

# Dielectric characterization and molecular interaction behaviour in binary mixtures of methyl acetate with 1-butanol and 1-pentanol

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The dielectric constant ( $\epsilon_s$ ) and relaxation time ( $\tau$ ) of binary mixtures of methyl acetate with alcohols (1-butanol and 1-pentanol) have been investigated at fifteen molar concentrations over the entire mixing range at 288 K, 298 K, 308 K and 318 K using time domain reflectometry technique over the frequency range from 10 MHz to 10 GHz. The relaxation in these mixtures can be described by a single relaxation time using the Debye model. The concentration dependent plots of excess dielectric constant ( $\epsilon^E$ ), excess inverse relaxation time ( $1/\tau^E$ ), Kirkwood correlation factor ( $g^{\text{eff}}$ ), thermodynamic parameters such as enthalpy of activation ( $\Delta H$ ) and Gibbs free energy ( $\Delta G$ ) of activation and Bruggman factor ( $f_B$ ) have been used to explore the complexes formed between unlike molecules, dipolar ordering, hydrogen bond molecular connectivity's and their strength in the binary mixtures. Results confirm that there are strong hydrogen-bond interactions between unlike molecules of ester-alcohol mixtures.

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

## 1 Introduction

Dielectric relaxation studies have been undertaken of binary mixtures of polar molecules under varying conditions of compositions to help in formulating adequate models of liquid relaxation and also in obtaining information about the relaxation process in mixtures. Hydrogen bonding is complex in the liquid state because of the uncertainty in identifying the particular bonds and the number of molecules involved. The presence of hydrogen bonds brings a considerable change in the dielectric properties of liquid mixtures such as dipole moment, dielectric constant, relaxation time, Kirkwood correlation factor, excess dielectric constant and excess inverse relaxation time. There is an increased interest in the study of liquid mixtures leading to formation of hydrogen bonding in the system due to solute-solvent interactions. Recently, we have investigated the effect of H-bonding on the dielectric properties of the binary mixtures of alcohol-alcohol<sup>1</sup>, amide-alcohol<sup>2-5</sup>, amine-alcohol<sup>6</sup>, acrylates-alcohol<sup>7-13</sup>, esters-alcohol<sup>14</sup>, DMSO-alcohol<sup>15</sup>, nitrobenzene-alcohol<sup>16</sup>, amine-amine<sup>17-18</sup>, amide-amine<sup>19-21</sup> and surfactants-amine<sup>22-24</sup> over the entire concentration range.

In view of special interest of mixed solvent, the dielectric relaxation study of methyl acetate mixed with 1-butanol and 1-pentanol over the whole composition range have been carried out. The aim of this study is to provide the precision dielectric constant and relaxation time values of these mixed solvents and to confirm the nature of H-bonded unlike molecular structures and the effect of the extent of substitution in ester and the number of alcohol molecules –OH groups on the hetero-molecular H-bonding interactions.

## 2 Experimental Details

### 2.1 Chemicals

Methyl acetate (MA), butanol (BU) and pentanol (PE) were purchased from Aldrich with purity >99 % and used as received. The solutions were prepared at fifteen different volume fractions of MA from 0 to 1 in step of 0.1 (0.05 in MA and BU/PE rich region) at room temperature.

### 2.2 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

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5 ns. Also 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:

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

This impedance for our transmission line is frequently 50  $\Omega$ . Here ‘a’ is the diameter of inner conductor and ‘b’ is the inner diameter of outer conductor. The  $\epsilon$  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  $Z = 50 \Omega$  (for air  $\epsilon = 1$  and for Teflon,  $\epsilon = 2.2$ ). 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  $\Omega$  impedance, a special design, when used with high frequency, is not required. The physical length of inner conductor can be changed. Due to the fringing field, the effective pin length<sup>27</sup> 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 length<sup>28</sup> 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 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 15 concentrations at 288 K, 298 K, 308 K and 318 K. The temperature of sample was maintained at desired value 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  $R_1(t)$  and with sample referred as  $R_x(t)$ .

### 2.3 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<sup>29-34</sup> as:

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

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,  $\omega$  is angular frequency,  $d$  is effective pin length and  $j = \sqrt{-1}$ .

The complex permittivity spectra<sup>27</sup>  $\epsilon^*(\omega)$  were obtained from reflection coefficient spectra  $\rho^*(\omega)$  by applying bilinear calibration method<sup>35</sup>.

The complex permittivity spectra measured using TDR was fitted by the non-linear least square fit method to the Havriliak Negami expression<sup>29</sup> to obtain various dielectric parameters.

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

Where,  $\epsilon^*(\omega)$  is the complex permittivity at an angular frequency  $\omega$ ,  $\epsilon_\infty$  is the permittivity at high frequency,  $\epsilon_s$  is the static permittivity,  $\tau$  is the relaxation time of the system,  $\alpha$  is the shape parameter

representing symmetrical distribution of relaxation time and  $\beta$  is the shape parameter of an asymmetric relaxation curve. The value of  $\epsilon_\infty$  was taken to be 3.2, for the frequency range considered here,  $\epsilon^*$  is not sensitive to  $\epsilon_\infty$ .

Equation (3) includes Cole-Cole<sup>30</sup> ( $\beta = 1$ ), Davidson-Cole<sup>31</sup> ( $\alpha = 0$ ) and Debye<sup>32</sup> ( $\alpha = 0, \beta = 1$ ) relaxation models. The dielectric model for fitting dielectric parameters suitable for present system is Davidson-Cole model. Therefore, the complex permittivity spectra has been fitted in Davidson-Cole model with  $\alpha = 0$  and  $\beta$  ( $0 < \beta \leq 1$ ) as one of the fitting parameter along with  $\epsilon_s$  and  $\tau$ . The value of fitting parameter  $\beta$  in Havriliak Negami equation obtained is in the range of 0.7 to 0.82 for different concentrations.

