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## Dielectric Relaxation and Thermodynamic Study of Erythritol in DMSO Using TDR Technique

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### ABSTRACT

*The measurement of complex permittivity spectra of binary mixtures of Erythritol with DMSO were carried out using picosecond time domain technique at the temperatures ranging from 10 °C to 25 °C To obtain the dielectric parameters, the measured complex permittivity spectra were fitted to the Cole-Davidson model These dielectric parameters are further used to evaluate the Kirkwood correlation factor and thermodynamic parameters to discuss the hydrogen bond interaction*

**Keywords:** Dielectric relaxation, Time domain reflectometry, Kirkwood correlation factor, Thermodynamic parameters

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### INTRODUCTION

Dimethyl Sulphoxide (DMSO) with structural formula  $(\text{CH}_3)_2\text{SO}$  is a highly polar, aprotic solvent However, it can act as a hydrogen bond acceptor DMSO is incorporated into several products for healthcare and drug delivery applications due to its ability to act as a carrier for transferring other drugs through the cell membrane [1] The literature survey shows that dielectric properties of binary mixtures of DMSO and Water [2-10], 2-Methoxy ethanol [11], 3-Nitrotoluene [12], benzene [13], N, N-dimethyl formamide [14], 2-amino ethanol [15], ethylene glycol [16] etc have been extensively investigated using various theoretical and experimental methods

Nakanishi and Nozaki have studied the dielectric behavior of various polyhydric sugar alcohols in pure form at a glass transition temperature [17, 18] Previously, we have studied the dielectric relaxation in binary mixtures of different concentrations of polyhydric sugar alcohols such as Erythritol, D-mannitol and Xylitol with water at various

temperatures using time domain reflectometry (TDR) technique [19-21] We have also investigated the dielectric properties of Sorbitol + DMSO binary mixtures using the TDR technique [22] Erythritol is a polyhydric sugar alcohol composed of linear backbone chain of four carbon atoms each carrying an OH group ( $N_C = N_{OH} = 4$ ) It is widely used in confectionery, pharmaceutical and food products [23, 24]

A DMSO molecule contains a highly polar S=O group while the Erythritol molecule contains OH groups which are dielectrically active the electronegative oxygen atom of DMSO favours the formation of hydrogen bond with electropositive hydrogen atom of OH group of Erythritol

In the present study, the complex permittivity spectra of the binary mixtures Erythritol and DMSO at various concentrations and temperatures were obtained and the dielectric parameters such as static dielectric permittivity ( $\epsilon_0$ ), relaxation time ( $\tau$ ) are evaluated and discussed Molecular interaction in the binary mixtures has been discussed using Kirkwood correlation factor ( $g^{eff}$ ) and thermodynamic parameter (activation energy)

## MATERIALS AND METHODS

### Chemicals

DMSO (995%) was obtained from Spectrochem Pvt Ltd while the sugar alcohol erythritol (99%) was purchased from Alfa Aesar and used without further purification

### Measurements

The TDR technique obtained the dielectric spectra The dielectric relaxation measurements were carried out in the frequency range of 10 MHz to 30 GHz using the Tektronix DSA8200 Digital Serial Analyzer sampling mainframe along with the sampling module 80E08 at the temperatures 10, 15, 20 and 25 °C A vertically positioned flat end coaxial line was immersed into the sample The binary mixtures of the erythritol with DMSO were prepared by taking different weight percent's of erythritol in DMSO depending upon the solubility The weight measurements were done at room temperature using an electronic balance with an accuracy of  $\pm 0005$  g The mole fractions of the mixture constituents were determined from the weight measurements and used wherever necessary The temperature of the sample under test was maintained using calibrated temperature controller system within the accuracy of  $\pm 0.1$  °C Data analysis to determine complex permittivity spectra  $\epsilon^*(\omega)$  were discussed elsewhere [25]

## RESULTS AND DISCUSSION

### Complex permittivity Spectra

The arcs in the Cole-Cole plot of 25% Erythritol in DMSO mixtures at different temperatures (Figure 1) are not semicircles but skewed at higher frequencies showing the asymmetric distribution of relaxation times It is a non-Debye type behavior and the dielectric dispersion can be well explained using the Cole-Davidson model

