

# Microwave dielectric relaxation, Thermodynamic and conformational studies of Hydrogen bonded binary mixtures of ethylene glycol with methyl butyrate and ethyl butyrate

K. Umamakeshvari <sup>a\*</sup>, A. Mozes Ezhil Raj <sup>b</sup> & R. Shabu <sup>c</sup>

<sup>a\*</sup> Department of Physics, Christopher Arts and Science College (Women),  
Nanguneri-627108, Tamilnadu,  
(Affiliated to Manonmaniam Sundaranar University, Tirunelveli - 627012, Tamilnadu.

<sup>b</sup> Department of Physics, Scott Christian College, Nagercoil.

<sup>c</sup> Department of Physics, St. Alphonsa College of Arts and Science, Karinkal.

Email : [chitra.uma86@gmail.com](mailto:chitra.uma86@gmail.com)

## Abstract

The dielectric relaxation studies of ethylene glycol (EG) with alkyl butyrates (Methyl butyrate (MB) and Ethyl butyrate (EB)) have been carried out, for various molefractions at different temperatures using LF impedance analyser, Plunger method and Abbe's refractometer in radio, microwave and optic frequency regions, respectively. Kirkwood effective correlation factor, corrective Kirkwood correlation factor, Bruggeman parameter, relaxation time and thermodynamical parameters are calculated using the experimental data. Conformational analysis of the formation of hydrogen bond in the equimolar binary mixture systems of ethylene glycol with alkyl butyrates is supported by experimental and theoretical FTIR values.

**Keywords:** Corrective Kirkwood correlation factor, Relaxation time, Hydrogen bond, FTIR.

## 1. Introduction

The dielectric relaxation study of solute solvent mixture at microwave frequency gives information about molecular interactions in the system, formation of monomers and multimers. Dielectric relaxation spectroscopy was proved to be powerful tool for the investigation of H-bond rearrangement dynamics and has been widely applied to study the pure solvent, solvent-solvent mixtures<sup>1,2</sup>. Dielectric investigation of binary polar liquid mixtures consisting of one associative and other non-associative liquids, provides valuable information regarding molecular complex

formation in solution. Alcohols are industrially and scientifically important organic compounds and their physical and chemical properties are largely determined by the –OH group. Alcohols are strongly associated in solution, good hydrogen bonding acceptors and important industrial chemicals that are widely used in perfumery and pesticides.

The strength of the molecular association depends on several factors including molecular structure, temperature, solvent and other factors<sup>3</sup>. The presence of hydrogen bond brings a considerable change in the dielectric properties of liquid mixtures. Therefore, the solution chemistry of these compounds can be strongly influenced by the aggregation phenomena, which can play a significant role in physical properties like refractive index, dielectric permittivity, density and molar volume. Further the thermodynamic properties of liquids and liquid mixtures have been used to understand the molecular interaction between the components of the mixture and also for engineering applications concerning heat transfer, mass transfer, fluid flow activation energy, enthalpy, entropy etc of the polar molecules<sup>4-9</sup>.

In the course of present study to get better understanding of the nature of molecular orientation process we studied the temperature dependent dielectric relaxation in pure and binary mixtures of ethylene glycol with methyl butyrate and ethyl butyrate at different frequencies. The dielectric data is used to calculate Kirkwood effective correlation, Corrective Kirkwood correlation factor, Bruggemann factor relaxation time and the thermodynamic parameters- Gibbs energy of activation, molar enthalpy and molar entropy<sup>10-14</sup>. Conformational analysis of the formation of hydrogen bond between equi molar mixtures of ethylene glycol with butyrates is studied from FTIR spectra. The theoretical vibrational frequencies of the pure and equi molar hydrogen bonded systems are obtained from Hamiltonian quantum mechanical calculations using sparton modeling software.

## 2. Experimental details

The compounds ethylene glycol, methyl butyrate, ethyl butyrate of AR grade are procured from E-merck germany are used without further purification and the binary mixtures are prepared for different molefractions (ie) molefraction ( $X_2$ ) of butyrates (MB and EB) are varied from 0 to 1 in EG (with a step increment of 0.1) the temperature controller system with a water bath supplied by sakti scientific instruments company India has been used to maintain the constant temperature within the accuracy limit of  $\pm 1K$ . Densities at different temperatures are measured by using a 10ml specific gravity bottle.

The static permittivity values at the spot frequencies 1 KHz, 10KHz, 100 KHz, 1 MHz and 100MHz for the above systems are measured using HP-LF impedance analyser at different temperatures. The real and imaginary part of the complex dielectric permittivity are determined in X-band using plunger technique<sup>15</sup> for the above temperatures. The error in the estimation of  $\epsilon_{static}, \epsilon', \epsilon_\infty$  and density is 1% and the error in the estimation of  $\epsilon''$  and  $\tau$  is 2%. Dipole moments of the liquids in gaseous state are taken from literature<sup>16</sup>, the FTIR spectra of pure and equi molar binary mixture systems were recorded in the 400-4000 $cm^{-1}$  region on Perkin Elmer series.

## 3. Theory

The molecular interaction between a polar solute and a polar solvent can be described by the modified Kirkwood –Frohlich correlation factor. The Kirkwood –Frohlich theory<sup>15</sup> takes in to account of the short-range interactions through the introduction of the dimensionless correlation factor  $g$ , which gives information regarding the orientation of the electric dipoles in polar liquids. The Kirkwood correlation factor ( $g$ ) for the pure liquids is given<sup>17</sup> by the expression:

$$\frac{4\pi N_A \mu^2 \rho}{9kTM} g = \frac{(\epsilon - \epsilon_\infty)(2\epsilon + \epsilon_\infty)}{\epsilon(\epsilon_\infty + 2)^2} \dots\dots\dots(1)$$

where  $N_A$  is the Avogadro's number,  $\mu$  the dipole moment in the gaseous phase.  $\rho$  the density,  $k$  the Boltzmann constant,  $T$  the temperature in Kelvin.  $M$  the molecular weight,  $\epsilon$  the dielectric permittivity at static frequency and  $\epsilon_\infty$  is the permittivity at optical frequency which is the square of refractive index.