### 3 Theory

#### 3.1 Excess dielectric constant and excess inverse relaxation time

The information regarding interaction of liquids 1 and 2 may be obtained from excess dielectric properties<sup>36,37</sup> like excess dielectric constant and excess relaxation time in the mixture. In the present work excess dielectric properties are determined corresponding to static permittivity and inverse relaxation time. The inverse relaxation time analogy is taken from spectral line broadening (which is the inverse of relaxation time) from the resonant spectroscopy<sup>38</sup>.

The excess dielectric constant ( $\epsilon_s^E$ ) is defined as:

$$\epsilon_s^E = (\epsilon_s)_m - [(\epsilon_s)_1 x_1 + (\epsilon_s)_2 x_2] \quad \dots (4)$$

Where,  $x$  - mole fraction and suffices  $m, 1, 2$  represents mixtures, liquid 1 (MA) and liquid 2 (BU/PE), respectively.

The excess dielectric constant may provide qualitative information about structure formation in the mixture as follows:

(i)  $\epsilon_s^E = 0$ : indicates the liquid 1 and 2 do not interact and do not change their individual structural properties in the presence of other liquid,

(ii)  $\epsilon_s^E < 0$ : indicates that liquid 1 and 2 which interact in such a way that the total effective dipoles get reduced. The liquid 1 and 2 may form multimers leading to the less effective dipoles. In general, the negative excess permittivity indicates the formation of multimers in the binary mixtures and

(iii)  $\epsilon_s^E > 0$ : indicates that liquid 1 and 2 interact in such a way that the total effective dipole moment increases. This may be due to breaking of multimer

structure into monomer structure due to presence of other molecule.

Similarly, the excess inverse relaxation time  $(1/\tau)^E$  may be defined as:

$$(1/\tau)^E = (1/\tau)_m - [(1/\tau)_1 x_1 + (1/\tau)_2 x_2] \quad \dots (5)$$

The information regarding the dynamic of liquids 1 and 2 can be retrieved from this excess inverse relaxation time  $(1/\tau)^E$  as follows:

(i)  $(1/\tau)^E = 0$ : There is no change in the dynamics of liquid 1 and 2,

(ii)  $(1/\tau)^E < 0$ : The liquid 1 and 2 interaction produces a field such that the effective dipoles rotate slowly and

(iii)  $(1/\tau)^E > 0$ : The liquid 1 and 2 interaction produces a field such that the effective dipoles rotate rapidly, i.e., the field will co-operate in rotation of dipoles.

The experimental values of both the excess parameters were fitted to the Redlich - Kister equation<sup>39</sup>.

$$A^E = x_1 \cdot x_2 \cdot \sum_{j=0}^n B_j \cdot (x_1 - x_2)^j \quad \dots (6)$$

Where,  $A$  is either  $\epsilon^E$  or  $(1/\tau)^E$ ,  $x_1$  and  $x_2$  are mole fractions of MA and BU/PE respectively, using these  $B_j$  values of excess parameters at various concentrations were calculated and used to draw the smooth curves.

#### 3.2 The Bruggeman factor

The static permittivity of two component mixture must lie somewhere between two extremes corresponding to static permittivity of two liquids. In order to understand the dipole interaction in the mixture of two liquids, the Bruggeman mixture formulae<sup>40</sup> have been proposed. The Bruggeman mixture formulae can be used as first evidence of molecular interactions in binary mixture. This formula states that static permittivity of binary mixture  $(\epsilon_s)_m$ , solute  $(\epsilon_s)_1$  and solvent  $(\epsilon_s)_2$  can be related to volume fraction of MA ( $v_2$ ) in mixture as:

$$f_B = \left( \frac{(\epsilon_s)_m - (\epsilon_s)_2}{(\epsilon_s)_1 - (\epsilon_s)_2} \right) \left( \frac{(\epsilon_s)_1}{(\epsilon_s)_m} \right)^{\frac{1}{3}} = 1 - v_2 \quad \dots (7)$$

#### 3.3 The Kirkwood correlation factor

The Kirkwood correlation factor<sup>41</sup> 'g' is also a parameter containing information regarding orientation

of electric dipoles in polar liquids. The  $g$  for the pure liquid is given by the following expression:

$$g = \frac{\epsilon_0(\epsilon_s - \epsilon_\infty)(2\epsilon_s + \epsilon_\infty)9KTM}{\epsilon_s(\epsilon_\infty + 2)^2 \mu^2 N\rho} \quad \dots(8)$$

Where,  $\mu$  is the dipole moment in gas phase,  $\rho$  is density at temperature  $T$ ,  $\epsilon_0$  is free space permittivity,  $M$  is molecular weight,  $K$  is the Boltzman constant and  $N$  is Avogadro's number.

Assuming that the Kirkwood factor,  $g$ , for mixtures can be expressed by an effective averaged correlation factor  $g^{\text{eff}}$  such that Kirkwood equation for the mixture can be approximated as:

$$g^{\text{eff}} = \frac{\epsilon_0(\epsilon_{sm} - \epsilon_{\infty m})(2\epsilon_{sm} + \epsilon_{\infty m})9KT}{N\epsilon_{sm}(\epsilon_{\infty m} + 2)^2 \left( \frac{\mu_1^2 \rho_1}{M_1} v_1 + \frac{\mu_2^2 \rho_2}{M_2} v_2 \right)} \quad \dots (9)$$

Where,  $v_1$  and  $v_2$  are the volume fraction of liquid 1 and 2,  $\epsilon_{sm}$  is the dielectric constant of mixture and  $\epsilon_{\infty m}$  is high frequency dielectric constant of mixture.

The another way to visualize variation in the Kirkwood correlation factor is to assume that correlation factors for molecules 1 and 2 in mixture contribute to effective  $g$  in equal proportion to their values corresponding to pure liquids, i.e.,  $g_1$  and  $g_2$ . Under this assumption the Kirkwood equation for the mixture can be approximated as:

$$g_f = \frac{\epsilon_0(\epsilon_{sm} - \epsilon_{\infty m})(2\epsilon_{sm} + \epsilon_{\infty m})9KT}{N\epsilon_{sm}(\epsilon_{\infty m} + 2)^2 \left( \frac{\mu_1^2 \rho_1 g_1}{M_1} v_1 + \frac{\mu_2^2 \rho_2 g_2}{M_2} v_2 \right)} \quad \dots (10)$$

Where,  $g_f$  is a fractional change in correlation factor for mixture. The values of  $g^{\text{eff}}$  in Eq. (10) will changes from  $g_1$  (MA) to  $g_2$  (BU/PE). The value of  $g^{\text{eff}}$  change from  $g_1$  to  $g_2$  as concentrations of MA

varies from 0 % to 100 %. In Eq. (10),  $g_f$  is unity for pure liquids and will remain close to unity if there is no interaction between 1 and 2.