The dielectric relaxation parameters are obtained by using the least squares curve fitting procedure on the complex permittivity spectrum of the binary mixtures The data best fits with minimum variance to the well-known Cole-Davidson model [26] It was also pointed out for neat DMSO by Lu et al [3] The shape parameter  $\alpha = 0$  and  $\beta$  varies such that  $0 \leq \beta < 1$  which indicates the asymmetric distribution of relaxation times Figure 2 shows the dielectric permittivity  $\epsilon'$ , b) dielectric loss  $\epsilon''$  of the complex permittivity spectra of the binary mixtures of erythritol with DMSO at 25 °C

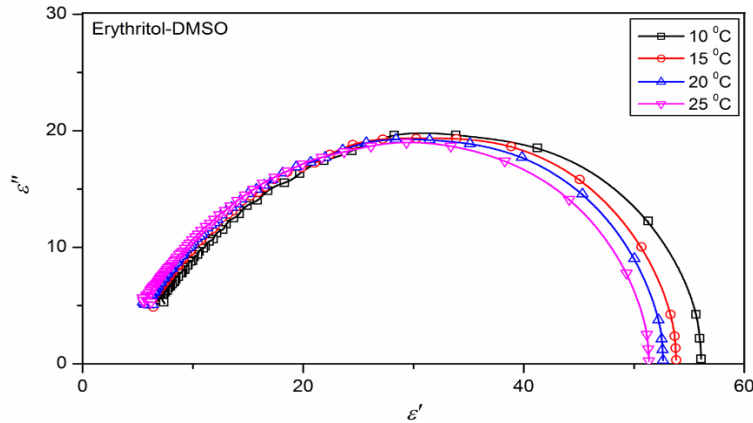


Figure 1: Cole-Cole plot of the 25% Erythritol in DMSO at different temperatures

The solid lines are the fit lines. The measured values of static permittivity of DMSO are in good agreement with the literature data [14, 16]. It can be observed from Figure 2 that on addition of erythritol, the dielectric permittivity increases while the dielectric loss peak shifts considerably towards lower frequency. This may be due to H-bond formation. H atom in hydroxyl group of the erythritol molecules and O atom of the S=O group of DMSO molecules. The evaluated values of the static permittivity and relaxation time are reported in Table 1.

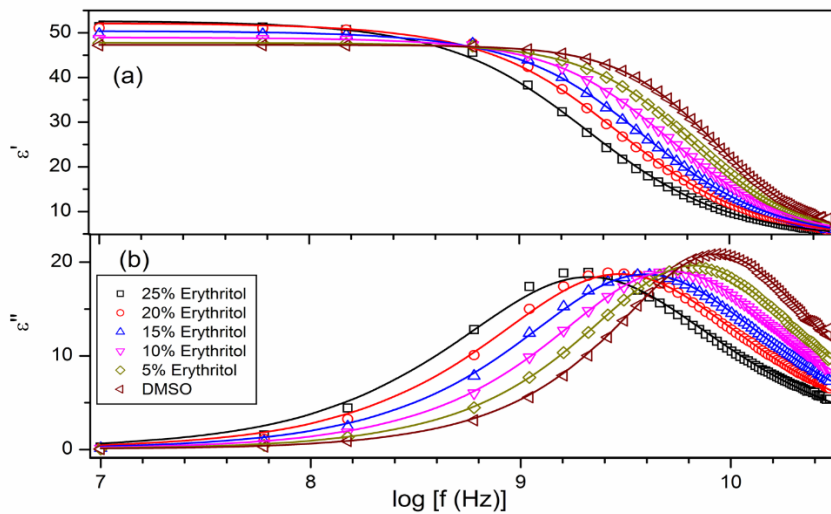


Figure 2: Frequency dependent a) dielectric permittivity ( $\epsilon'$ ) and b) dielectric loss ( $\epsilon''$ ) for Erythritol-DMSO concentrations at 25 °C