For a mixture of two polar liquids, say 1 and 2 the Eq. (1) could be modified<sup>18</sup> using different assumptions. Assuming that  $g^{\text{eff}}$  is the effective correlation factor for the mixture, the Kirkwood equation for the mixture can be expressed as:

$$\frac{4\pi N}{9kT} \left( \frac{\mu_A^2 \rho_A}{M_A} X_A + \frac{\mu_B^2 \rho_B}{M_B} X_B \right) g^{\text{eff}} = \frac{(\epsilon_{\text{om}} - \epsilon_{\infty\text{om}})(2\epsilon_{\text{om}} + \epsilon_{\infty\text{om}})}{\epsilon_{\text{om}}(\epsilon_{\infty\text{om}} + 2)^2} \dots\dots(2)$$

or

Assuming that the dipole moments of both the liquids are affected by the same amount  $g^f$  the Kirkwood equation for the mixture is modified as:

$$\frac{4\pi N_A}{9kT} \left( \frac{\mu_A^2 \rho_A g_A}{M_A} X_A + \frac{\mu_B^2 \rho_B g_B}{M_B} X_B \right) g^f = \frac{(\epsilon_m - \epsilon_{\infty m})(2\epsilon_m + \epsilon_{\infty m})}{\epsilon_m(\epsilon_{\infty m} + 2)^2} \dots\dots\dots(3)$$

where  $X_A$  and  $X_B$  are the molefractions of liquids 1 and 2 in the mixture respectively and the suffix 1, 2 and m represents liquid 1, liquid 2 and mixture, respectively. Here the value of  $g^{\text{eff}}$  in Eq. (2) varies from  $g_A$  to  $g_B$  as the concentration (molefraction) of liquid 2 increases from 0 to 1 and the value of  $g^f$  in Eq. (3) is unity for pure polar liquids and close to unity if there is no interaction between the liquid mixtures. The deviation of  $g^f$  value from unity indicates the interaction between liquids 1 and 2.

The solute-solvent interaction between the components of a mixture can also be obtained from another dielectric parameter is Bruggemann factor ( $f_B$ ) and it is given by:

$$f_B = \left[ \frac{(\epsilon_m - \epsilon_2)}{(\epsilon_1 - \epsilon_2)} \right] \left( \frac{\epsilon_1}{\epsilon_m} \right)^{1/3} = (1 - \phi_2) \quad \dots\dots(4)$$

where  $\phi_2$  is the volume fraction of liquid 2 in liquid 1, If there is no interaction between the components in the mixture then the Bruggemann factor<sup>19</sup> ( $f_B$ ) should vary linearly with volume fraction  $\phi_2$ , but if there is interaction between the components then  $f_B$  varies non-linearly with  $\phi_2$ .

The dielectric data obtained i.e.,  $\epsilon_{static}$ ,  $\epsilon^*(\omega) = \epsilon'(\omega) - i\epsilon''(\omega)$ ,  $\epsilon_\infty$  and the data from impedance analyser is used to fit in an Argand diagram to calculate the relaxation time ( $\tau$ ). The distribution of relaxation time is witnessed from Cole-Cole are plot. Although Cole-Cole equations which signify the distribution of relaxation time is measured using the equation:

$$\omega\tau = \left( \frac{v}{u} \right)^{1-\alpha} \quad \dots\dots\dots(5)$$

Where  $\alpha$  (distribution parameter),  $u$  and  $v$  values are determined from their respective Cole-Cole plots.

Eyring<sup>20,21</sup> treated the dipolar rotation on the basis assumed to jump from one equilibrium position to another, depending on the following factors:

- (a) The number of collisions that it makes with the neighbouring molecules;
- (b) The entropy  $\Delta S^*$ , which describes the disturbance of the local structure of the medium during orientation;
- (c) The heat of activation  $\Delta H^*$ , which is equal to the potential barrier separating the successive equilibrium positions. Using this concept a relation between the microscopic relaxation time and the free energy of activation is given as:

$$\tau = \frac{h}{kT} \exp\left[\frac{\Delta G^*}{RT}\right] = \frac{h}{kT} \exp\left[\frac{\Delta H^* - T\Delta S^*}{RT}\right] \dots\dots\dots(6)$$

Where  $h$  is the Planck's constant,  $k$  the Boltzmann constant,  $T$  the temperature in Kelvin and  $R$  is the gas constant. By using Eq. (6), the thermodynamic parameters Gibb's energy of activation  $\Delta G^*$ , molar enthalpy of activation  $\Delta H^*$ , molar entropy of activation  $\Delta S^*$  for various molefractions and at different temperatures can be determined.

Minimum energy structures of the monomers of ethylene glycol, methyl butyrate, ethyl butyrate and the equimolar hydrogen bonded complexes for the vibrational frequencies are obtained from semi-empirical Hamiltonian quantum mechanical calculations<sup>22,23</sup> such as Austin model 1 (AM1), Parameterized model number 3 (PM 3) and Modified Neglect of Differential Overlap (MNDO) converged geometry optimization procedure using Spartan Modeling software<sup>24</sup>.