**3.4 Thermodynamic parameters**

According to Eyring rate equation<sup>42</sup> the relation between activation enthalpy and entropy and relaxation time  $\tau$  is given by:

$$\tau = (h/kT) \exp\left[\frac{(\Delta H - T\Delta S)}{RT}\right] \quad \dots (11)$$

Where,  $\Delta H$  is the molar enthalpy of activation and  $\Delta S$  is the molar entropy of activation for the dipole reorientation process.  $\Delta H$  is obtained from the slope of  $\ln(\tau T)$  versus  $1/T$ . It follows from this equation that, if  $\Delta H$  and  $\Delta S$  are independent of the temperature, the plot of  $\ln(\tau T)$  versus  $1/T$  is linear.

$$\Delta H - T\Delta S = RT(\ln \tau) - RT[\ln(h/kT)] \quad \dots (12)$$

The order of magnitude of the enthalpy of activation and entropy of activation can give some clue to the molecular energy and order of molecules in the relaxation process.

**4 Results and Discussion**

Measurements of the complex permittivity, i.e., dielectric dispersion ( $\epsilon'$ ) and absorption ( $\epsilon''$ ) were carried out over a frequency range 10 MHz – 20 GHz by employing the TDR at different four temperatures. The maximum errors in the evaluated values of  $\epsilon'$  and  $\epsilon''$  are  $\pm 2$  and  $\pm 3$  %, respectively. Frequency dependent of  $\epsilon'$  and  $\epsilon''$  curves for MA, BU, PE and their mixtures MA-BU and MA-PE with increase in volume percentage of MA at 25° C are depicted in Fig. 1(a and b) and Fig. 2 (a and b), respectively.

It has been found that the complex dielectric data of pure MA, BU, PE, MA-BU and MA-PE systems

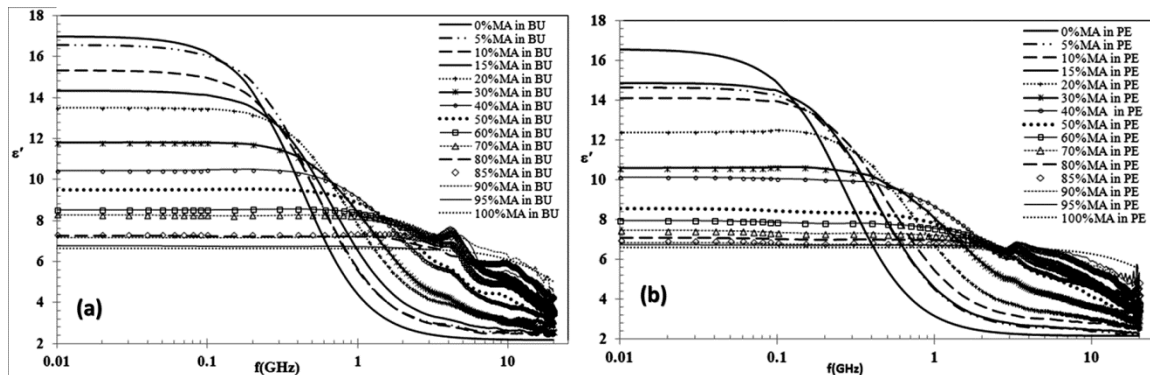


Fig. 1 – (a) Frequency dependent dielectric constant (dispersion- $\epsilon'$ ) curves for methyl acetate, 1-butanol and their mixtures at 25 °C and (b) frequency dependent dielectric constant (dispersion- $\epsilon'$ ) curves for methyl acetate, 1-pentanol and their mixtures at 25 °C.

obey the Debye dispersion model faithfully. Both the  $\epsilon'$  (Fig. 1) and  $\epsilon''$  (Fig. 2) decrease with increasing volume percentage of MA in the binary mixture MA-BU and MA-PE at the low frequency end and increase at the high-frequency end.

The frequency at which the loss factor is a maximum,  $f_{\max}(\tau=1/2\pi f_{\max})$ , shifts to higher values with increasing the volume percentage of MA in the mixture, corresponding to their individual relaxation times, because the individual molecular values are sufficiently different ( $\tau$  values of PE (582.57 ps), BU (355.27 ps) and MA (4.37 ps) to allow their resolution in practice. However, in a mixture of two associated

liquids it seems that the individual principle relaxation processes of the components coalesce, and hence the mixture exhibits a single relaxation time. Earlier, Kumar *et al.*<sup>43</sup> had observed Debye-type behavior in amines (aliphatic/ aromatic)–alcohol mixtures, despite the large differences in the values of individual molecule relaxation times. From Fig. 4, it is observed that the relaxation time is shorter for MA compared with BU and PE, which can be ascribed to the fact that BU/PE is an associated liquid while MA is an aprotic one. On the other hand, the temperature dependence of the dielectric constant (Fig. 3) and of the relaxation time (Fig. 4) is stronger in BU/PE

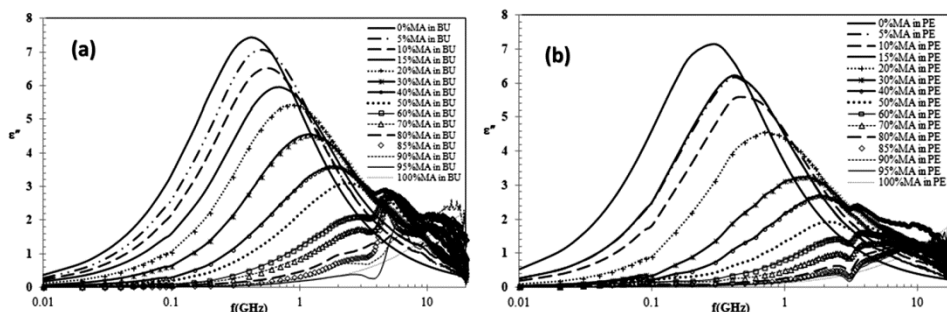


Fig. 2 – (a) Frequency dependent dielectric loss (absorption- $\epsilon''$ ) curves for methyl acetate, 1-butanol and their mixtures at 25 °C and (b) frequency dependent dielectric loss (absorption- $\epsilon''$ ) curves for methyl acetate, 1-pentanol and their mixtures at 25 °C.

