Study of dielectric relaxation and dipole moment of some hydrogen bonded solvent binary mixtures in 1,4-dioxane

R J Sengwa*, Madhvi, Abhilasha & Sonu Sankhla
Dielectric Research Laboratory, Department of Physics, J N V University, Jodhpur 342 005
E-mail: rjsengwa@rediffmail.com

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The dielectric relaxation and dipole moment of different concentration binary mixtures of mono methyl, mono ethyl and mono butyl ethers of ethylene glycol with four polar solvents i.e. ethyl alcohol, glycerol, dimethyl sulphoxide and dimethyl formamide have been measured in dilute solutions of 1,4-dioxane at 35°C. The measured values of permittivity ($\varepsilon'$) and dielectric loss ($\varepsilon''$) at 10.1 GHz, static dielectric constant ($\varepsilon_o$) at 1 MHz and high frequency limiting dielectric constant ($\varepsilon_\infty$) have been used to determine the values of molecular relaxation time ($\tau_o$), and dipole moment ($\mu$) of the different composition binary mixtures. The analysis of the results based on hetero-association in these binary systems, indicates the existence of different characteristic heterogeneous species in dilute solutions. The comparative values of $\tau_o$ and $\mu$ of the various binary mixtures of different composition also suggest that the nature of heterogeneous interaction varies with the type of polar solvent and also constituents composition in the binary mixture.

Keywords: Dielectric relaxation, Dipole moment, Binary mixtures, Polar solvents, Heterogeneous interactions, Molecular dynamics

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1 Introduction

Microwave dielectric relaxation and dipole moment studies$^1$ are useful to investigate molecular and intramolecular motions, solute-solute interactions, solute-solvent interactions and their molecular conformations. Earlier dielectric studies$^2-8$ were centered at single component system either in pure state or in non-polar solvents. In the last two decades, dielectric relaxation behaviour of binary mixture of industrial and biological useful associating polar solvents$^9-25$ in their pure liquid state and also in non-polar solvents under varying conditions of compositions has evoked considerable interest. It helps in formulating adequate models of liquid relaxation and also in obtaining information about the relaxation processes and formation of heterogeneous interactions between the polar molecules in their binary mixtures.

Mono alkyl ethers of ethylene glycol are commercially known as cellosolves. These are used as industrial solvents, surfactants, detergents and wetting agents. The molecules of these compounds have hydrogen bonding sites and can enter into intra and intermolecular hydrogen bonding giving rise to several different conformations. In pure liquid state, the molecules of mono alkyl ethers of ethylene glycol exist in hydrogen bonded linear structures in dynamical equilibrium$^{25}$. The values of Kirkwood correlation factor $g$ for mono methyl, mono ethyl and mono butyl ethers of ethylene glycol are 1.49, 1.35 and 1.23, respectively at 35°C, which were determined using $\mu$ values of these molecules in benzene solvent$^{25}$. The $g$ values greater than unity show that ethers molecules form multimers with parallel dipole moment, which decreases with increase in molecular size. Similarly, ethyl alcohol (EA) molecules also exist in linear structure with the switch-over mechanism$^4,26,29$ in their inter-molecular associated structure, which is confirmed by the observed values of Kirkwood correlation factor and relaxation time. In case of glycerol (GLY), due to presence of two primary alcohol groups and one secondary alcohol group, the glycerol molecules form cross-linkage hydrogen bonded structure, which is also confirmed by its value of Kirkwood correlation factor $g = 2.6$ and high value of relaxation time$^{29,30}$. Dimethyl sulphoxide (DMSO) and dimethyl formamide (DMF) also show the $g$ value greater than unity i.e. 1.49 and 1.50, respectively, which favours the existence of self-associated structures of these
molecules in their pure liquid state. When self-associated ether molecules are mixed with self-associated molecules of EA, GLY, DMSO and DMF, the heterogeneous molecular interaction gives rise to different species in their binary mixtures. The dynamics of associating polar molecules in their pure liquid state binary mixtures can be interpreted by using the heterogeneous structure with cooperative domains (CDs) of different behaviour and sizes in dynamical equilibrium. The CD is defined as a domain in which the reorientation of molecules occurs cooperatively with dipole correlations, and a CD has a microscopic relaxation time. The cooperative motion of the constituents of binary mixture can be explored by comparing the evaluated values of relaxation time. Stronger interactions among the moving units can yield a larger CD, and a variation of the size of the CD results in a corresponding variation of the microscopic relaxation time with a symmetric relaxation curve. In these mixtures, the coexistence of three kinds of CDs can be assumed to interpret the observed values of dielectric relaxation in dilute solutions. CD_{Eth} includes only ether molecules, CD_{Sol} includes only polar solvent molecules i.e. EA, GLY, DMSO, and DMF, and CD_{Eth-Sol} includes both types of molecules. This CD model can explain the concentration dependence of the dielectric behaviour of these binary mixtures.

