

# Temperature dependent dielectric studies of ethanol and ethylene glycol using time domain reflectometry

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**Abstract :** Dielectric properties of ethanol and ethylene glycol have been investigated using time domain reflectometry technique in the frequency range of 10 MHz to 10 GHz over the temperature  $-30^{\circ}\text{C}$  to  $40^{\circ}\text{C}$ . The activation energies of both the systems are compared. The relaxation approximately follows the Cole-Davidson behaviour at lower temperature range whereas it becomes the Cole-Cole behaviour at higher temperature range.

**Keywords :** Dielectric relaxation, time domain technique, ethanol, ethylene glycol, activation energy.

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## 1. Introduction

Ethanol is an ideal example of primary alcohol whereas ethylene glycol (EG) or 1,2-ethanedial is classified as a polyhydric alcohol with two hydroxyl groups. Ethylene glycol is good solvent for biological molecules. These two systems were chosen to compare the dielectric properties of primary alcohol and polyhydric alcohol.

It is interesting to note that at room temperature, static permittivity of ethanol [1] with one hydroxyl group is smaller (24.5) than corresponding value (41.3) of EG [2], whereas relaxation times of both molecules are quite identical ( $\cong 140$  ps).

The objective of this paper is to report dielectric study of the systems over a wide temperature range of  $-30^{\circ}\text{C}$  to  $40^{\circ}\text{C}$  between 10 MHz to 10 GHz range of frequency using time domain reflectometry (TDR) method.

## 2. Experimental

TDR is a technique which involves a study of change in fast rising voltage pulse due to the sample placed in the cell at the end of the transmission line. In our experiment, the Tektronix 7854 sampling oscilloscope along with S-52 pulse generator and S-6 sampling head has been used to monitor these pulses.

It is necessary to compare two pulses in time domain one; the pulse  $[R_1(t)]$  with

empty cell and second; the pulse  $[R_x(t)]$  with the sample in the cell. Then these two pulses are added  $[q(t)]$  and subtracted  $[p(t)]$  in the oscilloscope memory, and transferred to PC/XT system via GPIB card for the Fourier transformation and data analysis.

The reflection coefficient [3] which called here as a Raw data are computed by the following expression

$$\rho^* = \frac{c}{i\omega d} \frac{p(\omega)}{q(\omega)} \quad (1)$$

where 'c' is the velocity of light, ' $\omega$ ' is the angular frequency, 'd' is the effective length of inner conductor used in the cell, and  $[p(\omega)]$  and  $[q(\omega)]$  are the Fourier transformation of  $[p(t)]$  and  $[q(t)]$  respectively.

The complex permittivity which called here as Cor data is determined by the following expression

$$\epsilon^* - 1 = \frac{(1 + A)\rho^*}{1 - B\rho^*} \quad (2)$$

where A and B are unknown complex quantities which have to be determined experimentally with some fairly known liquids. Further details of the experiment is described elsewhere [4] and is very similar to the work done by the Cole *et al* [3].

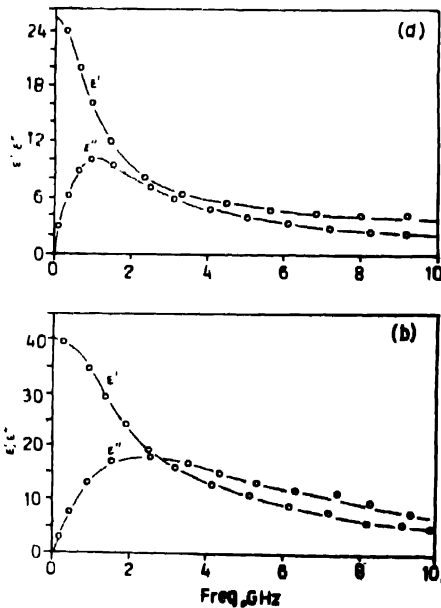


Figure 1. Complex permittivity spectra at 25°C for (a) ethanol; (b) ethylene glycol.

### 3. Results and discussion

The complex permittivity spectra as obtained from eq. (2) for ethanol and ethylene glycol are shown in Figure 1, at 25°C. The Cole-Cole plots at various temperature are illustrated

in Figure 2, for both the systems. To evaluate the values of dielectric parameters, the complex permittivity data as obtained from eq. (2) is fitted by the least squares fit method to the Havriliak-Negami [5] expression,

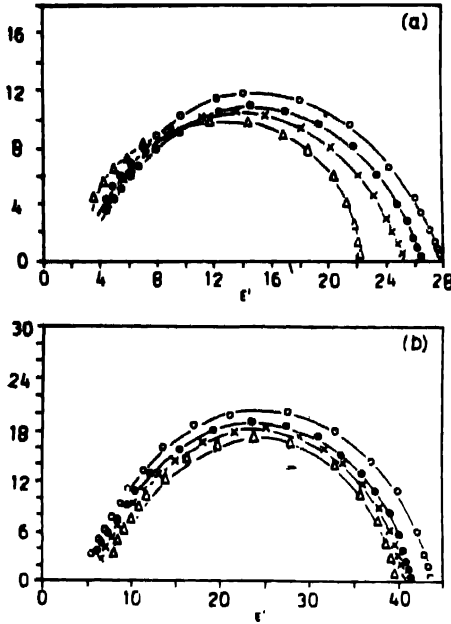


Figure 2. The Cole-Cole plots at various temperatures for (a) ethanol; (b) ethylene glycol. (o), -30°C; (•), 0°C; (x), 25°C; (Δ), 40°C.