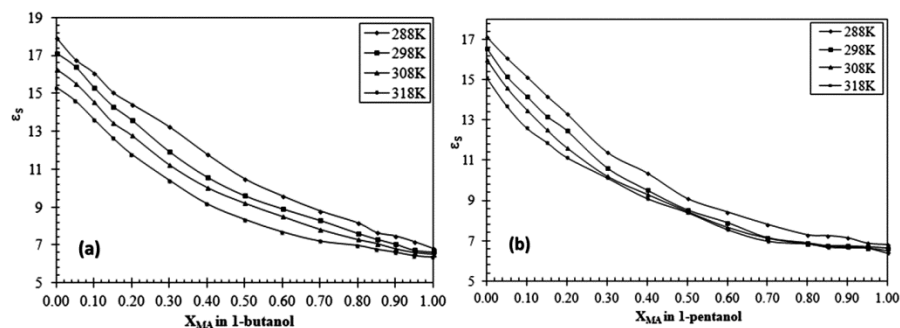


Fig. 3 – (a) Variation of dielectric constant with volume fraction of methyl acetate in 1-butanol at various temperatures and (b) variation of dielectric constant with volume fraction of methyl acetate in 1-pentanol at various temperatures.

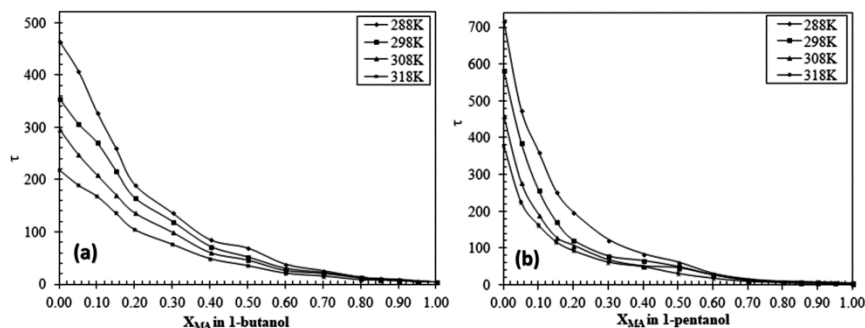


Fig. 4 – (a) Variation of relaxation time with volume fraction of methyl acetate in 1-butanol at various temperatures and (b) variation of relaxation time with volume fraction of methyl acetate in 1-pentanol at various temperatures.

compared with MA, as a consequence of the reported differences between the two liquids.

The evaluated values of dielectric constant ( $\epsilon_s$ ) and relaxation time ( $\tau$ ) obtained from fitting into the Eq. (3) for MA, BU, PE and their mixtures with change in volume fraction of MA in BU and PE ( $X_{MA}$ ) are recorded in Table 1. The temperature dependent variation in dielectric constant and relaxation time with change in  $X_{MA}$  in BU and PE is also presented in Fig. 3 and Fig. 4, respectively.

From Fig. 3 (a and b), it is observed that the  $\epsilon_s$  values gradually decrease with increase in mole fraction of MA in BU and PE, respectively. Decrease in  $\epsilon_s$  with increase in percentage of MA indicates the decrease in effective dipole moment (decreased polarization) of the system. The non-linear behavior of concentration dependent  $\epsilon_s$  values of MA-BU and

MA-PE binary mixtures (Fig. 3 (a and b)) is the experimental evidence of unlike molecular interactions such as H-bonding, dipole-dipole and dipole-induced dipole interactions in these mixed solvents. The deviation in  $\epsilon_s$  values from ideal behavior in mixed solvents is mainly due to H-bond hetero molecular interactions with dipolar orientation.<sup>2-17, 21-24</sup>. In case of MA-PE mixtures, the deviation in  $\epsilon_s$  values from ideal behavior is significantly more in comparison to the deviation in MA-BU mixtures. MA forms H-bond complexes through its O atoms with BU and PE, whereas, the ability of BU and PE molecules to act as acceptors of hydrogen bonds promotes the MA-BU/PE complications. It is also observed that the  $\epsilon_s$  decreased by increasing the number of carbon atoms in the alkyl chain of alcohol. This could be attributed to the decrease in the number of dipoles in the

Table 1 – Temperature dependent dielectric parameters for binary mixtures of methyl acetate - 1-butanol and methyl acetate -1-pentanol.