#### 4.Results and Discussion

The permittivity values  $\epsilon_{static}$  and  $\epsilon_{\infty}$  for various mole fractions at different temperatures of the binary systems EG+ MB (System 1) and EG+EB (System 2) are determined experimentally and their variation with mole fraction is shown in Figs 1 and 2

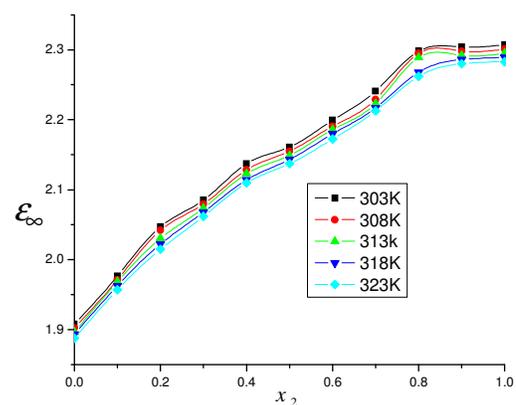
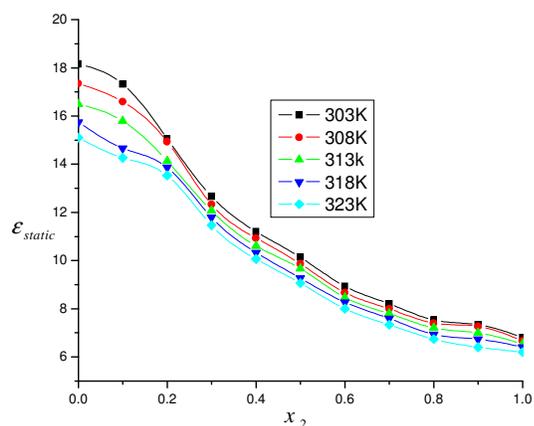


Fig. 1

Fig. 1- Static permittivity ( $\epsilon_{\text{static}}$ ) versus mole fraction ( $X_2$ ) of methyl butyrate in EG at different temperatures

Fig. 2

Fig.2 – High frequency permittivity ( $\epsilon_{\infty}$ ) versus mole fraction of methyl butyrate in EG at different temperatures

(System 1), 3 and 4 (System 2). From Figs 1-4, it is observed that there is non-linear variation of  $\epsilon_{\text{static}}$  and  $\epsilon_{\infty}$  with mole fractions at all temperatures, which indicates the interaction between the compounds. Similar results were reported by Kroeger<sup>6</sup> for the mixture of alcohols and polar liquids. The values of  $g^{\text{eff}}$ ,  $g^{\text{f}}$  for system 1 and system 2 at different temperatures are presented in Table 1 and 2, EG and MB are greater than unity at all temperatures, which suggest that molecular dipoles have parallel orientation among themselves. For the pure compound EB, the values of  $g^{\text{eff}}$  are less than unity at all temperatures indicating anti-parallel orientation of the electric dipoles. But both the mixture systems, the parameter  $g^{\text{eff}}$  exhibits a steadily decreasing tendency as the concentration of MB or EB goes on increasing in EG at all temperatures. This tendency leads to the conclusion that the heterogeneous interaction between the compounds in binary systems, possibly between the-OH group of alcohol and -CH group of butyrates, is in such a way to form multimers with decreasing parallel orientation of electric dipoles<sup>25</sup>. The strength of this heterogeneous interaction is found to depend on the temperature and concentration of the mixture, which shows that temperature and concentration variations impact the structural properties.

The Corrective Kirkwood correlation factor ( $g^{\text{f}}$ ) is a dielectric parameter, which can give information regarding the interaction between the compounds in the mixture. For an ideal non-

interacting mixture,  $g^f$  must be unity and the magnitude of deviation of  $g^f$  from unity indicates the strength of interaction between the compounds (i.e) greater the deviation from unity larger the strength of interaction<sup>26</sup>.

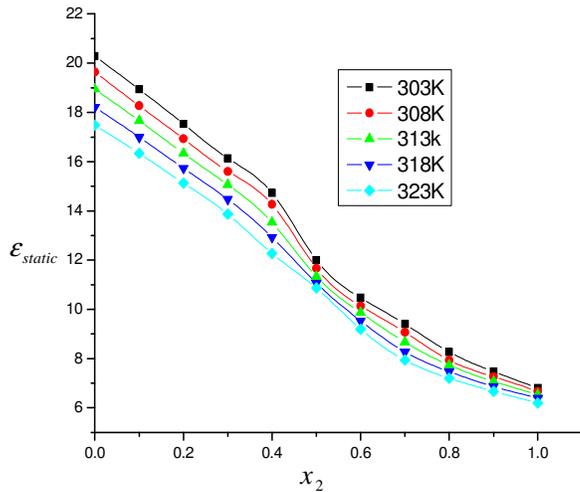


Fig. 3

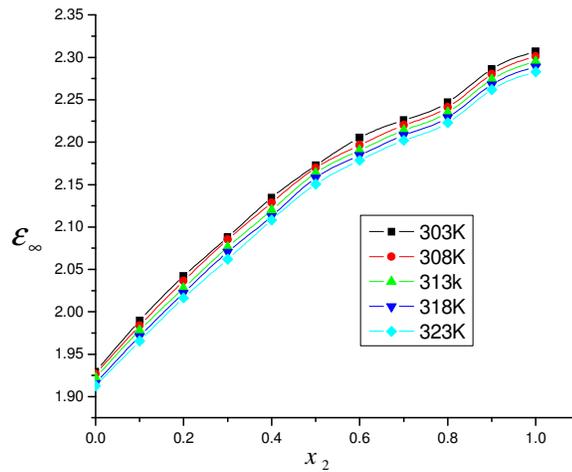


Fig. 4

Fig. 3- Static permittivity ( $\epsilon_{static}$ ) versus mole fraction ( $X_2$ ) of ethyl butyrate in EG at different temperatures

