

Dielectric Relaxation in Ethylene Glycol - Dimethyl Sulfoxide Mixtures as a Function of Composition and Temperature

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ABSTRACT. Using time domain reflectometry, the complex dielectric spectra between 10 MHz to 20 GHz has been measured in the whole composition range at 10, 20, 30 and 40 °C for the binary mixtures of ethylene glycol and dimethyl sulfoxide. For all the mixtures, only one dielectric loss peak was observed in this frequency range. The relaxation in these mixtures can be described by a single relaxation time using the Debye model. A systematic variation is observed in dielectric constant (ϵ_0) and relaxation time (τ). The excess permittivity (ϵ^E), excess inverse relaxation time ($1/\tau$)^E, Kirkwood correlation factor (g) and thermodynamic parameters viz. enthalpy of activation (ΔH) and Gibbs free energy of activation (ΔG) have been determined, to confirm the formation of hydrogen bonded homogeneous and heterogeneous cooperative domains, the dynamics of solute - solute interaction and the hindrance to molecular rotation in the hydrogen bonded glass forming ethylene glycol - dimethyl sulphoxide system.

Key words: Dielectric relaxation, Dimethyl sulfoxide, Ethylene glycol, Time domain reflectometry, Thermodynamic parameters

INTRODUCTION

Dielectric studies involve measurements of permittivity and dielectric loss. The measurements can be used to find dielectric relaxation times and distribution parameters. The relaxation time depends upon the molecular size, shape, intramolecular and intermolecular forces, and can be used to investigate molecular and intramolecular motions and their relation to molecular structure. These studies can be used to evaluate the barrier height hindering internal rotation; problems of complex formation, dipole-dipole interactions and other short range intermolecular forces. Although NMR, ESR and IR spectroscopy are powerful tools for studying hydrogen bonding, dielectric relaxation measurements have great potential for studying weak molecular interactions. An extensive study of dielectric behaviour of polar solutes at low concentration (to minimize solute-solute interactions) in polar solvents has led to valuable information regarding hydrogen bonding and solute-solvent interaction.¹⁻⁹ To gain some insight into the nature of molecular interactions between the associating molecules, a dielectric study of ethylene glycol (EG) - dimethyl sulphoxide (DMSO) system would be helpful. No attempt, so far, seems to have been made to study the dielectric behaviour in the microwave region.

The interest in this system does not only spring from its unique biological properties^{10,11} but also from the wide use of DMSO. The DMSO can interact strongly with EG through hydrogen bonds. The methyl groups, on the other hand, may induce cooperative ordering of EG molecules by hydrophobic hydration effects. The dipole forces may result in self association of DMSO molecules.

Several workers have reported the dielectric properties of binary mixture of DMSO-water,¹²⁻¹⁵ DMSO-alcohol,¹⁶ DMSO-benzophenone and its derivatives,¹⁷ EG-benzene,¹⁸ EG-water.^{15,19}

It is appropriate to report the recent work on the dielectric behaviour of ethylene glycol and dimethyl sulphoxide molecules, and also their conformations, because the dielectric behaviour and molecular dynamics of the EG-DMSO system can be explored more clearly only by comparing the dielectric data of the mixture system with the dielectric data of the individual molecular and their dynamics.

The dimethyl sulfoxide is a highly polar self-associated solvent ($\mu=4.06$ D) and is able to participate in hydrogen bonding.²⁰ The hydrogen bonding ability of the sulfoxide group and ability to act as an electron donor in charge-transfer complex formation have been unambiguously established. The structure and dynamics of the hydrogen bonded ethylene glycol (HOCH₂CH₂OH) molecules are

very interesting and have been studied by various workers using different measurement techniques.^{21,22} The four sites available for H-bonding in EG molecules promote a set of transient crosslinks between neighboring molecules. In such a case, relevant transient structures such as branched associated species and/or chains are formed. In addition many conformations can be generated for each molecule by the rotation of the CH₂OH group around the CC axis.

EXPERIMENTAL

Chemicals

The analytical grade DMSO and EG were purchased from Spectrochem Laboratories Ltd., Bombay, India with purity >99%. The solutions were prepared at different volume percentage of DMSO 0 to 100% in the step of 10% in EG at room temperature. The concentrations were prepared for 5 ml solution at room temperature assuming ideal mixing behavior, within 0.02% error limit. Both EG and DMSO are strongly hygroscopic. Their binary mixtures were kept in desiccator containing anhydrous CaCl₂ that absorbs the moisture in the surrounding and keeps the solutions dry.