When a binary mixture consisting of three kinds of CDs in pure liquid state is added into non-polar solvent to prepare very low concentration dilute solutions, the non-polar solvent molecules penetrate into the homogeneous and heterogeneous CDs, which results in the quasi-isolated behaviour of CDs in dilute solutions. The measurement of microwave dielectric relaxation time can be used to explore the size and nature of different CDs and hindrance to the dynamical behaviour of such CDs in different non-polar solvents at quasi-isolated state because the values of microwave dielectric relaxation time depend upon the molecular size, shape and intermolecular interactions. The molecular reorientation in intermolecularly associated liquids requires breaking and reforming of hydrogen bonds in an alternating electric field. Therefore, it is of great interest to study the dielectric behaviour of different concentration binary mixtures of the molecules of homologous series of mono alkyl ethers of ethylene glycol with hydrogen bonded molecules in non-polar solvent to understand the role of hydrogen bonding with variation of concentration of the mixture constituents and the existence of heterogeneous structures. Further, the effect of number of carbon atoms (i.e. chain length) on dielectric relaxation and molecular dynamics can be explored by the comparative values of different dielectric parameters.

The dielectric behaviour of mono alkyl ethers of ethylene glycol in benzene and carbon tetrachloride solvent, and in their pure liquid state has been investigated for their molecular conformation in pure liquid state and also to confirm the effect of non-polar solvent environment on the molecular dynamics. For small size polar molecules in non-polar solvents, the dielectric measurements at single frequency in microwave X-band frequency region provide fair results regarding their molecular relaxation because these molecules in dilute solutions have dielectric dispersion in microwave region.

In the present paper, the dielectric relaxation and dipole moment study of different concentration binary mixtures of the homologous series of mono alkyl ethers of ethylene glycol with EA, GLY, DMSO and DMF were carried out in dilute solutions of 1,4-dioxane. The dielectric parameters i.e. relaxation time ($\tau_0$), distribution parameter ($\alpha$), free energy of activation ($\Delta F$) and dipole moment ($\mu$) of these polar binary mixtures at four different mixing concentrations were determined for their molecular conformations in binary mixtures.

## 2 Experimental Details

### 2.1 Materials

Mono alkyl ethers of ethylene glycol, ethyl alcohol (EA), glycerol (GLY) and 1,4-dioxane of AR grade were obtained from E Merck, India. Dimethyl sulphoxide (DMSO) and N,N-dimethyl formamide (DMF) of LR grade were obtained from Qualigens Fine Chemicals, India.

### 2.2 Dielectric measurements

Dielectric permittivity ($\varepsilon'$), dielectric loss ($\varepsilon''$), static dielectric constant ($\varepsilon_0$), and high frequency limiting dielectric constant ($\varepsilon_\infty$) of mono alkyl ethers of ethylene glycol, EA, GLY, DMSO, DMF and their binary mixtures of four different concentrations in dilute solutions of dioxane (in the range from $\approx 0.01$ to $0.05$ weight fraction of the binary mixture) were determined using the methods described elsewhere. The values of $\varepsilon'$ and $\varepsilon''$ were determined by the precise waveguide method suggested by
Heston et al.\textsuperscript{36} adopted to short-circuited termination. The heterodyne beat method was used for determination of $\varepsilon_{\infty}$ at 1 MHz. The high frequency limiting $\varepsilon_{\infty}$ was taken as square of the refractive index ($n_0$), which was measured with an Abbe’s refractometer at wavelength of sodium light. The accuracy of measurements of $\varepsilon_{\infty}$, $\varepsilon'$, $\varepsilon''$ and $\varepsilon_{\infty}$ are $\pm 0.5$, $\pm 1$, $\pm 3$ and $\pm 0.05\%$, respectively. The density of solutions was measured with a pycknometer having two fine capillary of uniform bore. Liquid viscosity was measured using the fine capillary Ostwald’s viscometer with reference to the viscosity of water at the same temperature. All measurements were made at 35°C and the temperature was controlled thermostatically within $\pm 0.5$°C.