Fig.4 – High frequency permittivity ( $\epsilon_{\infty}$ ) versus mole fraction of ethyl butyrate in EG at different temperatures

Table 1 – Values of  $g^{eff}$  and  $g^f$  with mole fraction( $X_2$ ) of methyl butyrate in EG at different temperatures

$X_2$	T = 303 K		T = 308 K		T = 313 K		T = 318 K		T = 323 K	
	$g^{eff}$	$g^f$								
0	3.1316	1.0000	3.0592	1.0000	2.9730	1.0000	2.8936	1.0000	2.8340	1.0000
0.1	2.9538	0.7739	2.7912	0.9630	2.7085	0.9607	2.6834	0.9771	2.5784	0.9584
0.2	2.3349	0.6514	2.3347	0.8555	2.3554	0.8864	2.3209	0.8958	2.3110	0.9101
0.3	1.9008	0.5698	1.8837	0.7387	1.8429	0.7415	1.8512	0.7629	1.8933	0.7955
0.4	1.7074	0.5560	1.6403	0.6948	1.6423	0.7126	1.6422	0.7288	1.6215	0.7331
0.5	1.4158	0.5079	1.3954	0.6459	1.3916	0.6586	1.3982	0.6756	1.4098	0.6931
0.6	1.4093	0.5678	1.3445	0.6903	1.3506	0.7072	1.3260	0.7071	1.3196	0.7147
0.7	1.2980	0.6023	1.2527	0.7275	1.2552	0.7410	1.2579	0.7538	1.2617	0.7660
0.8	1.1638	0.6461	1.1126	0.7511	1.1254	0.7686	1.1377	0.7852	1.1366	0.7916
0.9	1.0714	0.7556	1.0276	0.8391	1.0398	0.8527	1.0515	0.8655	1.0463	0.8640
1	0.9432	1.0000	0.9503	1.0000	0.9578	1.0000	0.9649	1.0000	0.9715	1.0000

Table 2 – values of  $g^{\text{eff}}$  and  $g^{\text{f}}$  with mole fraction( $X_2$ ) of ethyl butyrate in EG at different temperatures

$X_2$	T = 303 K		T = 308 K		T = 313 K		T = 318 K		T = 323 K	
	$g^{\text{eff}}$	$g^{\text{f}}$								
0	3.1316	1.0000	3.0592	1.0000	2.9730	1.0000	2.8936	1.0000	2.8340	1.0000
0.1	2.9538	0.7739	2.7912	0.9630	2.7085	0.9607	2.6834	0.9771	2.5784	0.9584
0.2	2.3349	0.6514	2.3347	0.8555	2.3554	0.8864	2.3209	0.8958	2.3110	0.9101
0.3	1.9008	0.5698	1.8837	0.7387	1.8429	0.7415	1.8512	0.7629	1.8933	0.7955
0.4	1.7074	0.5560	1.6403	0.6948	1.6423	0.7126	1.6422	0.7288	1.6215	0.7331
0.5	1.4158	0.5079	1.3954	0.6459	1.3916	0.6586	1.3982	0.6756	1.4098	0.6931
0.6	1.4093	0.5678	1.3445	0.6903	1.3506	0.7072	1.3260	0.7071	1.3196	0.7147
0.7	1.2980	0.6023	1.2527	0.7275	1.2552	0.7410	1.2579	0.7538	1.2617	0.7660
0.8	1.1638	0.6461	1.1126	0.7511	1.1254	0.7686	1.1377	0.7852	1.1366	0.7916
0.9	1.0714	0.7556	1.0276	0.8391	1.0398	0.8527	1.0515	0.8655	1.0463	0.8640
1	0.9432	1.0000	0.9503	1.0000	0.9578	1.0000	0.9649	1.0000	0.9715	1.0000

Table 3 – Values of Bruggemann factor ( $f_B$ ) with volume fraction ( $\phi_2$ ) of methyl butyrate and ethyl butyrate in ethylene glycol at different temperatures

$X_2$	T = 303 K		T = 308 K		T = 313 K		T = 318 K		T = 323 K	
	EG+MB	EG+EB								
0	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
0.1	0.9456	0.9545	0.9368	0.9400	0.9427	0.9315	0.9459	0.9341	0.9461	0.9302
0.2	0.8876	0.9020	0.8884	0.8830	0.8878	0.8725	0.8875	0.8756	0.8909	0.8660
0.3	0.8299	0.8470	0.8242	0.8280	0.8244	0.8077	0.8214	0.8011	0.8240	0.7978
0.4	0.7546	0.7428	0.7519	0.7342	0.7546	0.7257	0.7369	0.7303	0.7428	0.7395
0.5	0.6733	0.5979	0.6707	0.5953	0.6730	0.5978	0.6445	0.6123	0.6359	0.6202
0.6	0.5029	0.4393	0.5055	0.4419	0.4996	0.4361	0.5029	0.4505	0.5140	0.4475
0.7	0.3522	0.3369	0.3548	0.2794	0.3607	0.2801	0.3404	0.2853	0.3522	0.2804
0.8	0.2447	0.2827	0.2303	0.1693	0.2158	0.1647	0.2040	0.1660	0.1929	0.1654
0.9	0.1116	0.0867	0.1236	0.0828	0.0917	0.0826	0.0887	0.7789	0.0854	0.0808
1	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

In the present case for both the systems at low concentrations of butyrates in EG, the values of  $g^{\text{f}}$  are closer to unity indicating weaker intermolecular interactions between the compounds, but

as the concentration of MB and EB increases in EG  $g^f$  values deviate more from unity indicating the increment in the strength of hetero interaction between the compounds. The values of  $g^f$  are found to depend more on concentration than temperatures as reported by Krishnan S et al<sup>27</sup>. Further, it is observed that  $g^f$  values deviate more from unity, in system 2 than in system 1, at all temperatures indicating stronger hetero interaction in case of system 2.