TDR Setup and Data Acquisition

The Hewlett Packard HP54750A sampling oscilloscope with HP54754A TDR plug in module has been used. After observing TDR response for sample under study, the time window was kept to 5 ns. By observing TDR response for sample under study, the SMA sample cell with 1.35 mm effective pin length has been used. The sample cell holds the liquid under consideration. The physical dimensions of the cell are very important, so one must be careful while designing the sample cell. The impedance of the cell should be matched with coaxial transmission line to which cell is connected. If there is impedance mismatch then unwanted reflections may disturb the wave thereby causing some errors in the measurements. The proper design of cell includes the inner conductor and outer conductor diameters. The length of the inner conductor is called as 'pin length' of the cell and is very important factor in analysis. The sample length must be enough to avoid unwanted reflections.

In total reflection method, the sample length must be long enough to produce an adequate difference signal but short enough to keep less complication of resonance effects at frequencies above the range of interest.

The characteristics impedance of a coaxial line is given

by

$$Z = \frac{138.2}{\sqrt{\epsilon}} \text{Log}_{10} \left[\frac{b}{a} \right] \quad (1)$$

This impedance for our transmission line is frequently 50 Ω. Here 'a' is the diameter of inner conductor and 'b' is the inner diameter of outer conductor. The ε is the relative permittivity of the dielectric between the conductors. Using Teflon and air, and taking appropriate 'a', 'b' a cell can be designed to have a matching impedance of Z=50 Ω (for air ε=1 and for Teflon, ε=2.2). The sample cell consists of standard military applications (SMA) coaxial connector with matched impedance with 3.5 mm inner diameter of outer conductor. The inner conductor of SMA connector itself is considered as 'inner conductor' and hex-nut is treated as an outer conductor. Since these SMA connectors have already been designed for precise 50 Ω impedance, a special design, when used with high frequency, is not required. The physical length of inner conductor can be changed. When cell is filled with sample above the physical length of inner conductor the fringing effect^{23,24} takes place. Due to the fringing field the effective pin length²⁵ will not be equal to physical pin length. The effective electrical pin length will be more than the physical pin length. The accurate determination of effective pin length 'd' is very important for the accurate evaluation of dielectric parameters. It is found that for SMA type cell effective pin length²⁶ is greater than actual physical length by 0.1-0.2 mm.

To reduce noise, time dependent response curve was averaged for 64 times and then was stored in TDR oscilloscope memory with 1024 points per waveform. First, the response waveform for empty cell is acquired and stored in memory and then secondly, the response waveform for sample is acquired and stored in other memory. The empty cell waveform is used as reference waveform. Both the response waveforms are the reflected waveforms from the sample cell with open termination transmission line.

The data acquisition is carried out for 11 concentrations at 10, 20, 30 and 40 °C. The temperature of sample was maintained at desired value, within accuracy limit of ±1 °C, by circulating constant temperature water through heat insulating jacket surrounding sample cell.

At each time the response waveforms without sample and with sample were recorded. The time dependent response waveform without sample is referred as R₁(t) and with sample referred as R_x(t).

Data Analysis

The time dependent data were processed to obtain complex reflection coefficient spectra $\rho^*(\omega)$ over the frequency range from 10 MHz to 10 GHz using Fourier transformation as^{27,28}

$$\rho^*(\omega) = \left(\frac{c}{j\omega d} \right) \left[\frac{p(\omega)}{q(\omega)} \right] \quad (2)$$

where $p(\omega)$ and $q(\omega)$ are Fourier transformations of $(R_1(t) - R_x(t))$ and $(R_1(t) + R_x(t))$, respectively, c is the velocity of light, ω is angular frequency, d is effective pin length and $j = \sqrt{-1}$.

The complex permittivity spectra $\varepsilon^*(\omega)$ ²⁵ were obtained from reflection coefficient spectra $\rho^*(\omega)$ by applying bilinear calibration method.²⁹

The complex permittivity spectra measured using TDR are fitted by the non-linear least square fit method to the Havriliak Negami expression³⁰ to obtain various dielectric parameters.