2.3 Analysis of data

It has been observed that $\varepsilon_{oo}$, $\varepsilon'_o$, $\varepsilon''_o$ and $\varepsilon_{oo}$ are linear functions of the weight fraction of polar solvent (or binary mixture of polar solvents) in dilute solutions of non-polar solvent. These relations are $\varepsilon' = a'_w + \varepsilon'_w$; $\varepsilon'' = a''_w$; $\varepsilon_o = a_o w_o + \varepsilon'_o$ and $\varepsilon_{oo} = a_{oo} w_{oo} + \varepsilon_{oo}$.

Subscript 1 refers to pure non-polar solvent; $w_2$ is the concentration of the solute in weight fraction, $a$’s are the slopes of the straight lines obtained by plotting the dielectric quantity against $w_2$. Linear slopes $a_w$, $a'_w$, $a''_w$ and $a_o$, corresponding to $\varepsilon'_w$, $\varepsilon''_w$ and $\varepsilon_o$ versus $w_2$ of solute (binary mixture or their constituents) at different concentration were used for the evaluation of different dielectric parameters. Distribution parameter $\alpha$, and average relaxation time $\tau_o$ were calculated by using Higasi’s et al.\textsuperscript{37} equations proposed for single frequency measurements in the dispersion region with solute concentration variation in non-polar solvent. For Cole-Cole dispersion\textsuperscript{38} in dilute solutions, the Higasi’s equations\textsuperscript{37} for $\tau_o$ and $\alpha$ are:

$$\tau_o = 1/\omega \left[ (A^2 + B^2) / C^2 \right]^{1/2} (1-\alpha)$$

... (1)

$$1 - \alpha = 2/\pi \tan^{-1}(A/B)$$

where $\omega$ is the angular frequency and

$$A = a''_w(a_o - a_o)$$

$$B = (a_o - a') (a'_w - a_o)$$

and

$$C = (a'_w - a_o)^2 + a''_w$$

... (2)

The dielectric free energy of activation $\Delta F$ was evaluated using Eyring’s rate equation\textsuperscript{1}.

$$\Delta F = RT \ln \left[ \frac{(kT/h)^{\tau_o}}{(kT/h)^{\tau_{so}}} \right]$$

... (3)

where $R$ is the gas constant, $T$ the absolute temperature, $k$ the Boltzmann’s constant, $h$ the Planck’s constant and $\tau_o$ is the experimentally determined value of the relaxation time. The evaluated values of $\alpha$, $\tau_o$ and $\Delta F$ are given in Table 1.

The dipole moment of individual polar molecules and their binary mixtures in dilute solutions of non-polar solvents were determined using Higasi’s equation\textsuperscript{39}:

$$\mu_{1} = \left[ (27kT/4\pi N) \left( \frac{M}{(\varepsilon_i + 2)} d_i \right) \right]^{1/2} (\alpha_{1} - \alpha_{o})$$

... (4)

where $\varepsilon_i$ and $d_i$ are the values of permittivity and density of non-polar solvent, respectively, $T$ the absolute temperature, $N$ the Avogadro’s constant and $M$ is the molecular weight of solute. For binary mixture, solute of polar molecules A and B, $M$ is given by the relation:

$$M = (X_iM_i/m_i) \left[ (1-X_i) m_o \right]$$

... (5)

where $X_i$ is the mole fraction of the non-polar solvent, $M_i$ the molecular weight of the non-polar solvent, $m_i$ and $m_o$ are the weights of the polar solvents binary mixture (solute) and non-polar solvent, respectively, in the solution.