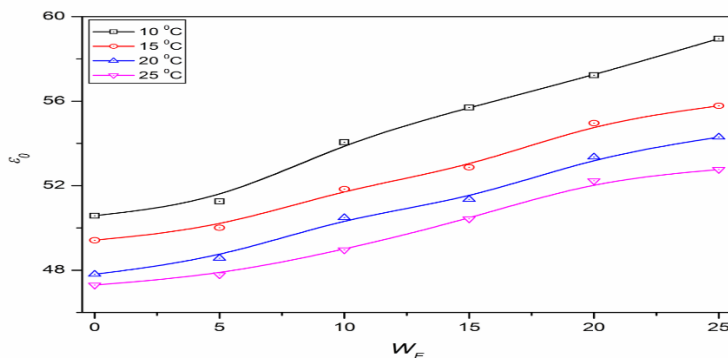
Table 1: Temperature dependent dielectric parameters for Sugar alcohol – DMSO binary mixtures

Weight % of Erythritol in DMSO ( $W_E$ )	25 °C		20 °C		15 °C		10 °C	
	$\epsilon_0$	$\tau$ (ps)	$\epsilon_0$	$\tau$ (ps)	$\epsilon_0$	$\tau$ (ps)	$\epsilon_0$	$\tau$ (ps)
0%	4730 (3)	1861 (2)	4781 (2)	1934 (1)	4942 (3)	2044 (2)	5058 (2)	2192 (3)
5%	4778 (2)	2391 (2)	4857 (2)	2582 (2)	5001 (2)	2722 (3)	5126 (3)	2828 (4)
10%	4896 (2)	3066 (2)	5049 (2)	3443 (3)	5184 (3)	3635 (5)	5406 (7)	3849 (11)
15%	5043 (3)	4045 (6)	5135 (3)	4470 (8)	5287 (5)	4884 (13)	5570 (11)	5505 (29)
20%	5223 (5)	5375 (13)	5336 (6)	6246 (20)	5496 (8)	7014 (28)	5723 (14)	7902 (57)
25%	5277 (7)	7567 (28)	5430 (9)	8890 (41)	5578 (12)	10010 (62)	5896 (19)	12565 (130)

### Static Dielectric Permittivity ( $\epsilon_0$ )

The static dielectric permittivity  $\epsilon_0 = \lim_{f \rightarrow 0} \epsilon'(f)$  helps us to know the structural properties of polar substances

The static dielectric permittivity's of binary mixtures of Sugar alcohol-DMSO ( $\epsilon_0$ ) are plotted against the weight percent of Erythritol ( $W_E$ ) and shown in Figure 3 Generally, such plots are linear for non-interacting solute and solvent In the present study, the variations in static dielectric permittivity are non-linear for all systems This non-linearity can be attributed to the intermolecular association between the solute and solvent molecules of the systems

Figure 3: Static dielectric permittivity ( $\epsilon_0$ ) Vs Weight percent of Erythritol in DMSO ( $W_E$ ) at different temperatures

### Relaxation time ( $\tau$ )

The functional groups which are capable of hydrogen bonding strongly influence the relaxation time. The other factors affecting the relaxation time are chain length, viscosity, temperature etc. As observed from Figure 4, the relaxation time increases non-linearly with increase in the weight percent of Erythritol in DMSO. The non-linearity in the relaxation time confirms the association between the sugar alcohol and DMSO molecules. The hydrogen bonds between the like molecules of Erythritol gets broken and new bonds may be formed between the hydrogen atom of –OH groups of Erythritol and oxygen atom of DMSO molecule. Initially, the relaxation time increases slowly up to 10% of Erythritol in DMSO. On further increase of sugar alcohol in the mixture, the relaxation time increases rapidly. This can be attributed to the increase in number of hydrogen bonds between Erythritol and DMSO molecules because of increase in number of hydrogen bond donor sites and formation of H-bonded complexes in the mixtures. It can also be seen in Figure 4 that in the low concentration region, there is a minor effect of the number of –OH groups in an Erythritol molecule on the relaxation time. The number of OH groups in sugar alcohols is proportional to the molecular weight and Nozaki et al have shown that the relaxation time for pure sugar alcohols strongly depends upon number of OH-groups per molecule [18].