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{[1 + (j\omega\tau)^{(1-\alpha)]^\beta} \quad (3)$$

where $\varepsilon^*(\omega)$ is the complex permittivity at an angular frequency ω , ε_∞ is the permittivity at high frequency, ε_0 is the static permittivity, τ is the relaxation time of the system, α is the shape parameter representing symmetrical distribution of relaxation time and β is the shape parameter of an asymmetric relaxation curve. Equation (3) includes Cole-Cole ($\beta=1$),³¹ Davidson-Cole ($\alpha=0$)³² and Debye ($\alpha=0, \beta=1$)³³ relaxation models.

RESULTS AND DISCUSSIONS

Measurements of the complex permittivity i.e. dielectric dispersion (ε') and absorption (ε'') were carried out over a frequency range 10 MHz-10 GHz by employing the TDR at different four temperatures. The maximum errors in the evaluated values of ε' and ε'' are ± 2 and $\pm 3\%$, respectively. Frequency dependent of ε' and ε'' curves for EG, DMSO and EG-DMSO mixtures volume percentage of DMSO at 20 °C are depicted in Fig. 1 and 2, respectively.

It has been found that the complex dielectric data of pure EG, DMSO and EG-DMSO systems obey the Debye dispersion model faithfully. These Debye type complex plane plots (ε'' vs. ε') of these systems are also shown in Fig. 3. The values of dielectric parameters such as dielectric constant (ε_0) and relaxation time (τ) obtained from fitting into the Eq. (3) for EG, DMSO and EG-DMSO

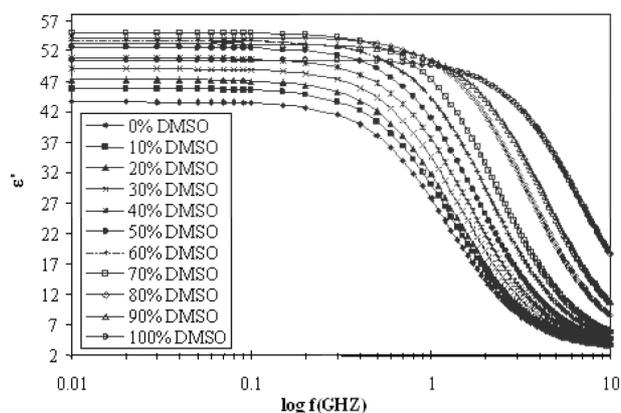


Fig. 1. Frequency dependent dielectric constant (dispersion- ε') curves for ethylene glycol, dimethyl sulfoxide and their mixtures at 25 °C.

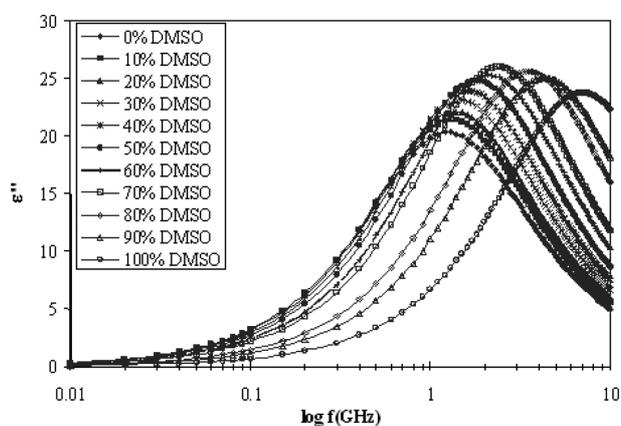


Fig. 2. Frequency dependent dielectric loss (absorption- ε'') curves for ethylene glycol, dimethyl sulfoxide and their mixtures at 20 °C.

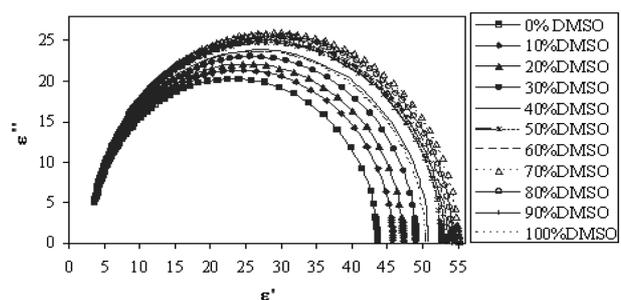


Fig. 3. Cole-Cole plot for ethylene glycol, dimethyl sulfoxide and their mixtures at 20 °C.