The other dielectric parameter, which gives information about the interaction between the components in the mixture, is Bruggemann parameter ( $f_B$ ). The values of  $f_B$ , for both the systems, are found to vary non-linearly with volume fraction  $\phi_2$  at all temperatures are provided in Table 3. This phenomenon indicates that there is an interaction taking place between the components of the binary systems<sup>28</sup>.

The relaxation times ( $\tau$ ) of pure EG are higher and is due to the formation of intra molecular hydrogen bonding between one alcohol molecule and another (R-O-H...OH-R), which leads to the formation of self associated groups. The increase in the number of self associated groups causes to absorb more electromagnetic energy. Due to this, molecules relax very slowly leading to higher relaxation times<sup>29</sup>. But the relaxation times of pure MB and EB are very low<sup>30</sup> compared to pure EG. The relaxation times of pure EB are greater than that of pure MB due to the increase in molecular size and effective radius of the rotating unit<sup>31</sup>. The relaxation times are found to decrease as the concentration of MB and EB increases in EG at all temperatures as shown in Fig 5 and 6, respectively.

At high concentrations of alcohol in the mixture, there are a large number of EG molecules surrounding the butyrate molecules are forming hydrogen bond with the butyrate molecules.

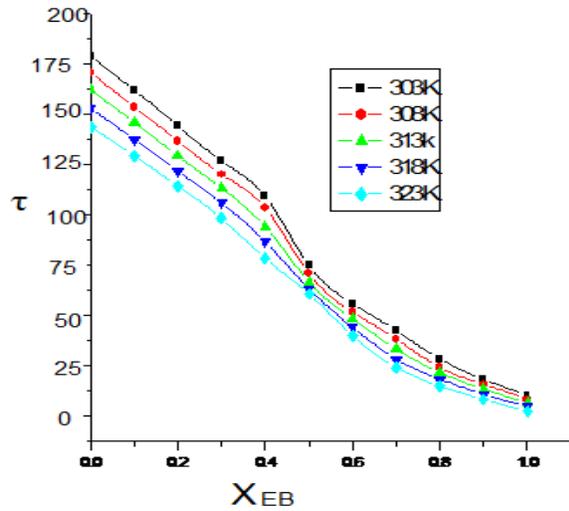


Fig. 5

Fig. 5- Relaxation time ( $\tau$ ) with mole fraction ( $X_2$ ) of methyl butyrate in EG at different temperatures

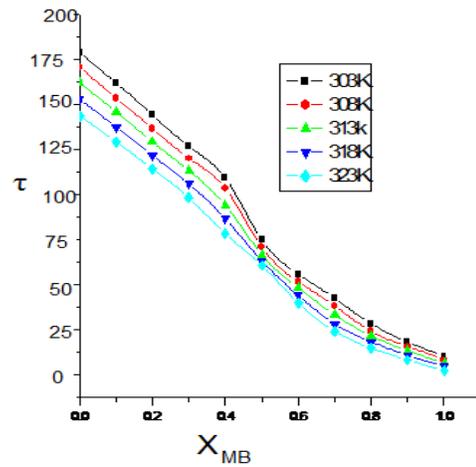


Fig. 6

Fig. 5- Relaxation time ( $\tau$ ) with mole fraction ( $X_2$ ) of ethyl butyrate in EG at different temperatures

Table-4 – Values of Gibb's energy of activation ( $\Delta G^*$  KJ Mol<sup>-1</sup>) with mole fraction( $X_2$ ) of methyl butyrate in EG at different temperatures

$X_2$	T = 303 K	T = 308 K	T = 313 K	T = 318 K	T = 323 K
1	17.6192	17.8196	18.0406	18.2755	18.2410
0.9	17.0911	17.3478	17.5286	17.7039	17.9216
0.8	16.7613	16.9619	17.1173	17.3108	17.4815
0.7	16.3498	16.5364	16.6530	16.8155	16.9312
0.6	15.8793	15.9884	16.1582	16.2709	16.3484
0.5	15.2877	15.4007	15.4416	15.5502	15.6035
0.4	14.5869	14.6175	14.6879	14.6536	14.5402
0.3	13.9784	13.9355	13.9769	13.6871	13.6580
0.2	13.1428	13.1130	12.9524	13.0044	12.8241
0.1	12.4432	12.4153	12.1716	11.4013	11.1530
0	11.0641	11.0082	10.3672	10.2441	9.7950

Table-5 – Values of Gibb's energy of activation ( $\Delta G^*$  KJ Mol<sup>-1</sup>) with mole fraction( $X_2$ ) of ethyl butyrate in EG at different temperatures