$X_{MA}$	288 K		298 K		308 K		318 K	
	$\epsilon_s$	$\tau$ (ps)	$\epsilon_s$	$\tau$ (ps)	$\epsilon_s$	$\tau$ (ps)	$\epsilon_s$	$\tau$ (ps)
Methyl acetate +1-Butanol								
0.00	17.93	463.99	17.11	355.27	16.25	295.76	15.31	219.07
0.05	16.79	407.52	16.40	307.52	15.52	247.54	14.61	189.93
0.10	16.07	328.57	15.29	271.39	14.52	208.32	13.62	168.29
0.15	15.05	260.1	14.31	217.56	13.44	170.77	12.65	136.03
0.20	14.43	190.36	13.58	165.67	12.76	136.01	11.79	104.40
0.30	13.23	136.42	11.92	120.6	11.21	99.07	10.42	76.12
0.40	11.79	85.23	10.58	73.06	10.02	60.35	9.18	48.58
0.50	10.49	69.34	9.60	52.48	9.19	46.03	8.36	35.33
0.60	9.59	38.48	8.91	30.81	8.49	26.06	7.70	20.80
0.70	8.80	26.04	8.30	22.70	7.81	20.56	7.22	15.26
0.80	8.17	13.59	7.62	13.49	7.28	11.70	6.99	8.11
0.85	7.66	10.81	7.31	10.69	7.07	7.98	6.79	7.79
0.90	7.48	9.68	7.05	8.09	6.79	6.67	6.64	6.61
0.95	7.18	6.66	6.73	5.81	6.60	4.86	6.45	4.94
1.00	6.82	4.46	6.63	4.37	6.51	4.12	6.38	3.67
Methyl acetate +1-Pentanol								
0.00	17.15	717.64	16.56	582.57	16.01	459.92	15.11	378.68
0.05	16.10	476.72	15.16	386.57	14.60	278.83	13.70	224.98
0.10	15.17	362.78	14.17	256.28	13.50	191.11	12.6	162.79
0.15	14.21	254.69	13.18	172.01	12.51	129.66	11.89	118.48
0.20	13.33	197.49	12.46	121.10	11.62	107.21	11.14	93.83
0.30	11.42	123.4	10.62	78.10	10.21	67.77	10.13	62.96
0.40	10.38	84.56	9.51	65.69	9.31	51.08	9.10	50.57
0.50	9.12	61.95	8.53	49.66	8.46	46.50	8.41	31.90
0.60	8.45	30.83	7.90	27.18	7.67	26.28	7.56	19.38
0.70	7.83	15.60	7.15	13.12	7.13	11.76	6.98	10.70
0.80	7.31	9.31	6.89	8.08	6.85	7.86	6.84	7.25
0.85	7.27	8.36	6.75	6.59	6.74	6.57	6.68	5.52
0.90	7.16	7.02	6.74	6.55	6.70	5.99	6.65	4.98
0.95	6.89	5.80	6.70	4.97	6.64	4.73	6.63	4.30
1.00	6.82	4.46	6.63	4.37	6.51	4.12	6.38	3.67

complex, which may lead to a decrease in the molar volume of the rotating molecules<sup>14</sup>. Earlier, Shirke *et al.*<sup>44</sup> observed the similar variation in  $\epsilon_s$  and  $\tau$  in binary mixture of methyl acetate-methanol, methyl acetate-ethanol and methyl acetate-propanol. Kumar *et al.*<sup>45</sup> observed that  $\epsilon_s$  values decrease with increase in percentage of methyl acetate in 2-methoxyethanol, 2-ethoxyethanol and 2-butoxyethanol. Whereas, Meenachi *et al.*<sup>46</sup> observed that  $\epsilon_s$  values increase with increase in the percentage of methyl acetate in *o*-xylene and *p*-xylene.

From Fig. 4, it is observed that the relaxation time values gradually decrease with increase in mole fraction of MA in BU and PE. With increase in temperature, the  $\tau$  values are decreasing by maintaining same type of variation with change in concentration. This may possibly be due to the decrease in the molar volume and the increase in the effective length of the dipole with increase in temperature and also due to increase in the thermal agitation and partly to decrease in the viscosity<sup>22-24</sup>. In PE rich region the  $\tau$  values are so much sensitive with change in temperature. In comparison with BU the observed relaxation time,  $\tau$  of BU (463.99 ps) is smaller than  $\tau$  of PE (717.64 ps), which confirms that there is substantial hindrance to molecular reorientation due to the bulky methyl side group. The increase in  $\tau$  with chain length is to be expected in view of the fact that the hydroxyl group reorientation depends to some extent on the length of the alkyl group, and the viscosity of the liquid. It also indicates that the degree of cooperativity for reorientation of the molecules increases with increasing length and the bulk of the cluster increases.<sup>8,11,15,25</sup>. In case of alcohol molecules, the observed relaxation time is very large which suggests that primary relaxation of the BU and PE molecules is

due to a co-operative process of multimers, (i.e., clusters of BU and PE molecules) with (O-H...O) linkage. The evaluated value of Kirkwood correlation factor for BU and PE,  $g = 3.08$  and  $3.18$ , respectively also confirms the formation of multimers in alcohol molecules. Increase in mole fraction of MA in BU/PE,  $\tau$  decreases, is a manifestation of the dielectric orientation of the clusters containing both MA and BU/PE molecules, which is because of the continuous breaking and making of H-bonds in the heterogeneous mixture. It is also noticed that, the  $\epsilon_s$  and  $\tau$  values of mixtures lie between the individual component values, which indicated the solute-solvent interaction between the -OH group of alcohol and C=O group of ester<sup>14</sup>.

The excess dielectric constant  $\epsilon^E$  values of the binary mixtures of polar solvents provide information in relation to the molecular conformation<sup>1-21</sup>. The  $\epsilon^E$  values of MA-BU and MA-PE mixtures are negative over the entire mixing range (Fig. 5 (a and b)), which confirms the formation of H-bonded complexes with decrease in effective number of parallel aligned dipoles. The negative  $\epsilon^E$  values also confirm that the MA and alcohol molecules are apt to coalesce and form hetero-molecular structures by breaking some of the self-associated structures. It is observed that the magnitude of  $\epsilon^E$  values of MA-PE mixtures is higher than the MA-BU mixtures, which is evidence of the formation of comparatively stronger interactions between MA and PE molecules. Further, the magnitude of the negative  $\epsilon_s^E$  values of these mixtures increases with increase of the alcohols molecular size and also with the decrease of the  $\epsilon_s$  values of the alcohol molecules (around  $X_{MA}=0.37$  and  $X_{MA}=0.33$  MA-BU and MA-PE mixtures, respectively), which also confirms the enhance in breaking of MA structure with increase of co-solvent molecular size in these mixtures. Excess inverse relaxation time  $(1/\tau)^E$