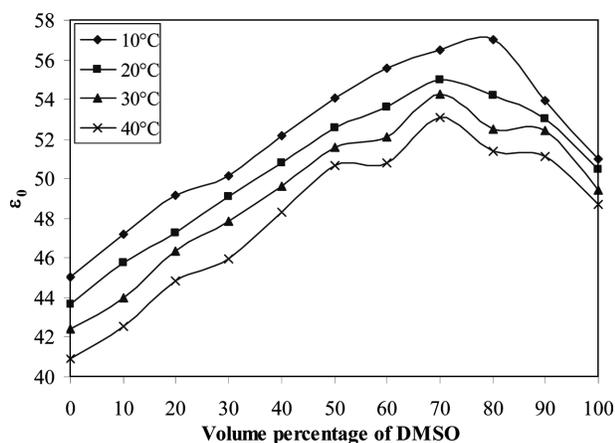
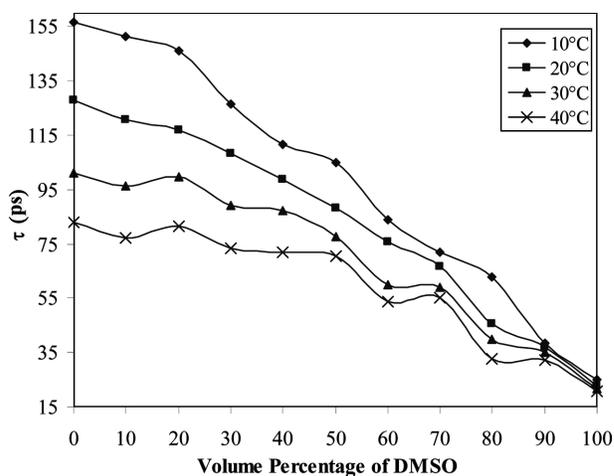
mixtures with volume percentage of DMSO are recorded in Table 1. The evaluated values of τ are within the $\pm 3\%$ error. The temperature dependent variation in dielectric constant and relaxation time with change in volume percentage of DMSO is presented in Figs. 4 and 5, respectively.

Table 1. Temperature dependent dielectric parameters for binary mixture of dimethyl sulphoxide - ethylene glycol

Volume fraction of DMSO in EG	10 °C		20 °C		30 °C		40 °C	
	ϵ_0	τ (ps)						
0	45.03	156.67	43.67	127.73	42.42	101.31	40.90	82.80
0.1	47.21	151.59	45.75	120.84	43.99	96.51	42.52	77.12
0.2	49.17	146.01	47.26	116.85	46.36	99.90	44.82	81.44
0.3	50.15	126.27	49.07	108.12	47.84	89.34	45.98	73.17
0.4	52.20	111.44	50.81	98.61	49.64	87.20	48.31	71.93
0.5	54.06	105.15	52.58	88.21	51.57	77.50	50.64	70.43
0.6	55.60	84.11	53.60	75.8	52.10	59.92	50.80	53.93
0.7	56.49	71.85	55.00	66.62	54.30	58.82	53.10	55.00
0.8	57.00	62.80	54.18	45.54	52.51	39.95	51.39	32.65
0.9	53.95	38.63	53.03	36.95	52.43	35.16	51.16	32.28
1	51.00	24.90	50.50	22.79	49.40	21.60	48.70	20.64

In Figs. 1 and 2 only one peak is observed for EG, DMSO and EG-DMSO mixtures. The dielectric loss peaks for these molecules and their mixtures are found in the frequency range from approximately 1.2 to 6.9 GHz. From Fig. 2 it is observed that the relaxation time is shorter for DMSO compared with EG, which can be ascribed to the fact that EG is an associated liquid while DMSO is an aprotic one. On the other hand, the temperature dependence of the dielectric constant (Fig. 4) and of the relaxation time (Fig. 5) is stronger in EG compared with DMSO, as a consequence of the reported differences between the two liquids. Moreover, the dielectric strength of the relaxation is higher in DMSO compared with EG, which indicates that the relaxing dipole moment is higher in DMSO.