Table 1. Values of dielectric parameters at different temperatures.

Tem. °C	$\epsilon_0$	$\epsilon_\infty$	$\tau/PS$	$\alpha$	$\beta$
Ethanol					
-30	29.66 (3)	4.35 (1)	416.0 (13)	0.000	0.982 (1)
-10	27.00 (3)	4.15 (1)	288.3 (11)	0.000	0.988 (5)
0	26.61 (3)	5.86 (3)	270.0 (21)	0.000	0.996 (7)
10	26.00 (6)	4.25 (3)	212.3 (12)	0.000	1.000 (3)
20	24.93 (10)	3.62 (2)	138.0 (10)	0.000	1.000 (7)
25	24.40 (1)	3.53 (18)	136.0 (9)	0.000	1.000 (9)
40	22.20 (1)	3.00 (2)	92.0 (1)	0.000	1.000 (1)
Ethylene glycol					
-30	44.20 (11)	3.59 (2)	525.8 (35)	0.000	0.940 (2)
-10	43.81 (11)	4.76 (2)	308.7 (43)	0.000	0.995 (5)
0	42.49 (80)	4.01 (1)	280.1 (67)	0.165 (11)	1.000 (1)
10	41.12 (15)	3.99 (4)	214.5 (56)	0.116 (18)	1.000 (1)
20*	41.38	7.10	140.0	—	—
25	40.89 (6)	4.44 (4)	104.6 (18)	0.121 (10)	1.000 (1)
40	39.00 (50)	4.00 (5)	60.5 (15)	0.132 (11)	1.000 (1)

\* Values from reference [8] for comparison.

$$\epsilon^*(\omega) = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{[1 + (j\omega\tau)^\alpha]^\beta} \quad (3)$$

with  $\epsilon_0$ ,  $\epsilon_\infty$ ,  $\tau$ ,  $\alpha$  and  $\beta$  as fitting parameters.

The evaluated values of dielectric parameters, namely static permittivity ( $\epsilon_0$ ), permittivity at high frequency ( $\epsilon_\infty$ ) and relaxation time ( $\tau$ ) are listed in Table 1, along with the Cole-Cole and the Cole-Davidson distribution parameters  $\alpha$  and  $\beta$  respectively. Figure 2 reveals that EG shows the Cole-Cole like behaviour, whereas ethanol shows Debye type nature at higher temperature, but both shows slightly the Cole-Davidson relaxation at lower temperature.

It is well known that as number of carbon atoms in alcohol increases ( $C_1$  to  $C_{10}$ ), the static permittivity decreases but relaxation time increases. In case of ethanol and EG, the number of carbon atoms are equal, but not the oxygen atom. Hydrogen bond rupture rate in both, ethanol and EG seems to be not very much different because the values of relaxation times are nearly similar. The higher values of static permittivity in case of EG may be because of reorientation of OH groups around the C-O bond.

Table 2. Values of activation energies ( $\Delta H$ ) for the systems

System	$\Delta H$ KJ/mol	
	This work	other work
Ethanol	17.13 (3)	17.0 Ref [6]
Ethylene glycol	25.6 (5)	22.0 Ref [8]

Numbers in brackets denote uncertainties in last significant digits as obtained by least squares fit methods.

e.g. 29.66 (3) means  $29.66 \pm 0.03$ , 416.0 (13) means  $416.0 \pm 1.3$ , 0.982 (1) means  $0.982 \pm 0.001$ .

The values of activation energies ( $\Delta H$ ) are given in Table 2, along with the values reported earlier. Note that  $\Delta H$  of EG is higher than that of ethanol. This

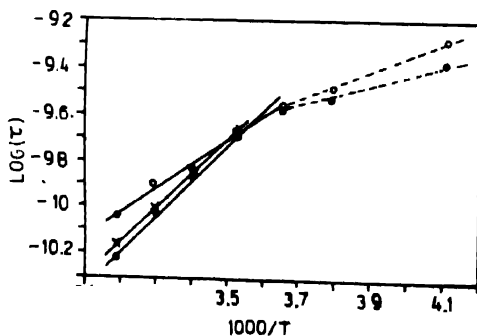


Figure 3. Arrhenius plot of  $\log(\tau)$  vs  $1000/T$ °K. (o), ethanol; (•), ethylene glycol; (x), values corresponding to EG from ref. [2]

suggests that hydrogen bonding in EG is stronger than corresponding hydrogen bonding in ethanol because of the presence of two OH groups in EG. Further, it has been quoted [6] that the activation energy is not merely a matter of the -OH group position but also one of its steric interference. Therefore, it seems to be likely that the steric interference in EG may be stronger than ethanol.

The Arrhenius behaviour for both the systems is shown graphically in Figure 3. Note that both systems follow nearly identical behaviour over all temperatures. As can be seen from Figure 3, a deviation (change of slope) from the linear Arrhenius behaviour being found for the systems at the lower temperatures (below 0°C). Such deviation indicating distinctly a different activation energy may be due to chain formation at lower temperature. Similar deviation was reported earlier for 3-bromopentane [7] at lower temperatures.

#### 4. Conclusion

Dielectric parameters for ethanol and ethylene glycol over temperature range -30°C to 40°C are reported. It can be concluded from this investigation that dielectric parameters, particularly static permittivity for polyhydric alcohols, having two OH groups, is much higher than corresponding value of primary alcohol having one OH group. The activation energies of EG is found to be larger than the corresponding value of ethanol, indicating stronger hydrogen bonding in polyhydric alcohols.

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