The values of dipole moment of these molecules and their mixtures were also determined using the Guggenheim’s equation\textsuperscript{40}:

$$\mu_{o} = \left[ \left( \frac{(27kT/4\pi N)(\varepsilon_i + 2)(n_i^2 + 2)}{(\Delta/C)_{C=0}} \right) \right]^{1/2}$$

... (6)

where $\Delta = (\varepsilon_{12} - n_{12}^2) - (\varepsilon_i - n_i^2)$. Here subscript 1 indicates the non-polar solvent and 12 the solution, respectively. $C$ is the concentration of the solute in mole/cc and $n$ is the refractive index. $(\Delta/C)_{C=0}$ is the slope of the $\Delta$ versus $C$ plot for the concentration of $C = 0$. For binary mixture of solute C is determined by the relation:

$$C = (md_{12}/M m_{12})$$

... (7)
where \( m_{12} \) and \( m \) are the weights of the solution and polar solvents binary mixture (solute), respectively, \( d_{12} \) is the density of the solution and \( M \) is the molecular weight of the polar solvent binary mixture.

The evaluated values of \( \mu_H \) and \( \mu_G \) are presented in Table 2. The evaluated values of \( \tau_o \) and \( \mu \) of these studied binary mixtures have also been shown in Figs. 1-4, respectively with ethers concentration \( (X_A) \).

### 3 Results and Discussion

#### 3.1 Dielectric relaxation time

Table 1 shows that the \( \tau_o \) values of binary mixtures of mono alkyl ethers of ethylene glycol with EA,
GLY, DMSO and DMF vary anomalously with the increase in concentration ($X_A$) in dioxane solvent. The anomalous variation in comparative observed $\tau_o$ values suggest the existence of heterogeneous cooperative domains (CDs) of polar solvents in dilute solutions of dioxane and these CDs changes with the change in the composition of the constituents of the polar molecules mixture. The anomalous deviation in $\tau_o$ values of the studied mixtures from the $\tau_o$ values of EA, GLY, DMSO and DMF can be seen from Fig. 1.

To explore the molecular dynamics and hindrance to the binary polar molecular mixtures due to the

| $X_A$ | $\mu_G$ | $\mu_H$ | $\mu_{(\text{theor})}$ | $\Delta \mu$ | $X_A$ | $\mu_G$ | $\mu_H$ | $\mu_{(\text{theor})}$ | $\Delta \mu$
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**Ethers-ethyl alcohol mixtures**

**Ethers-glycerol mixtures**

**ME-DMF**

| $X_A$ | $\mu_G$ | $\mu_H$ | $\mu_{(\text{theor})}$ | $\Delta \mu$ | $X_A$ | $\mu_G$ | $\mu_H$ | $\mu_{(\text{theor})}$ | $\Delta \mu$
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**Ethers-dimethyl sulphoxide mixtures**

**Ethers-dimethyl formamide mixtures**

**Table 2**—Values of dipole moment (Debye) of binary mixtures at different mole fractions of mono alkyl ethers of ethylene glycol ($X_A$) in dioxane solutions at 35°C
interactions between their constitutes, first we consider the dynamics of the mixture constitutes in dilute solutions of dioxane.

The $\tau_o$ values of mono methyl (MM), mono ethyl (ME) and mono butyl (MB) ethers of ethylene glycol in dioxane solvent were found to be 4.30, 6.29 and 9.77 ps respectively. The increase in $\tau_o$ value from MM to MB is due to the increase in their molecular size, although the Kirkwood correlation factor $g$ values in pure liquid state decrease from MM to MB i.e. 1.49 to 1.23. These observed $\tau_o$ values along with $g$ values suggest that the increase in molecular size mask the effect of the decrease in their intermolecular association.