Fig. 2 shows that the relaxation time decreases with increasing volume percentage of DMSO, and Fig. 5 shows that this decrease is monotonous. Moreover, Fig. 2 indicates that the dielectric strength of the relaxation is higher

**Fig. 4.** Variation of dielectric constant with volume percentage of dimethyl sulphoxide in ethylene glycol at various temperatures.**Fig. 5.** Variation of relaxation time with volume percentage of dimethyl sulphoxide in ethylene glycol at various temperatures.

for the mixture with 70-80 volume percentage of DMSO. Figs. 4, 6, 7 and 9 suggest that the mixture with this composition has particular features. As DMSO is added to EG, the H-bonded network of EG is progressively destroyed. At the same time, some kind of 1:1 short lived EG/DMSO molecular association is formed, which probably is strongly polar (eventually more polar than DMSO itself). The experimental results seem to be compatible with such a scenario, and the mixture with 70-80 volume percentage of DMSO is probably that where the concentration of the EG/DMSO is higher. Such a relaxation would involve the cooperative motion of a number of monomer units. A Debye-type relaxation corresponds to a single, non-distributed mobility, to an individual mode of motion, characterized by a single relaxation time. In non H-bonded liquids like acetone or methyl cyanide the observed relaxations

are also Debye-type. Further in case of DMSO molecules, the observed Debye type dielectric dispersion behaviour is not surprising. Recently, Gabrielian et al.³⁴ also confirmed the Debye dielectric dispersion behaviour of DMSO by means of coaxial and waveguide setups (dielectric spectroscopy method). Debye type relaxation in these molecules and their mixtures reflect the behaviour of clusters of molecules as large species. Further, the Debye process in case of pure polar liquids also suggests the cooperative process involving the relaxation of the structure. Furthermore, it seems that in the mixture of these associating liquids, the individual principal relaxation processes of the components coalesce, and hence the mixture exhibits a single relaxation time.

From Fig. 4, it is found that dielectric constant values increase with increase in DMSO up to ($X_{\text{DMSO}}=0.7$) in EG, above that they decrease to the corresponding value of pure DMSO. The observed ϵ_0 value is significantly high in comparison to the ϵ_0 values of EG and DMSO molecules ($X_{\text{DMSO}}=0.4$ to 1). Same type of change in ϵ_0 values has been observed at all four temperatures under study. Earlier, Khirade et al.¹⁶ investigated the molecular dynamics of binary mixture of ethyl alcohol (ethanol) and propan-1-ol with dimethylsulfoxide using dielectric spectroscopy and confirmed that the dielectric constant increases with increase in volume percentage of DMSO (up to 90%) in alcohol, above that it decreases to the corresponding value of pure DMSO. Increase in ϵ_0 with increase in percentage of DMSO indicates the increase in effective dipole moment (increased polarization) of the system up to 0.7 X_{DMSO} above that effective dipole moment decreases. In general, ideal binary mixtures in the absence of heteromolecular H-bond interactions follow the linear behaviour of ϵ_0 values with one of mixture constituent volume-fraction concentration. The non-linear dielectric behaviour of DMSO-EG mixed solvent (Fig. 4), confirms the formation of H-bond molecular complexes in the mixture over the entire concentration range. DMSO forms H-bond complexes through its S and O atoms with EG, whereas the ability of EG molecules to act as acceptors of hydrogen bonds promotes the DMSO-EG complexations.

From Fig. 5, it is observed that the relaxation time values gradually decrease with increase in volume percentage of DMSO in EG. Khirade et al.¹⁶ also reported that the relaxation time value gradually decreases with increase in volume percentage of DMSO in ethyl alcohol. EG is derivative of ethyl alcohol in which two hydroxyl groups are attached to the terminal carbon atom of ethane. In comparison with EG the observed relaxation time τ of EG

(101.2 ps) is smaller than τ of ethyl alcohol³⁵ (136 ps), which confirms that there is substantial hindrance to molecular reorientation due to the bulky methyl side group. With increase in temperature, the τ values are decreased by maintaining same type of variation with change in concentration. In EG rich region the τ values are so much sensitive with change in temperature. In case of EG molecules, the observed relaxation time ($\tau=156.67$ ps) is very large which suggests that primary relaxation of the EG molecules is due to a co-operative process of multimers (i.e. clusters of EG molecules) with (O-H...O) linkage. The evaluated value of Kirkwood correlation factor $g=1.19$ also confirms the formation of multimers in EG molecules.

