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DIELECTRIC RELAXATION STUDY ON TWO ISOMERS OF BUTANEDIOLS

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ABSTRACT

The dielectric relaxation studies on the two isomers of butanediols have been done by using the time domain raflectometry (TDR) technique at various temperaturs. The complex permittivity spectra of 1, 3 and 1, 4-butanediol have been measured in the frequency range from 10MHz to 50GHz.The complex permittivity spectrum shows the Cole-Davidson type relaxation. From the complex permittivity spectra the dielectric parameters such as static dielectric constant and relaxation time are obtained using the nonlinear least square fit method. The orientation of electric dipoles was studied using the Kirkwood correlation factor for both the butanediols.

KEYWORDS: *Complex permittivity spectra, Time domain reflectometry, static dielectric constant, relaxation time and Kirkwood correlation factor.*

1. INTRODUCTION

Understanding molecular interactions in hydrogen-bonded liquids like diols can be done by using the dielectric relaxation spectroscopy. The dielectric relaxation behaviour of diols is of great interest because of presence of two hydroxyl group in a molecule, the solution chemistry of these compounds can be strongly influenced by the intermolecular and intramolecular hydrogen bond formation. It also plays an important role in the physical properties of the molecules.[1-2] The dielectric permittivity of a liquid is an important property because it provides valuables information on the intermolecular interactions. Butanediols are four carbon diols with many industrial and biological applications.[1-4] In last few years several investigation were done on the diols to understand dielectric behaviour and hydrogen bond formation in presence of polar and non polar solvents.[1-6]

The present investigation is done on the temperature dependent dielectric relaxation studies of two isomers of butanediols in the frequency range 10MHz to 50GHZ using a TDR technique to understand the effect of position of hydroxyl group on the dielectric properties. The static dielectric constant, relaxation time and Kirkwood correlation factors have been determined from the complex permittivity spectra.

2. Experimental details

The chemicals 1,3 and 1,4-butanediol where purchased commercially with 99% purity from Merck specialties private Ltd. and used without further purification. The complex permittivity spectra of both butanediols were measured in the frequency range from 10MHz to 50GHz using the time domain reflectometry (TDR) technique at various temperatures. A Tektronix digital serial analyzer DSA 8300 sampling oscilloscope with dual channel sampling module 80E10B was used. The experimental setup is done as mentioned in reference[7] and shown in Fig.1.

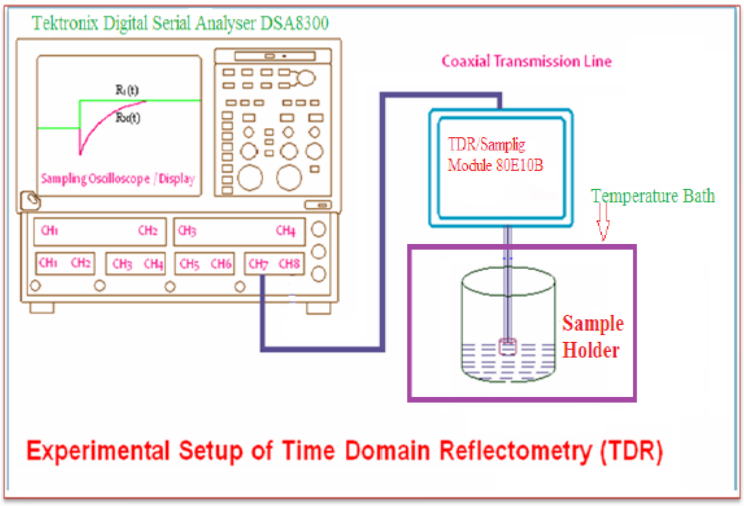

Fig. 1: Experimental Setup of TDR.

3. RESULT AND DISCUSSION

The fig.2 shows the Cole-Cole (ε’ vs. ε”) plot for both butanediols. From fig.2 it is observed that the Cole-Cole plot is not exact semicircle it is a semicircle with a skewed arc. Fig.3 represents the frequency dependent complex permittivity spectra of butanediols at 25^{o}C which represent the systematic variation in dielectric permittivity and dielectric losses with respect to frequency ranging from 10MHz to 50GHz.To calculate static dielectric constant (ε_0), dielectric permittivity at high frequency (ε_∞) relaxation time (τ) and distribution parameters α and β the experimentally obtained complex permittivity spectra $\varepsilon^*\left(\frac{1}{16}\right)$ where fitted into Havriliak-Negami equation[8]:

$$\varepsilon * (\omega) = \varepsilon_\infty + \frac{\varepsilon_S - \varepsilon_\infty}{[1+(j\omega\tau)^{1-\alpha}]^\beta} \quad ....(1)$$

The diols under study shows the Cole Davidson type of relaxation where the distribution parameters α=0 and β is ranging from 0 to 1. Therefore the complex permittivity spectra fitted into Cole Davidson equation by using least square fit method.[9] It is observed from Fig.2 that the dielectric permittivity (ε’) value decreases for both the diols as the frequency increases this is due to the dielectric dispersion phenomenonwhereas, the dielectric loss (ε”) shifted towards lower frequency incase of 1,3 butanediol this suggest increase in relaxation time.