The $\tau_o$ values of EA, GLY, DMSO and DMF in dioxane were found 3.58, 6.31, 5.71 and 6.81 ps, respectively. The $g$ values for EA, GLY, DMSO and DMF in pure liquid state are 3.12, 2.6, 1.49 and 1.50 respectively. The observed $\tau_o$ values and comparative $g$ values suggest that there is a significant variation in the self-associated structures of these polar solvents in dilute solutions. Further, the $\tau_o$ values of these solvents are not corresponding to the molecular size. This also confirms that interaction of these molecules with dioxane significantly influences their pure liquid state self-associated structures when added in dioxane to make the dilute solutions. Further, it seems that the behaviour of self-association also varies in dilute solutions with the polar solvents. In case of DMF and DMSO, Sharma and Sharma observed the $\tau_o$ values 6.5 and 4.5 ps, respectively in carbon tetrachloride solvent at 35°C. These values are slightly lower than the values observed in dioxane, which confirm the existence of the interactions of DMSO and DMF in dioxane solvent (solute-solvent interactions).

Fig. 1 shows that the $\tau_o$ values of binary mixtures of mono alkyl ethers of ethylene glycol with EA, GLY, DMSO and DMF vary with mixtures constituents composition and also with the type of the constituents. In case of mono alkyl ethers of ethylene glycol-EA mixture, the observed $\tau_o$ values of the mixtures were found lower than the corresponding $\tau_o$ values of mono alkyl ethers of ethylene glycol in dioxane. Critical examination of $\tau_o$ of binary mixtures [Fig. 1(a)] confirms that at lower concentration of $X_A$, the interaction of ethers-EA reduces the hindrance to the reorientation of heterogeneous cooperative domains. But at higher mole fraction of $X_A$, $\tau_o$ of binary mixtures increases which may be due to the decrease in the number of heterogeneous co-operative domain density with EA mixtures.

In case of the mixtures of mono alkyl ethers of ethylene glycol with GLY, it is found that the $\tau_o$ values of binary mixtures below 0.4 mole fraction of

![Fig. 1](image-url)
ethers ($X_A$) are lower than the $\tau_o$ values of GLY in dioxane solvent [Fig. 1(b)]. This finding also suggests that the interaction of the ethers molecules with GLY molecules facilitates the dynamics of the cooperative molecular reorientation. Mono ethyl (ME) ethers of ethylene glycol and GLY have their equal $\tau_o$ values ($\approx 6.3$ps). But the evaluated $\tau_o$ values of ME-GLY mixtures were found lower in comparison to their individual $\tau_o$ values at all the studied concentration. This confirms that the interaction of ME with GLY favours the dynamics of the CDs at all the mixing concentrations in dioxane solution. But in case of MM-GLY and ME-GLY, the $\tau_o$ values of mixtures tend to approach their corresponding ethers value for $X_A > 0.4$.

The variation in $\tau_o$ values of the mixtures of MM and ME with DMSO shows a typical variation with $X_A$ [Fig. 1(c)]. The observed $\tau_o$ values of these binary systems are higher and lower than the $\tau_o$ values of mixture constituents, confirm that the heterogeneous interactions at the studied concentrations alternately slow down or facilitate the molecular motion of the mixture molecules [Fig. 1(c)]. In case of MB-DMSO, the $\tau_o$ values of mixtures tend to approach the $\tau_o$ of mono butyl ether from $X_A > 0.1$.

In case of the binary mixtures of mono alkyl ethers of ethylene glycol-DMF, the observed $\tau_o$ values of different ethers suggest different kind of heterogeneous interaction characteristics. In case of ME-DMF mixtures, the mixtures $\tau_o$ values were found higher than their constituents $\tau_o$ values [Fig. 1(d)]. This confirms that there is increase in the hindrance to the molecular reorientation due to heterogeneous interactions between these molecular binary systems. But in case of MM-DMF and MB-DMF the observed $\tau_o$ values confirm the anomalous nature of the heterogeneous interaction, which either slow down or favours the resultant molecular dynamics with the variation in $X_A$ values.