The excess parameters^{36,37} related to ϵ_0 and τ provide valuable information regarding interaction between the (solute-solvent) polar-polar liquid mixtures. These properties are also useful for detection of the cooperative domain in the mixture and may evidence for formation of multimers in the mixture due to intermolecular interaction. The excess permittivity is defined as³⁸

$$\epsilon^E = (\epsilon_0 - \epsilon_\infty)_m - [(\epsilon_0 - \epsilon_\infty)_A x_A + (\epsilon_0 - \epsilon_\infty)_B x_B] \quad (4)$$

where x -mole fraction and suffices m , A , B represents mixture, liquid A and B respectively.

The excess permittivity provides qualitative information about structure formation in the mixture as follows:

(i) $\epsilon^E=0$: indicates that the solute and solvent do not interact at all.

(ii) $\epsilon^E<0$: indicates that the solute and solvent interaction act so as to reduce total effective dipoles. This suggests that the solute-solvent mixture may form multimers leading to the less effective dipoles.

(iii) $\epsilon^E>0$: indicates that the solute and solvent interact in such a way that the effective dipole moment increases. There is formation of monomers and dimers.

The excess inverse relaxation time is defined as,

$$(1/\tau)^E = (1/\tau)_m - [(1/\tau)_A x_A + (1/\tau)_B x_B] \quad (5)$$

where $(1/\tau)^E$ is excess inverse relaxation time, which represents average broadening of dielectric spectra. The inverse relaxation time analogy is taken from spectral line broadening (which is the inverse of relaxation time) from the resonant spectroscopy.³⁹ The information regarding the dynamics of solute solvent interaction from this excess property is as follows.

(i) $(1/\tau)^E=0$: There is no change in the dynamics of solute solvent interaction, i.e. the dynamics of EG and a DMSO molecule is similar to their dynamics in homogeneous medium.

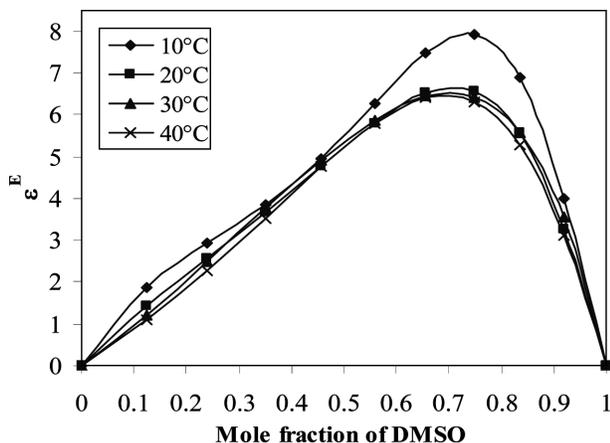


Fig. 6. Variation of excess permittivity with mole fraction of dimethyl sulfoxide in ethylene glycol at various temperatures.

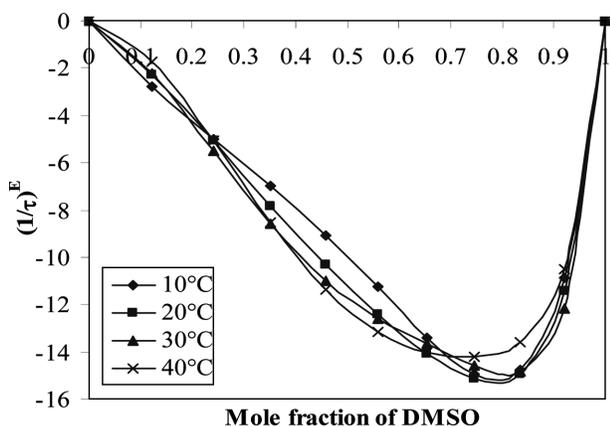


Fig. 7. Variation of excess inverse relaxation time with mole fraction of dimethyl sulphoxide in ethylene glycol at various temperatures.

(ii) $(1/\tau)^E < 0$: The solute-solvent interaction produces a field such that the effective dipoles rotate slowly as the strength of the heterogeneous H-bond increases.

(iii) $(1/\tau)^E > 0$: The solute-solvent interaction produces a field such that the effective dipoles rotate rapidly i.e. the field will co-operate in rotation of dipoles.