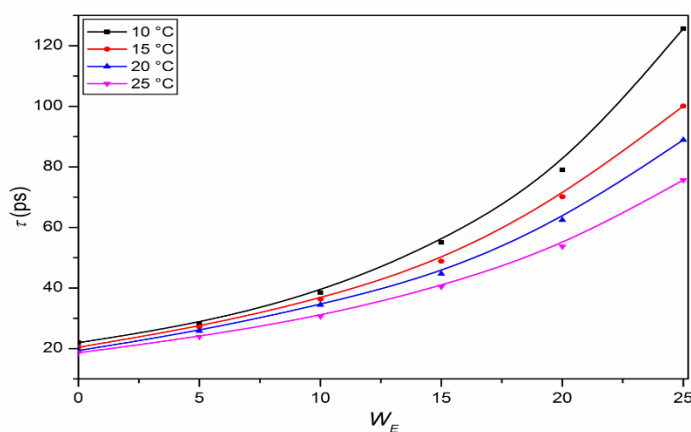


Figure 4:  $\tau$  (ps) Vs Weight percent of Erythritol in DMSO ( $W_E$ ) at different temperatures

### Kirkwood correlation factor

The orientationally correlation between a dipole and its neighboring dipoles in short range can be expressed by Kirkwood correlation factor which can be calculated by Kirkwood Frohlich equation for pure liquids [27]

$$\frac{(\epsilon_0 - \epsilon_\infty)(2\epsilon_0 + \epsilon_\infty)}{\epsilon_0(\epsilon_\infty + 2)^2} = g\mu^2 \frac{4\pi N\rho}{9\kappa TM} \quad (1)$$

where  $g$  is Kirkwood correlation factor,  $N$  is Avogadro's number,  $\mu$  is dipole moment,  $M$  is molecular weight,  $\rho$  is density of the liquid,  $\epsilon_0$  is static dielectric permittivity,  $\epsilon_\infty$  is dielectric permittivity at high frequency and  $k$ ,  $T$  has usual meanings. The deviation of  $g$  value from unity is a measure of orientation correlation among the associating molecules. The quantity  $\epsilon_\infty$  is a crucial parameter since it has a strong impact on the  $g$  values [10]. The frequency range covered in the present study is inadequate to determine the value of  $\epsilon_\infty$ . The value of  $\epsilon_\infty$  is generally estimated by using  $\epsilon_\infty = n^2$  where  $n$  is refractive index of the liquid [7, 14, 15, 19-21, 25]. For Erythritol, the high frequency permittivity is estimated by using  $\epsilon_\infty = n^2$ . In case of DMSO, we have used the value of  $\epsilon_\infty = 43$  determined by Kaatz [10].

The information on dipole-dipole correlation in associating polar liquid can be determined from effective Kirkwood correlation factor ( $g^{\text{eff}}$ ) in binary mixtures by modified Kirkwood equation [28]

$$\frac{4\pi N}{9kT} \left[ \frac{\mu_{OH}^2 \rho_S}{M_S} X_S + \frac{\mu_D^2 \rho_D}{M_D} (1 - X_S) \right] g^{\text{eff}} = \frac{(\epsilon_{0m} - \epsilon_{\infty m})(2\epsilon_{0m} + \epsilon_{\infty m})}{\epsilon_{0m}(\epsilon_{\infty m} + 2)^2}$$

While determining the  $g^{\text{eff}}$  value, we have used the same method as earlier discussed by Nakanishi et al [17] Usually the dipole moment of the whole molecule is chosen as the unit dipole moment But sugar alcohols have number of OH groups that rotate individually Therefore, instead of dipole moment of whole molecule in this paper, we used the dipole moment of OH group The dipole moments are: for DMSO  $\mu_D = 396$  D [29], for OH group  $\mu_{OH} = 169$  D [17]  $\rho_D$ ,  $\rho_S$  are the densities of DMSO and Erythritol respectively  $X_E$  is the mole fraction of the Erythritol in DMSO Figure 5 shows the  $g^{\text{eff}}$  values plotted against the mole fractions of erythritol at different temperatures The evaluated  $g$  value for pure DMSO is 0.5 which is in good agreement with literature value [3, 16, 30] Nozaki et al has shown that the  $g$  values for orientationally correlation of OH-OH groups in pure sugar alcohols are greater than one which shows the parallel orientation Also, OH groups form hydrogen bonds in hydrogen bonding liquids [17] In case of Erythritol-DMSO binary mixture, the  $g^{\text{eff}}$  value goes on increasing on addition of Erythritol in DMSO but remains below one for all the concentrations studied here This indicates the anti-parallel ordering of the dipoles and confirms the formation of complexes between Erythritol and DMSO through hydrogen bonding In our previous study on erythritol-water binary mixtures, we found the  $g^{\text{eff}}$  values greater than one showing parallel ordering of molecular dipoles [19]