The values of relaxation time of the binary mixtures of mono alkyl ethers of ethylene glycol with EA, GLY, DMSO and DMF were evaluated theoretically by using the simple mixing equation of uniform mixture of two polar liquids by the relation:

$$\tau_{\text{o(thereth})} = \tau_A X_A + \tau_B X_B$$

where $\tau_A$ and $\tau_B$ are the relaxation times, and $X_A$ and $X_B$ are the mole fractions of mono alkyl ethers of ethylene glycol and polar solvent i.e. EA, GLY, DMSO and DMF, respectively. Evaluated $\tau_{\text{o(thereth})}$ are presented in Table 1. Comparative values of $\tau_o$ and $\tau_{\text{o(thereth})}$ at same concentration show that at most of the concentrations, there is significant difference in these values, which support the assumption of the existence of heterogeneous CDs in dilute solutions of dioxane.

The values of distribution parameter $\alpha$ for these binary mixtures confirm the asymmetric distribution of relaxation. Significant $\alpha$ values of the mixtures also suggest that beside the molecular reorientation in the mixture, there is a large probability of the group rotations due to breaking and reforming of hydrogen bonds in dilute solutions.

Free energy of activation $\Delta F$, which is a measure of the energy require to lift the molecule over the potential barrier for the reorientation is also determined for these binary mixtures and presented in Table 1. The observed $\Delta F$ values are corresponding to the energy required for the breaking of hydrogen bonds in dilute solutions$^{26,27}$, which also confirms the dynamical behaviour of the homogeneous and heterogeneous structures of the studied binary mixtures in dilute solutions.

### 3.2 Dipole moment

Table 2 presents the values of dipole moment $\mu_G$ and $\mu_H$ of mono alkyl ethers of ethylene glycol, EA, GLY, DMSO and DMF molecules and their mixtures in dioxane solvent. Except EA, the $\mu$ values of mono alkyl ethers of ethylene glycol were found lower than the $\mu$ values of GLY, DMSO and DMF.

Dipole moment values for these molecules and their binary mixtures were determined using two different equations i.e. Higasi’s equation$^{39}$ ($\mu_H$), and Guggenheim’s equation$^{40}$ ($\mu_G$). In case of ethers-EA and ethers-GLY mixtures, the observed $\mu_G$ values are greater than the $\mu_H$ values for all the mixture concentrations (Table 2). But in case of ethers-DMSO and ethers-DMF mixtures, the value of $\mu_G$ is not found higher than the value of $\mu_H$ at all the studied concentration. From these observations it is inferred that for hydroxyl groups containing polar molecules and their mixtures Guggenheim’s equation$^{40}$ gives higher values of dipole moment as compared to the values of dipole moment determined from Higasi’s equation$^{39}$. To understand the nature of dipolar interactions that exist between two polar molecules of different sizes and shapes, the dipole moment values of the studied binary mixtures were also computed theoretically using the simple mixing equation:
\[
\mu_{(\text{theor})} = \mu_A X_A + \mu_B X_B \quad \ldots (9)
\]

where \(\mu_A\) and \(X_A\) are the dipole moment and mole fraction of ethers, respectively, while \(\mu_B\) and \(X_B\) are the values of dipole moment and mole fractions of other polar solvent in the mixture i.e. EA, GLY, DMSO and DMF. The calculated values of \(\mu_{(\text{theor})}\) using the mixture constituents values \(\mu_A\) and \(\mu_B\) determined from Higasi equation are presented in Table 2. The practical evaluated values of binary mixture from the Higasi Eq. (4) and also determined from Eq. (9) are plotted in Figs 2-4. Information

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**Fig. 2**—Plots of \(\mu\) versus \(X_A\) of mono methyl ethers of ethylene glycol with different polar solvents in dilute solutions of dioxane

**Fig. 3**—Plots of \(\mu\) versus \(X_A\) of mono ethyl ethers of ethylene glycol with different polar solvents in dilute solutions of dioxane
regarding the alignment of the dipoles of the constituents of the polar binary mixture due to dipolar interactions from the comparative values of $\mu_H$ and $\mu_{(theor)}$ of the binary mixtures is as follows:

(i) when $\mu_H = \mu_{(theor)}$, there is no change in the net alignment of the effective dipoles due to heterogeneous dipolar interaction; (ii) when $\mu_H > \mu_{(theor)}$, the heterogeneous dipolar interactions increases the number of parallel dipole alignment in the binary mixture. (iii) when $\mu_H < \mu_{(theor)}$, the heterogeneous dipolar interactions reduce the net number of parallel dipole alignment in the mixture.

