 0.01GHz to 1GHz.

To calculate the dielectric parameters (ϵ_0 , τ) the experimentally obtained CPS $\epsilon^*(\omega)$ where fitted into Havriliak-Negami equation [9]:

$$\epsilon^*(\omega) = \epsilon_\infty + \frac{(\epsilon_0 - \epsilon_\infty)}{[1 + (i\omega\tau)^{1-\alpha}]^\beta} \quad (1)$$

All the diols under study shows the Cole Davidson type distribution where $\alpha=0$ and β is ranging from 0 to 1. Therefore the CPS where fitted into Cole Davidson model [6].

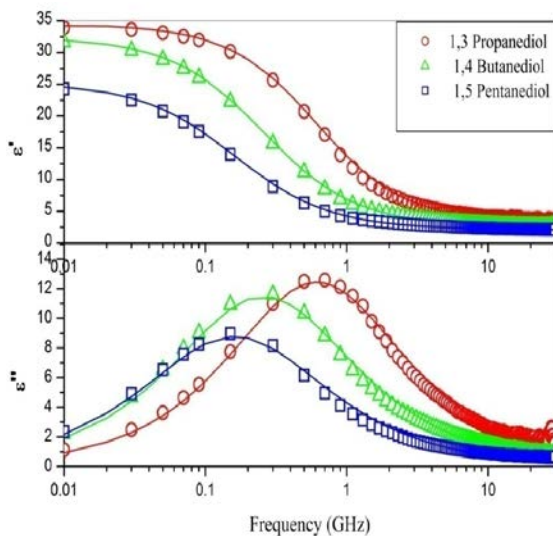


Fig.2 Complex dielectric permittivity spectra for all three diols at 25°C

Dielectric parameters (ϵ_0 & τ):

The calculated values of dielectric parameters (ϵ_0 , τ) for all three diols at various temperatures are reported in table1 and are agrees very well with those reported in the literature [3-6]. The static dielectric constant (ϵ_0) of liquids depends on temperature, number of carbon atoms present in the molecules and dipole moment. Table 1 show that the ϵ_0 decreases with increasing chain length and carbon atom number in diols, indicating that the molecular association reduces with increasing chain length. This phenomenon

is also seen in monohydric alcohols and amines [10]. For all three diols, the static dielectric constant (ϵ_0) was found to be affected by temperature; a decrease in temperature was shown to enhance orientation polarisation and H-bond strength. However in case of 1,4 butanediol the decrease in ϵ_0 at 10°C was due to the solidification of butanediol [11].

Table 1 show that the relaxation time in diols increases from propanediol to pentanediol. This might be because the increasing chain length of diols creates greater obstruction to molecular rotation, causing the molecule to relax slowly [10]. The relaxation time decreases as temperature rises, owing to an increase in the effective length of the dipoles [5].

Table 1.The dielectric parameters for all three diols at various temperatures.

The bracketed terms denote uncertainties in last significant digits i.e. 34.40(15) means

	1,3-Propanediol			
	25°C	20°C	15°C	10°C
ϵ_0	34.65(15)	35.16(21)	36.42(14)	37.12(13)
τ (ps)	315.6(33)	400.4(21)	463.9(44)	530.6(13)
	1,4-Butanediol			
ϵ_0	32.60(9)	33.17(10)	34.44(10)	10.53(20)
τ (ps)	616.7(52)	702.1(64)	845.2(77)	1068.8(47)
	1,5-Pentanediol			
ϵ_0	25.44(12)	27.45(14)	28.40(16)	30.43(19)
τ (ps)	986.4(13)	1211.2(17)	1376.7(21)	1656.2(25)

34.40±0.15

Kirkwood correlation factors (g):

The 'g' can offer information on the orientation of electric dipoles, molecule orientation, and liquid structure in a pure polar liquid. The strength of intermolecular H-bonding is measured by the deviation of g from unity. The following equation is used to calculate the value of g for a pure liquid [12].

$$\frac{(\epsilon_0 - \epsilon_\infty)(2\epsilon_0 + \epsilon_\infty)}{\epsilon_0(\epsilon_\infty + 2)^2} = g\mu^2 \frac{4\pi N\rho}{9kTM} \quad (2)$$

The symbols T, N, k, M, ρ , μ are temperature in Kelvin, Avogadro number, Boltzmann constant, molecular weight ,density and dipole moment of pure liquid in gaseous phase respectively. The calculated values of 'g' along with corresponding dipole moment is gas phase are reported in table 2 and agrees very well with those reported in the literature [3-6]. The value of 'g' greater than one indicates the parallel

orientation of electric dipoles. From table 2 its observed that the parallel orientation of electric dipoles attained more easily in 1,3 propanediol as compared to other two diols.

Table 2. Dipoles moments of all three diols and Kirkwood correlation factor (g)

Compound	Dipole moment (μ) Debye	Kirkwood correlation factor (g)
1,3-Propane diol	2.94 D	2.35
1,4-Butanediol	2.60 D	2.31
1,5-Pentane diol	2.45 D	2.19

IV. CONCLUSION

Using the TDR method, the CPS of the three diols is obtained in the frequency range of 10 MHz to 30 GHz. All the diols under study shows the Cole-Davidson type dispersion. At different temperatures, the values of the relaxation time and static dielectric constant are reported. In diols, the dielectric constant decreases with increasing carbon atom chain length, which indicates the decreases in molecular association. The parallel orientation of the electric dipole is indicated by a Kirkwood correlation factor value greater than one, which will decrease with an increase in the number of carbon atoms.

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