$X_2$	T = 303 K	T = 308 K	T = 313 K	T = 318 K	T = 323 K
1	17.6192	17.8196	18.0406	18.2755	18.2410
0.9	17.1433	17.4007	17.5478	17.7144	17.9266
0.8	16.8112	16.9965	17.1439	17.3283	17.5100
0.7	16.4015	16.5721	16.7114	16.8829	16.9846
0.6	15.9548	16.0735	16.2583	16.1934	16.3667
0.5	15.3782	15.4087	15.4018	15.4961	15.6271
0.4	14.5956	14.6660	14.6076	14.6220	14.5482
0.3	14.1101	14.0804	14.0628	13.7234	13.7543
0.2	13.2199	13.2372	13.0520	13.1412	13.0007
0.1	12.7235	12.5711	12.4194	11.7477	11.5501
0	11.1793	11.0785	10.9292	10.4735	10.3912

Thus dipole-dipole interaction occurs in such a way that the effective dipole moment get increased and linear  $\alpha$ - multimers are formed<sup>25</sup>. At low concentration of EG in the mixtures, there are only a small number of alcohol molecules to enable dipole-dipole interaction through hydrogen bonding with the non-associative butyrate molecules. As a result, weak intermolecular interaction occurs. The relaxation time increases with increasing alkyl chain length of butyrates indicating that the degree of cooperation for reorientation of the molecules increases with increasing length and the bulk of cluster increases. So the formation of hydrogen bonding between hydroxyl group (-OH) of EG and -CH group of butyrates restricts the free internal rotation of the molecules.

The values of thermodynamic parameter, Gibb's energy of activation ( $\Delta G^*$ ) exhibited positive deviation, increased with decreased concentrations of butyrates (MB and EB) in EG at different temperatures are presented in Table 4 and 5, respectively. The increasing positive values of  $\Delta G^*$  suggest the existence of molecular associations between unlike molecules in the mixture<sup>32</sup>. In the present study,  $\Delta G^*$  values of system 2 is high compared to system 1.

The molar enthalpy of activation ( $\Delta G^*$ ) and molar entropy of activation ( $\Delta S^*$ ) for various mole fractions of butyrates (MB and EB) in Ethylene glycol(EG) are also calculated and are given in Table 6. The positive value of  $\Delta H^*$  gives the amount of heat liberated in the process of dielectric reorientation<sup>33,34</sup>. The molar enthalpy values for both the systems (1 and 2) are positive indicating the bond formation. The negative values of  $\Delta S^*$  in both the systems, indicate that the activated complexes have lower entropy than the reactants, since entropy is a measure of disorder or chaos of the reaction. This is the situation encountered with most biomolecular reactions because the two molecules initially in random situation must come together with the resulting loss of entropy<sup>33</sup>. These values also indicate that there are fewer configurations possible in the activated state and for these configurations the molecules are ordered to higher extent than in the normal state<sup>34</sup>.

Observing the FTIR spectra for the equimolar mixture of EG+MB (System 1), there is a shift of  $10\text{cm}^{-1}$  wave number in the position of  $-\text{CH}$  for the mixture compared with the pure spectrums of EG and MB, respectively. Similarly, the FTIR spectra for the equimolar mixture of EG+EB (system 2), there is a shift of  $13\text{ cm}^{-1}$  wave number in the position of  $-\text{OH}$  and  $11\text{cm}^{-1}$  wavenumber in the position of  $-\text{CH}$  for the mixture compared with the pure spectrums of EG and EB, respectively. These shifts are caused by the strong interaction between the high electro-negative charge of oxygen in EG and hydrogen in butyrates (MB and EB). Thus the IR analysis convinces intermolecular hydrogen bonding of the equimolar binary mixtures (system 1 and system 2) effectively with proportionate variations in stretching frequencies of  $-\text{OH}$  and  $-\text{CH}$  compared to their respective pure systems<sup>35</sup>.

Table 6-Values of molar enthalpy ( $\Delta H^*$ ) and molar entropy ( $\Delta S^*$ ) with mole fraction ( $X_2$ ) methyl butyrate and ethyl butyrate in EG

$X_2$	$\Delta H^*$ (kJmol <sup>-1</sup> )		$\Delta S^*$ (kJmol <sup>-1</sup> K <sup>-1</sup> )	
	system 1	system 2	system 1	system 2
0	7.1357	7.1357	-0.0347	-0.0347
0.1	4.7641	5.6267	-0.0407	-0.0381
0.2	5.8028	6.2175	-0.0362	-0.0349
0.3	7.4590	7.2995	-0.0294	-0.0300
0.4	8.3108	10.0276	-0.0250	-0.0196
0.5	10.3517	11.6481	-0.0163	-0.0122
0.6	14.6131	15.1200	-0.00008	0.0015
0.7	18.9675	17.1716	0.0162	0.0097
0.8	17.3246	18.1438	0.0137	0.0095
0.9	23.4543	21.2555	0.0586	0.0307
1	30.4528	23.9028	0.0636	0.0417

The comparison of experimental and theoretical FT-IR values are provided in Table 7 and the obtained theoretical values are in good agreement with the experimental values<sup>38</sup>. The optimized geometrical structures for the formation of hydrogen bonding in EG+MB and EG+EB, which are obtained from Hamiltonian quantum mechanical calculations using Spartan Modeling software are shown in Fig.7 and 8, respectively.