All these studied molecules exist in multimers form with parallel dipole moment in their pure liquid state, which is confirmed by the values of Kirkwood correlation factor. Figs 2(a), 3(a) and 4(a) show that in case of MM-EA mixture $\mu_H > \mu_{(theor)}$, for ME-EA mixture $\mu_H < \mu_{(theor)}$, and for MB-EA mixture there is comparative anomalous behaviour of $\mu_H$ and $\mu_{(theor)}$ with the concentration variation of ethers ($X_A$). These observations suggest that MM-EA interaction increases the net dipole moment due to increase in parallel dipole alignment, whereas ME-EA interactions reduce the net dipole moments in these mixtures at all the studied concentrations. The anomalous variation in the comparative $\mu_H$ and $\mu_{(theor)}$ values of MB-EA mixtures shows that the dipolar interactions in these molecules are influenced by the concentration of the constituents’ composition. These results also suggest that the nature of dipolar interaction of ethyl alcohol vary with the molecular size of the molecules of mono alkyl ethers of ethylene glycol.

In case of mono alkyl ethers of ethylene glycol-GLY mixtures, the observed $\mu_H$ values were found lower than $\mu_{(theor)}$ for all the mono alkyl ethers at all the studied mixtures concentration (Fig. 2(b), 3(b) and 4(b)). From these results, it can be assumed that the GLY molecules interacted with ether molecules such that there is reduction in the parallel dipolar alignment and hence the net dipole moment of the mixture decreases. Further, comparatively significant decrease in $\mu_H$ as compared to $\mu_{(theor)}$ in case of ME-GLY mixtures suggest that GLY dipolar interactions are much higher with ME molecules in comparison to the interaction with MM and MB molecules. Furthermore, it also observed that the ethers-GLY dipolar interactions approaches maximum near equimolar concentration of these polar liquids in dioxane solutions.

Figures 2(c), 3(c) and 4(c) show that the nature of molecular dipolar interactions in MM-DMSO, ME-DMSO and MB-DMSO mixtures is affected by the size of mono alkyl ethers molecules, and it also vary anomalously with the ether concentration $X_A$ in case of MB-DMSO mixtures in dilute solutions. In case of mono alkyl ethers of ethylene glycol-DMF mixtures,
symmetrical nature of dipolar interactions is found for all the mixtures. Figs 2(d), 3(d) and 4(d) show that the $\mu_{H} > \mu_{\text{theor}}$ for all the ethers-DMF mixtures at all the studied concentrations. From these observations it can be concluded that the dipolar interaction between mono alkyl ether and DMF molecules favour the increase in net parallel dipolar alignment and it is more pronounced in case of MB-GLY mixtures [Fig. 4(d)].

4 Conclusions
The hindrance for molecular reorientation due to heterogeneous interaction of mono alkyl ethers of ethylene glycol with EA, GLY, DMSO and DMF binary mixtures in dioxane solutions influences by the nature of polar solvent and also by the composition of the mixture constituents. In most of the binary mixtures, heterogeneous interaction produces a field such that it facilitates the molecular dynamics.

From the dipole moment study of the binary mixture of mono alkyl ethers of ethylene glycol with EA (monohydric) and DMSO, it is inferred that the parallel or antiparallel dipolar alignment due to heterogeneous interactions changes with the size of molecule of the homologous series. GLY (trihydric alcohol) molecules interacted with all the molecules of homologous series at all the mixing concentration have resulted in decrease in net parallel dipole alignments in the mixture. Dipolar interactions of DMF with mono alkyl ethers of ethylene glycol favour the parallel ordering in the mixtures. The observations about heterogeneous interactions on the basis of dielectric relaxation and dipole moment study of different polar solvent can be applied to develop more suitable dielectric theories of hydrogen bonded binary mixtures, and can also be used for sketching the possible structures of heterogeneous species of these mixtures in dilute solutions.

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