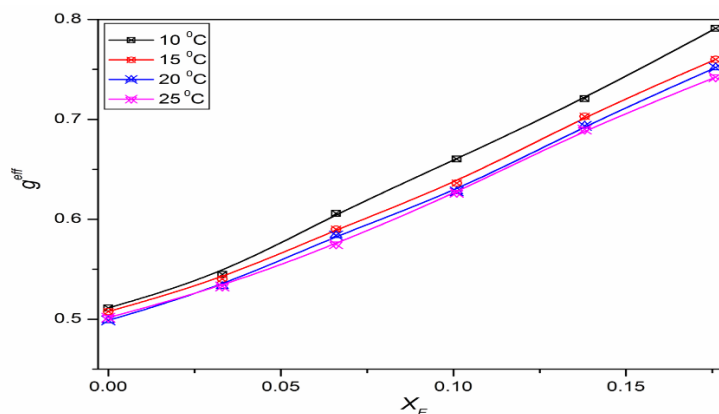


Figure 5: Kirkwood correlation factor ( $g^{\text{eff}}$ ) at 25 °C Vs Mole fraction of Erythritol in DMSO ( $X_E$ )

### Thermodynamic properties

The values of enthalpy of activation ( $\Delta H$ ) are evaluated for all the three systems by applying least square fit method to Eyring equation [31]

$$\tau = (h/kT) \exp(\Delta H/RT) \exp(-\Delta S/R) \quad (3)$$

where  $\Delta S$  is the entropy of activation,  $\Delta H$  is the activation energy in kJ/mol,  $\tau$  is the relaxation time in ps,  $T$  is the temperature in K and  $h$  is the Planck's constant The plot of enthalpy of activation ( $\Delta H$ ) against weight percent of Erythritol in DMSO is shown in Figure 6 For pure DMSO, the value of  $\Delta H$  is found to be 526 kJ/mol and it goes on increasing on addition of Erythritol in DMSO The increase in  $\Delta H$  value on addition of Erythritol may be due to the formation of complexes between the sugar alcohol molecules and DMSO molecules in the form of hydrogen bonding The activation energy ( $\Delta H$ ) is found minimum at 20% of erythritol in water [19]

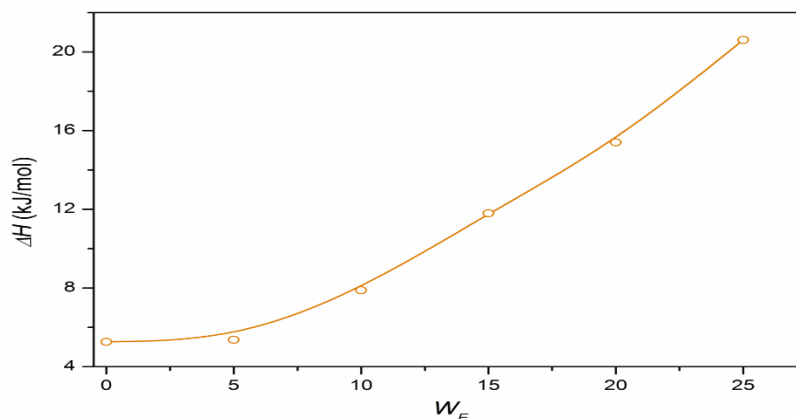


Figure 6: Activation energy( $\Delta H$ ) Vs Weight percent of Erythritol in DMSO ( $W_E$ )

### CONCLUSION

The temperature dependent complex permittivity spectra of Erythritol in DMSO have been studied using time domain reflectometry technique in the frequency range 10 MHz to 30 GHz the dielectric permittivity spectrum of binary mixtures of Erythritol with DMSO can be well described by Cole-Davidson model the molecular interaction among the unlike molecules is well studied using the Kirkwood correlation factor and thermodynamic parameters

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