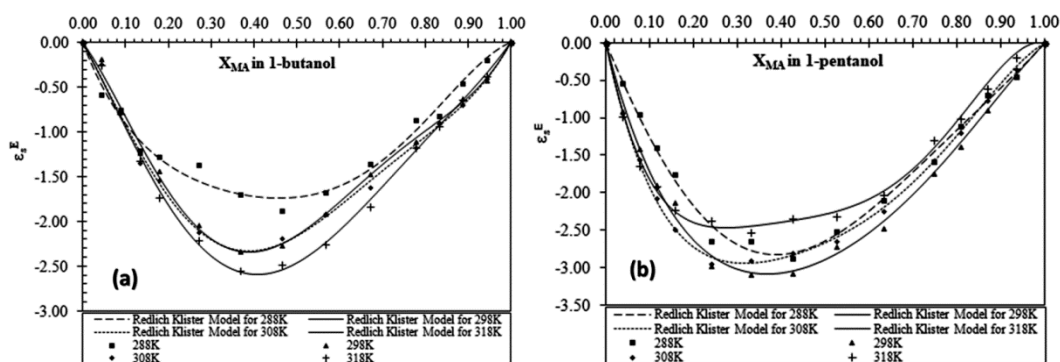


Fig. 5 – (a) Variation of excess permittivity with mole fraction of methyl acetate in 1-butanol at various temperatures and (b) variation of excess permittivity with mole fraction of methyl acetate in 1-pentanol at various temperatures.

values are found to be negative for all concentrations and temperatures for MA-BU (Fig. 6(a)) and MA-PE (Fig. 6(b)) mixtures, respectively. The negative values of  $(1/\tau)^E$ , indicate the formation of linear structures, probably, dimeric, and these rotate slowly under the influence of an external varying field. Both  $\epsilon_s^E$  and  $(1/\tau)^E$  were fitted by Redlich–Kister equation<sup>39</sup>. The estimated values of  $B_j$  coefficients are given in Table 2.

Different molecules are connected by hydrogen bonds, it will be necessary to break these bonds for the dielectric relaxation to be produced. This question has been envisaged by considering the Kirkwood correlation factor<sup>41</sup>  $g$  which itself expresses the existing dipolar correlation between the molecule and its surroundings. The variation in,  $g^{\text{eff}}$  with volume fraction of MA in BU and PE at various temperature represented in Table 3. For BU and PE,  $g$  values are greater than unity which are the evidence of long-range parallel dipolar ordering in their H-bonded self associated structures. The order of  $g$  values PE > BU > MA confirms that the strength of inter-molecular H-bonding in pure PE is strongest.

The  $g$  values of BU and PE are greater than unity at all temperatures that is a preferentially parallel

orientation of molecular dipoles which is likely to occur; again indicating the formation of self-aggregates probably due to the formation of inter-molecular hydrogen bonds (O-H $\cdots$ O). The  $g$  value of MA suggests that the formation of enolate ion is favorable as  $-\text{CH}_3$  present on C=O group and this shows hyper-conjugation, which promotes the H-bond self-association of MA molecules. It is observed that with increase in percentage of MA the  $g^{\text{eff}}$  values decrease in MA-BU and MA-PE mixtures. The concentration dependent non-linear behaviour of the investigated mixed solvents confirms the change in dipolar ordering of MA molecules due to their H-bond molecular interactions with BU and PE molecules.

The corrective Kirkwood correlation factor  $g_f$  of the investigated mixtures deviate from unity (Fig. 7) confirming the change in net dipolar ordering. The plots of  $g_f$  values of MA-BU and MA-PE mixtures have good resemblance with their corresponding  $\epsilon^E$  plots, i. e., the mixtures which have  $g_f$  values less than unity, their  $\epsilon^E$  values are negative, and vice versa (Fig. 5). The  $g_f$  values less than unity, which suggests that the addition of small amount of BU/PE breaks

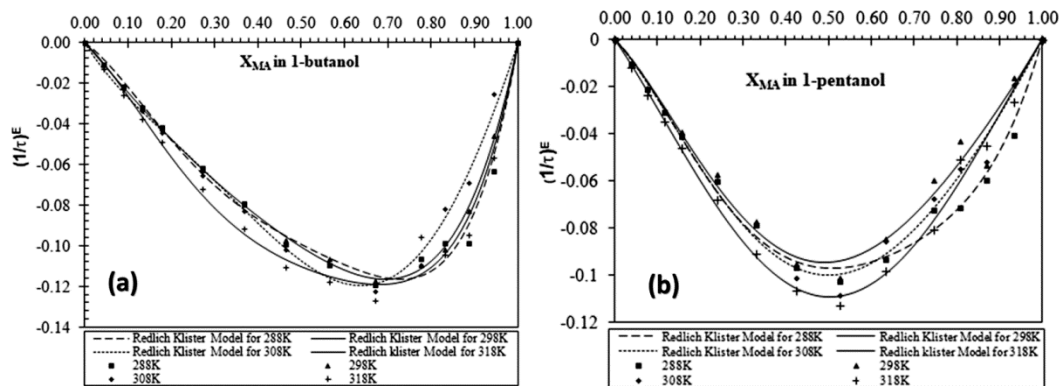


Fig. 6 – (a) Variation of excess inverse relaxation time with mole fraction of methyl acetate in 1-butanol at various temperatures and (b) variation of inverse relaxation time with mole fraction of methyl acetate in 1-pentanol at various temperatures.

Table 2 – Estimated values of  $B_j$  coefficients in Redlich–Kister equation along for methyl- acetate 1-butanol/1-pentanol mixtures at various temperatures.