The variation of excess permittivity (ϵ^E) and excess inverse relaxation time $(1/\tau)^E$ with mole fraction of DMSO in EG-DMSO mixture at all temperatures are presented in Fig. 6 and Fig. 7, respectively.

From Fig. 6, observed ϵ^E is found to be positive for all concentration and temperatures, which indicates that the total number of dipoles in EG-DMSO increases with formation of monomeric or dimeric structures. This is due to the parallel alignment of the dipoles of the interacting EG and DMSO molecules. It is interesting to observe that the excess permittivity is maximum at around 0.7 mole frac-

tion of DMSO at all temperatures, indicates that there is strong interaction between EG and DMSO molecules.

From Fig. 7, it is found that the excess inverse relaxation time $(1/\tau)^E$ are negative for all concentrations and temperatures. The negative peak value is observed at around 0.8 mole fraction of DMSO in EG-DMSO mixture. The negative values of $(1/\tau)^E$, indicates the formation of linear structures, probably, dimeric, and these rotate slowly under the influence of an external varying field.

The Kirkwood correlation factor⁴⁰ g is a measure for preferential local ordering of molecular dipole moments and thus a hint at the formation of self-aggregates. For perfectly random dipole orientation, there is $g=1$.

The g for pure liquid can be obtained by the expression

$$\frac{4\pi N\mu^2\rho}{9kTM}g = \frac{(\epsilon_o - \epsilon_\infty)(2\epsilon_o + \epsilon_\infty)}{\epsilon_o(\epsilon_\infty + 2)^2} \quad (6)$$

where μ is the dipole moment in gas phase, ρ is density at temperature T , M is molecular weight, k is Boltzman constant, N is Avogadro's number.

The effective angular correlation (g^{eff}) between molecules is calculated using modified form of equation (6).^{36,41} g^{eff} has been used to study the orientation of electric dipoles in binary mixtures. The Kirkwood equation for the mixture may be expressed as,^{13,41}

$$\frac{4\pi N}{9kT} \left(\frac{\mu_A^2 \rho_A \Phi_A}{M_A} + \frac{\mu_B^2 \rho_B \Phi_B}{M_B} \right) g^{\text{eff}} = \frac{(\epsilon_{om} - \epsilon_{\infty m})(\epsilon_{om} + \epsilon_{\infty m})}{\epsilon_{om}(\epsilon_{\infty m} + 2)^2} \quad (7)$$

where g^{eff} is the effective Kirkwood correlation factor for a binary mixture, and Φ_A, Φ_B are volume fraction of liquid A.

The g^{eff} values for EG are greater than unity at all tem-

Table 2. The value of Kirkwood correlation factor g^{eff} for dimethyl sulphoxide - ethylene glycol binary mixture at various temperatures

Volume fraction of DMSO in EG	g^{eff}			
	10 °C	20 °C	30 °C	40 °C
0	1.19	1.19	1.20	1.19
0.1	1.10	1.10	1.09	1.09
0.2	1.02	1.02	1.03	1.03
0.3	0.94	0.95	0.96	0.95
0.4	0.89	0.90	0.91	0.91
0.5	0.85	0.86	0.87	0.88
0.6	0.81	0.81	0.81	0.81
0.7	0.77	0.77	0.79	0.80
0.8	0.72	0.71	0.71	0.72
0.9	0.64	0.65	0.67	0.67
1	0.57	0.58	0.59	0.60

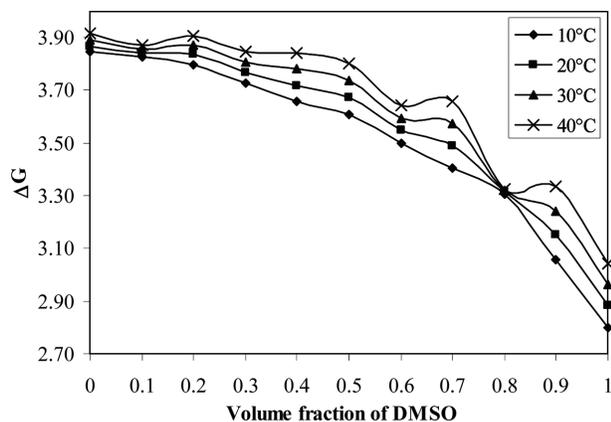


Fig. 8. Variation of Gibbs energy of activation for dimethyl sulfoxide - ethylene glycol binary mixture.