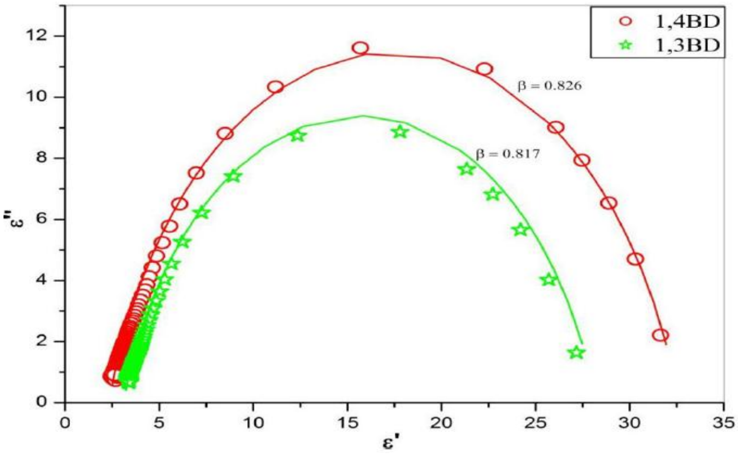

Fig. 2: The Cole-Cole (ε’ vs. ε”) plot for 1, 3 and 1, 4 butanediols at 25^{0}C.

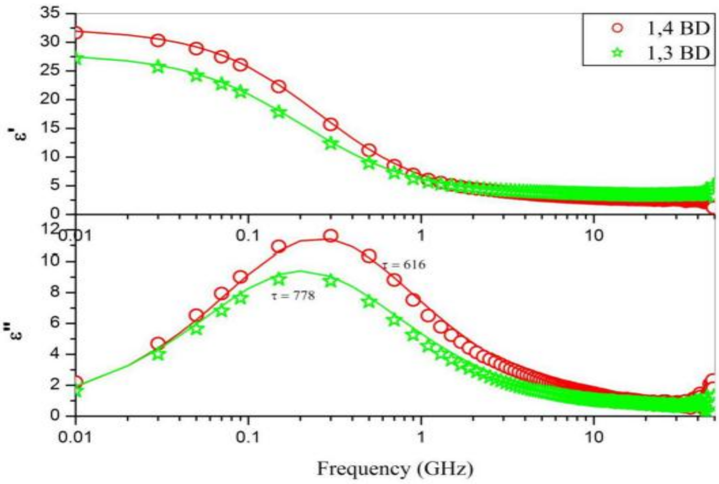

Fig. 3: Frequency dependent complex permittivity spectra of 1,3 and 1,4 butanediols at 25^{o}C.

3.1 Static dielectric constant (ε_0) and relaxation time (τ)

The static dielectric constant and relaxation time values of butanediols at various temperatures are reported in table1 and are agrees very well with those reported in the literature.[1-5] The dielectric constant of liquids depends on position of functional group, dipole moment and temperature. From table 1 it is observed that if the position of hydroxyl group is changed it affects the dielectric constant of liquid. The dielectric constant of 1, 3 buatnediol less than that of 1, 4 butanediol, which indicates the molecular association decreases with an position of hydroxyl group. The dielectric constant of diols decreases with increase in temperature indicating a decrease in orientation polarization and H-bond strength. However in case of 1, 4 butanediol the decrease in dielectric constant at 10^0C was due to the solidification of butanediol.[10]

From table 1 it can be observed that in butanediols relaxation time changes with the position hydroxyl group this is may be due to the change in viscosity causes more hindrance to molecular rotation due to which molecule relaxes slowly.[7] With the rise in temperature, the relaxation time decreased this is due to the increase in effective length of the dipoles with rising temperature.[5]

Table 1: The dielectric relaxation parameters of 1, 3 and 1, 4 butanediols.

Dielectric parameters	**1,3 Butanediol**			
	25^0C	**20^0C**	**15^0C**	**10^0C**
ε_0	28.21(11)	28.62(14)	29.30(14)	30.63(23)
τ (ps)	778.4(94)	917.1(13)	1104.5(15)	1206.8(28)
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)

Numbers in brackets denote uncertainties in the last significant digits i.e. 28.21(11)means 28.21± 11.

3.2 Kirkwood correlation factors (g)

The information regarding the liquid structure, molecular orientation and orientation of electric dipolesin pure polar liquid can be provided by the Kirkwood correlation factor (‘g’).The strength of intermolecular H-bonding is measured from the deviation of Kirkwood correlation factor g from unity. The value of g for pure liquid is obtained by following equation.[11]

$$\frac{(\varepsilon_0-\varepsilon_\infty)(2\varepsilon_0+\varepsilon_\infty)}{\varepsilon_0(\varepsilon_\infty+2)^2}=g\mu^2\frac{4\pi N\rho}{9kTM} \qquad \text{…………..(2)}$$

The symbols ρ= density, N= Avogadro number, k= Boltzmann constant, T= temperature in Kelvin, M= molecular weight and μ= dipole moment of pure liquid in gaseous phase respectively. The obtained values of Kirkwood correlation factor ‘g’ for both the butanediols along with corresponding dipole moment in gas phase are $g_{1,3BD}=2.19$,$g_{1,4BD}=2.35$ $\mu_{1,3BD}$=2.48, $\mu_{1,4BD}$=2.60 respectively and agrees with reported literature.[2] The value of ‘g’ greater than one indicates the parallel orientation of electric dipoles. From Kirkwood correlation factor ‘g’ its observed that the parallel orientation of electric dipoles attained more easily in 1,4 butanediol then that of 1,3 butanediol.

4. CONCLUSION

The temperature dependent dielectric relaxation study of 1,3 and 1,4-butanediols have been done. The complex dielectric permittivity spectra of both the butanediols were obtained by using the TDR technique in the frequency range from 10MHz to 50GHz. The butanediols shows the Cole-Davidson type relaxation. The values of static dielectric constant and relaxation time are reported at various temperatures and the effect of position of hydroxyl group and temperature on the dielectric properties has been discussed. The value of Kirkwood correlation factors is greater than one which indicates the parallel ordination of electric dipole and it will affect by the position of hydroxyl group.

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