Excess parameter	$B_j$ coefficient	MA-BU				MA-PE			
		288 K	298 K	308 K	318 K	288 K	298 K	308 K	318 K
$(\epsilon_s)^E$	$B_0$	-6.9023	-8.6203	-8.6473	-9.8497	-10.591	-11.557	-10.676	-9.1494
	$B_1$	1.0263	6.06862	5.44027	5.27339	6.18673	5.50677	5.34753	2.73613
	$B_2$	-0.2757	0.95342	-0.0406	2.12507	0.39193	-2.7472	-4.7528	-4.5014
	$B_3$	4.21087	-7.1828	-5.5126	-4.2793	-2.4566	2.73728	6.73788	11.9068
$(1/\tau)^E$	$B_0$	-0.3975	-0.4017	-0.4298	-0.4409	-0.3876	-0.378	-0.3995	-0.4375
	$B_1$	-0.2215	-0.2705	-0.3151	-0.1756	-0.0131	0.01805	-0.001	-0.0079
	$B_2$	-0.289	-0.2269	-0.058	-0.224	-0.0224	0.13233	0.12704	0.15263
	$B_3$	-0.3164	-0.115	0.16627	-0.2951	-0.2255	-0.0779	-0.0739	-0.0164



Table 3 – The value of Kirkwood correlation factor  $g^{\text{eff}}$  for methyl acetate in 1-butanol/ 1-pentanol binary mixture at various temperatures.

$X_{\text{MA}}$	MA-BU				MA-PE			
	288 K	298 K	308 K	318 K	288 K	298 K	308 K	318 K
0.00	3.08	3.03	2.96	2.86	3.18	3.16	3.15	3.05
0.05	2.84	2.87	2.79	2.69	2.92	2.83	2.81	2.70
0.10	2.68	2.63	2.57	2.47	2.70	2.59	2.54	2.42
0.15	2.48	2.42	2.34	2.25	2.48	2.36	2.30	2.24
0.20	2.34	2.27	2.19	2.06	2.27	2.18	2.08	2.05
0.30	2.09	1.92	1.85	1.76	1.86	1.77	1.75	1.79
0.40	1.81	1.65	1.60	1.49	1.62	1.52	1.53	1.54
0.50	1.56	1.45	1.42	1.31	1.36	1.30	1.33	1.36
0.60	1.38	1.31	1.27	1.17	1.21	1.16	1.15	1.17
0.70	1.23	1.18	1.13	1.06	1.08	1.00	1.03	1.03
0.80	1.11	1.05	1.02	1.00	0.97	0.93	0.96	0.99
0.85	1.01	0.99	0.98	0.96	0.96	0.90	0.93	0.95
0.90	0.98	0.94	0.92	0.93	0.93	0.89	0.91	0.93
0.95	0.92	0.88	0.88	0.89	0.88	0.88	0.89	0.92
1.00	0.86	0.86	0.86	0.87	0.86	0.86	0.86	0.87

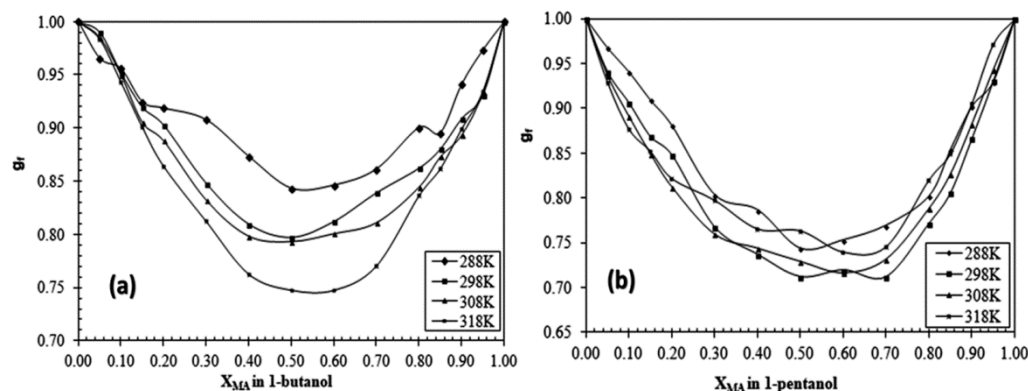


Fig. 7 – (a) Variation of corrective Kirkwood correlation factor  $g_f$  with volume fraction of methyl acetate in 1-butanol at various temperatures and (b) variation of corrective Kirkwood correlation factor  $g_f$  with volume fraction of methyl acetate in 1-pentanol at various temperatures.

large amount of H-bonded long-range ordered MA structures.

The Bruggeman plots of volume fraction of MA versus  $F_{\text{BM}}$  for MA-BU/PE mixtures are given in Fig. 8. It can be seen from these figures that  $F_{\text{BM}}$  is not a linear function of volume fraction of MA. The non-linearity of the curves indicates hetero-interaction which may be due to hydrogen bonding of the  $-\text{OH}$  group of BU and PE with  $-\text{C}=\text{O}$  of MA<sup>3,11,12,14,16,20</sup>

Since, the Arrhenius plots of  $\log \tau$  vs  $1/T$  displayed a good linearity for all the studied liquid mixtures, the kinetic parameters that characterise the molecular mobility in those systems were evaluated using the Eyring formula<sup>42</sup>. Figure 9(a and b) shows Gibbs energy of activation  $\Delta G$  of the MA-BU and MA-PE mixtures, respectively, as a function of solution composition at different temperatures. It is observed

that the  $(\Delta G)$  values of MA is 2.897 to 2.912 kJ/K mol and 2.647 to 2.583 kJ/K mol lower than those of PE and BU, respectively over the temperature range of 288 K – 318 K. Despite the distinctly difference in  $\Delta G$  values of MA and BU/PE and the presence of hydrogen bonding between MA and BU/PE molecules, there is a gradual decrease in  $(\Delta G)$  with increase in volume fraction of MA, which suggests that the MA and BU/PE molecules in the mixture react to the external field in a strongly cooperative way rather than individually over the entire temperature range. It also suggests that there is more hindrance to the rotation of the MA, BU and PE molecule clusters in MA-BU and MA-PE in comparison with the rotation of their homogeneous clusters. This also supports the conclusions drawn from the negative values of the excess inverse relaxation time.