peratures (Table 2) is a preferentially parallel orientation of molecular dipoles is likely to occur; again indicating the formation of self-aggregates probably due to the formation of intermolecular hydrogen bonds (O-H...O). In case of DMSO g^{eff} values are less than unity, indicates the antiparallel orientation of molecular dipoles due to the formation of intermolecular hydrogen bonds CH...O=S. It is observed that the g^{eff} values decrease from unity with increase in percentage of DMSO, indicates that the increase in dimerization with increase in percentage of DMSO in EG. According to Ref.⁴² the slight increase of g^{eff} with temperature for all concentrations suggests that ring structures and dimers break up in favor of chains.

Since the Arrhenius plots of $\log \tau$ vs $1/T$ displayed a good linearity for all the studied liquid mixtures, the kinetic parameters that characterize the molecular mobility in those systems were evaluated using the Eyring formula.^{43,44}

Fig. 8 shows Gibbs energy of activation (ΔG) of the EG-DMSO mixtures as a function of solution composition at different temperatures. It is observed that the (ΔG) values of EG are 0.83 to 1.04 KJ/K.mol higher than those of DMSO over the temperature range of 10-40 °C. Despite the distinctly difference in (ΔG) values of EG and DMSO and the presence of hydrogen bonding between EG and DMSO molecules, there is a gradual decrease in (ΔG) with increase in volume fraction of DMSO, which suggests that the DMSO and EG molecules in the mixture react to the external field in a strongly cooperative way rather than individually over the temperature range of 10-40 °C. It also suggests that there is more hindrance to the rotation of the DMSO and EG molecule clusters in EG-DMSO in comparison with the rotation of their homogeneous clusters.

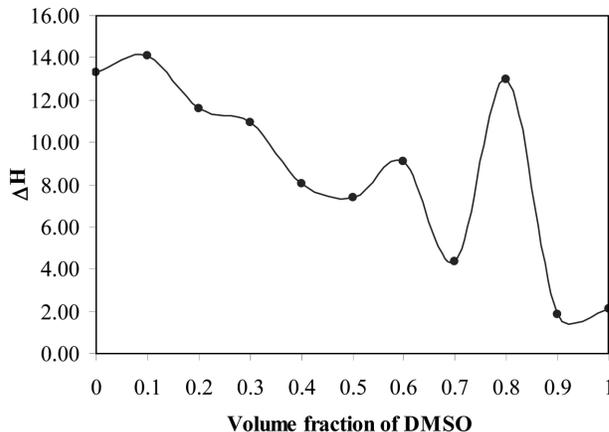


Fig. 9. Variation of Enthalpy of activation for dimethyl sulfoxide - ethylene glycol binary mixture.

This also supports the conclusions drawn from the negative values of the excess inverse relaxation time.

The values of molar enthalpy of activation (ΔH) in KJ/K.mol are obtained from Eyring's rate equation for EG, DMSO and EG-DMSO binary mixtures. The plot of change in enthalpy of activation (ΔH) with variation in volume fraction of DMSO in EG-DMSO mixtures is shown in Fig. 9. From this figure it is clear that the (ΔH), has got low value at 0.9 volume fraction of DMSO, which indicates that less energy is required to achieve group dipole reorientation at this composition. The large value of ΔH is observed at around 0.8 volume fraction of DMSO, indicates strong hydrogen bonding in this solution mixture.

CONCLUSION

The dielectric relaxation study of binary mixtures of DMSO and EG confirms the formation of hetero-molecular H bond interactions over the entire concentration range. The excess permittivity is found to be positive for all concentration and temperature. The excess inverse relaxation time values are negative for all concentration and temperature indicating the solute-solvent interaction hinders the rotation of the dipoles of the system. The g^{eff} values decrease with increase in percentage of DMSO in EG. The studied systems show Arrhenius behavior. The Gibbs energy of activation is dependent of the temperature for all concentrations. The enthalpy of activation decreases with increase in volume fraction of DMSO (except at $X_{\text{DMSO}}=0.6$ and 0.8) in the mixture. The singular mobility observed for the mixture with 0.8 volume fraction of DMSO.

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