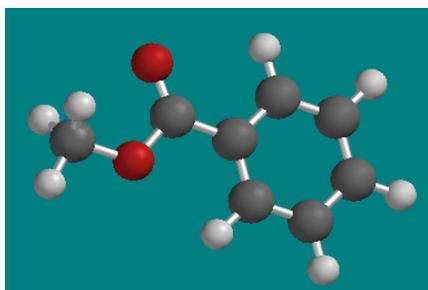


Fig. 7

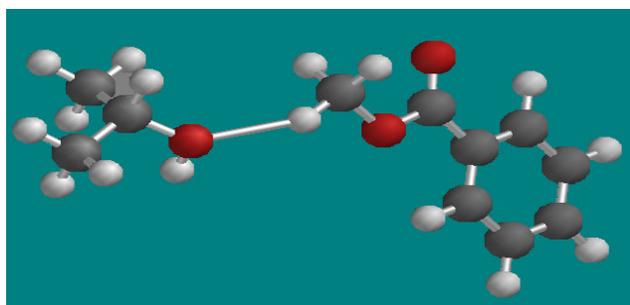


Fig. 8

Fig. 7-Optimized converged geometrical structure of hydrogen bonded EG and methyl butyrate (red: oxygen, black: carbon, white: hydrogen)

Fig. 7-Optimized converged geometrical structure of hydrogen bonded EG and ethyl butyrate (red: oxygen, black: carbon, white: hydrogen)

Table 7-Experimental and Theoretical FT-IR analysis for the pure and binary mixtures of EG, MB and EB

Compound	Band	Experimental		Theoretical (Pc Spartan)					
		$\nu$ ( $\text{cm}^{-1}$ )	$\Delta\nu$ ( $\text{cm}^{-1}$ )	AM1		PM3		MNDO	
				$\nu$ ( $\text{cm}^{-1}$ )	$\Delta\nu$ ( $\text{cm}^{-1}$ )	$\nu$ ( $\text{cm}^{-1}$ )	$\Delta\nu$ ( $\text{cm}^{-1}$ )	$\nu$ ( $\text{cm}^{-1}$ )	$\Delta\nu$ ( $\text{cm}^{-1}$ )
EG	OH	3550	---	3503	---	3903	---	4006	--
MB	CH	2952	---	2983	---	3141	---	3234	---
EB	CH	2984	---	3071	---	3185	---	3276	---
EG + MB	HO--HC	3540	10 --(OH)	3497	06--(OH)	3964	61 --(OH)	4150	144 --(OH)
		2959	07 --(CH)	2997	14 --(CH)	3197	56 --(CH)	3198	36 --(CH)
EG + EB	HO--HC	3537	13 --(OH)	3527	24--(OH)	3963	60--(OH)	4193	187--(OH)
		2973	11 --(CH)	3107	36 --(CH)	3177	08 --(CH)	3350	74--(CH)

## 5. Conclusions

The dielectric parameters Kirkwood effective correlation factor, Corrective Kirkwood correlation factor, Bruggemann parameter, relaxation time and thermodynamic parameters, Gibb's energy of activation, molar enthalpy of activation and molar entropy of activation are computed for the pure and binary mixture systems of ethylene glycol with methyl butyrate and ethyl butyrate at different temperatures for various mole fractions. The formation of hydrogen bond between the mixture systems is identified by studying the variations in the parameters determined. The existence of hydrogen bond between –OH group of ethylene glycol with –CH group of methyl butyrate and ethyl butyrate is confirmed through FT-IR spectra. The FT-IR values are determined theoretically using quantum mechanical calculations and are in good agreement with the experimental values.

## References

1. Ediger M D, Angell C A & Nagel S R, 1996. Supercooled liquids and glasses, *J Chem Phys*, 100: 13200
2. Nath G, Sahu S and Paikaray R, 2009. Study of acoustic parameters of binary mixtures of a nonpolar liquid with polar liquid at different frequencies, *Indian J. Phys.* 83: 429
3. Gupta K K, Bnashal A K, Singh P J & Sharma K S, 2003. Temperature dependence of dielectric relaxation of rigid polar molecules acetophenone, pyridine and their mixtures in dilute solutions of benzene, *Indian J Pure & Appl Phys*, 41: 57
4. Rowlinson J S & Swinton F L, 1982. *Liquids and Liquid Mixtures* (Butterworth, London), 3<sup>rd</sup> Edn.

5. Liakath Ali Khan F, Sivagurunathan P, Raja Mohamed Kamil S & Mehrotra S C, 2007. Dielectric studies of methyl methacrylate and butyl methacrylate with primary alcohols using time domain reflectometry, *Indian J Pure & Appl Phys*, 44: 754
6. Kroeger M K, 1987. Clustering and dielectric behavior of alcohols, *J Mol Liq*, 36:101
7. Sengwa R J, Vinita Khatri & Sonu Sankhla, 2009. Static dielectric constants and Kirkwood correlation factor of the binary mixtures of N-methylformamide with formamide, N, N-dimethylformamide and N, N ..., *J Sol Chem*, 38:763
8. Jacobo Troncoso, Claudio Cerdeirna A, Yolanda Sanmamed A, Luis Romani & Luis Paulo N Rebelo, 2006. Thermodynamic Properties of Imidazolium-Based Ionic Liquids: Densities, Heat Capacities, and Enthalpies of Fusion of [bmim][PF6] and [bmim][NTf2], *J Chem Eng Data*, 51:5
9. George A J, 1997. Hydrogen-Bonded Complexes of Aromatic Crown Ethers with (9-Anthracenyl) methylammonium Derivatives. *Supramolecular Photochemistry and Photophysics. pH ...An Introduction to hydrogen bonding (Oxford University Press, London).*
10. Parthipan G, Arivazhagan G & Thenappan T, 2008. Dielectric and thermodynamic studies on a binary mixture of anisole with butyric or caprylic acid, *Philosophical Magazine Letters*, 88:125.
11. Bruggemann D A G, 1935. Six-vector mixing formulae defended. Reply to comment on Effective medium formulae for bi-anisotropic mixtures, *Ann Phys*, 5:636.
12. Cole K S & Cole R H, 1941. Dispersion and absorption in dielectrics I. Alternating current characteristics, *J Chem Phys*, 9:341.