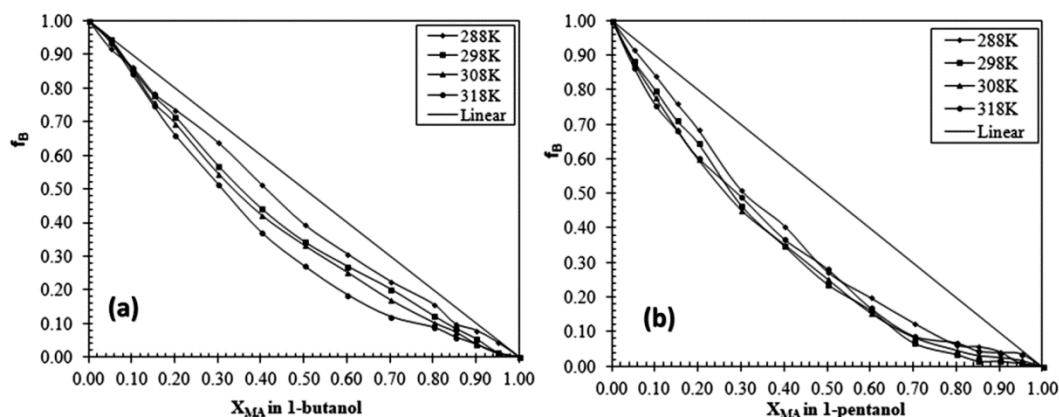


Fig. 8 – Bruggeman plot for (a) methyl acetate - 1-butanol and (b) methyl acetate - 1-pentanol at various temperatures.

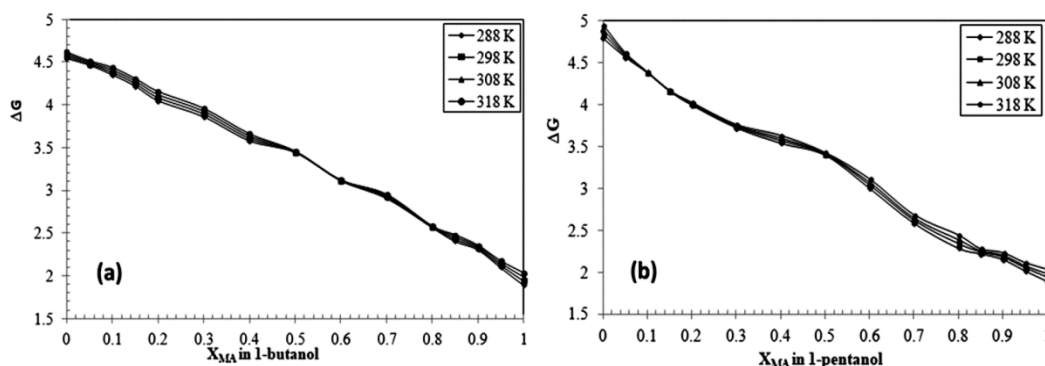


Fig. 9 – (a) Variation of Gibbs energy of activation ( $\Delta G$ ) with volume fraction of methyl acetate in 1-butanol at various temperatures and (b) variation of Gibbs energy of activation ( $\Delta G$ ) with volume fraction of methyl acetate in 1-pentanol at various temperatures.

The values of molar enthalpy of activation ( $\Delta H$ ) in kJ/K.mol are obtained from Eyring's rate equation for BU, PE, MA and MA-BU/PE binary mixtures. The plot of change in enthalpy of activation ( $\Delta H$ ) with variation in volume fraction of MA in MA-BU and MA-PE mixtures is shown in Fig. 10. From this figure it is clear that the  $\Delta H$ , has got low value at pure MA in MA-BU and MA-PE mixture, which indicates that less energy is required to achieve group dipole reorientation at this composition. The large value of  $\Delta H$  is observed in alcohol rich region, indicates strong hydrogen bonding in this solution mixture. An interesting trend may be observed in the temperature dependent relaxation time for the MA-BU and MA-PE binary mixture. The most probable relaxation time determined for the MA-BU and MA-PE binary mixture decreases with increasing temperature. In general, this type of temperature-dependent effect could indicate either a temperature-dependent rate process with activation energy or an equilibrium process with an enthalpy change between the two (or perhaps more) states, ( $\Delta H$ ).

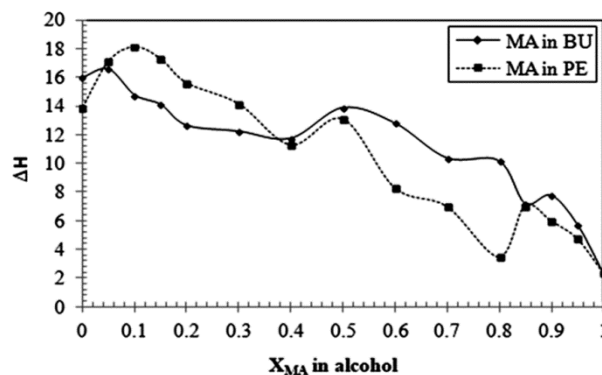


Fig. 10 – Variation of enthalpy of activation for methyl acetate in 1-butanol/1-pentanol mixture.

## 5 Conclusions

The dielectric study of binary mixtures of MA with BU and PE confirms the formation of H-bond interactions that favors parallel structures over the entire concentrations range. The proton donating ability or tendency of complex formation of alcohol increases with alkyl chain length. The strength of H-bond complication between MA and PE molecules

is stronger than the H-bond strength of MA and BU molecular interactions. The  $\epsilon_s$  as well as  $\tau$  values decrease with increase in volume fraction of MA in BU and PE, which indicates that with decrease in the number of dipoles in the solution the intermediate structures formed rotate rapidly thereby giving the decrease in the values of  $\tau$  in the solution. The plots of  $g_f$  values of MA-BU and MA-PE mixtures have good resemblance with their corresponding  $\epsilon^E$  plots, i. e., the mixtures which have  $g_f$  values less than unity, have negative  $\epsilon^E$  values, and vice versa. The  $g_f$  values less than unity for MA-BU and MA-PE mixtures reveal enhancement in the effective dipolar ordering due to hetero-molecular H-bond interactions. The excess inverse relaxation time values are negative for all concentrations and temperatures indicating the solute-solvent interaction which hinders the rotation of the dipoles of the system. The  $g^{\text{eff}}$  values decrease with increase in percentage of MA in BU and PE. The systems studied show Arrhenius behaviour.

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