13. Chaudhari A & Mehrotra S C, 2002. Dielectric relaxation study of pyridine-alcohol mixtures using time domain reflectometry, *Mol Phy*, 100:3907.
14. Dharmalingam K, Ramachandran K, Sivagurunathan P, Prabhakar under B, Khirade P W, & Mehrotra S C, 2007 Dielectric relaxation of butyl acrylate—alcohol mixtures using time domain reflectometry, *.Chem Pap* 61:300.
15. Nora E Hill, Vaughan E, Price A H & Davies M, 1968. Microwave dielectric relaxation, thermodynamic and conformational studies of hydrogen bonded binary mixtures of propan-1-ol with methyl benzoate and ethyl ..., *Dielectric properties and Molecular Behaviour (Northland Reinhold Company, London)*.
16. D R Lide, 1971. CRC. Handbook of Chemistry and Physics (*CRC Press, Boca Raton*) 78<sup>th</sup> Edn.
17. Kirkwood J G, 1939. The dielectric polarization of polar liquids, *J Chem Phys*, 7:911.
18. Puranic S M, Kumbharkhane A C & Mehrotra S C, 1991. Dielectric relaxation spectra for N, N-Dimethylacetamide-water mixures using picosecond time domain reflectometry, *J Mol. Liq*, 50:143.
19. Kaatze U, 1987. Dielectric properties of aqueous solutions of pyrazine and some of its alkyl derivatives, *Z Phys Chem*, 153:141.
20. Eyring H, Cernuschi F, 1939. An elementary theory of condensation, *J Chem Phys*, 7:547.
21. Kauzmann W, 1942. Dielectric relaxation as a chemical rate process, *Rev Mod Phys*, 14:12.
22. Chitra M, Subramanyam B & Murthy V R K, 2001. Conformational and dielectric analysis of hydrogen bonded polar binary mixtures of methyl benzoate with aniline, *Indian J Pure & Appl Phys*, 39:461.

23. Sundaraganesan N, Dominic Joshua B, Rajamoorthy M & Gangadhar C H, 2007. FT-IR, FT-Raman spectra and ab-initio DFT vibrational analysis of 2-chloro-5-aminopyridine, *Indian J Pure & Appl Phys*,45:969.
24. Spartan Version 5.1.1,1999 Quadrupolar moment calculations and mesomorphic character of model dimeric liquid crystals (*Wave Function Inc, CA:USA*)
25. Thenappan T, Prabakar Devaraj A,2006 Dielectric studies on binary polar mixtures of propanoic acid with esters, *J Mol Liq*,123:72
26. Ajay Chaudhari, Antia Das, Garigipati Raju, Harish Chaudhari, Prakash Khirade, Navinkumar Narain, Suresh Mehrotra,2001 Complex permittivity spectra of binary mixture of ethanol with nitrobenzene and nitrotoluene using the time domain technique, *Proc Natl Sci Counc Roc (a)*, 25:205
27. Balamurugan D, Kumar S, Krishnan S, 2005 Dielectric relaxation studies of higher order alcohol complexes with amines using time domain reflectometry, *J Mol Liq*, 122:11
28. Sivagurunathan P, Dharmalingam K,Ramachandran K, Prabhakar Undre B, Khirade P W & Mehrotra S C, 2007 Dielectric studies on binary mixtures of ester with alcohol using time domain reflectometry, *J Mol Liq*, 133:139
29. Vyas A D, Rana V A, Bhatnagar S P & Vashisth V M, 2008 Structural aspects in the dielectric properties of pentyl alcohols , *Indian J Pure & Appl Phys*, 46:521
30. Rajala G E & Crossley J,1972 Canadian, Dielectric and association behavior of 1-propanol, 2-propen-1-ol, and 2-propyn-1-ol in non-polar solvents, *J Chem*,50:99
31. Chitra M,Subramanyam B & Murthy V R K,2001, Conformational and dielectric analysis of hydrogen bonded polar binary mixtures of methyl benzoate with N-methylaniline, *Mol, Phys* 99:1569

32. Patil S P, Chaudari A S, Lokhande M P, Landle M K & Mehrotra S C, 1999 Dielectric measurements of aniline and alcohol mixtures at 283, 293, 303, and 313 K using the time domain technique, *J Chem Eng Data*, 44:875
33. Pal A & Kumar S, 2004, Viscometric and volumetric studies of some amino acids in binary aqueous solutions of urea at various temperatures, *J Mol Liq*, 109:23
34. Sharma V, Thakur N, Sharma D R, Rangra V S & Negi N S, 2008, Dielectric relaxation studies of binary mixtures of ethyl alcohol and N, N-dimethylacetamide in the benzene solution from microwave absorption data, *Indian J Pure & Appl Phys*, 46:212
35. Bansal R K, 1998 Organic Reaction Mechanisms, Heterocyclic chemistry (*Tata McGraw-Hill, New Delhi*)
36. Singh A, Misra R, Shukla J P, Sexena M C, 1983, Evaluation of the thermodynamic parameters for association process of hydrogen bond complexes from the dielectric relaxation measurements, *J Mol Liq*, 23:29
37. Silverstein R M, Bassler G C & Morrill T C, 1991, Spectroscopic Identification of Organic Compounds, Computational study of 2-bromo-4-chloroacetophenone (*John Wiley & sons, Singapore*) 5<sup>th</sup> Edn
38. Singh H J, & Srinivasan P, 2009, Computational studies on the structure and vibrational spectra of 2-hydroxy-5-methyl-3-nitropyridine, *Indian J Pure & Appl Phys*, 47:557