# Dielectric Relaxation studies of Methyl acetate with 2-Alkoxyethanols using Time Domain Reflectometry Technique

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**ABSTRACT** — Complex Dielectric spectra of Methyl acetate (MA) with 2-Alkoxyethanols like 2-methoxyethanol (2-ME), 2-ethoxyethanol (2-EE), 2-butoxyethanol (2-BE) for various concentrations over the frequency ranges from 10MHz to 20GHz at 308.15K were recorded using Time Domain Reflectometry (TDR). The dielectric constant, dielectric permittvity and dielectric loss were obtained from the TDR measurement. The molecular interaction parameters like relaxation time, Kirkwood correlation factors, Bruggeman factor, excess dielectric constant, excess inverse relaxation time and excess Helmholtz free energy of activation were also calculated. This study gives the information about the nature of molecular interaction between the participating liquid molecules.

*Keywords* — *Complex Dielectric spectra, Relaxation time, Methyl acetate, 2-Alkoxyethanols, Time Domain Reflectometry.*

## I. INTRODUCTION

When two liquids of different chemical properties are mixed together, it results into a state which has properties widely different from the constituent liquids. Understanding such behavior, in particular the molecular interaction present between the pure liquids and solutions becomes a necessity as they find a variety of applications in industries. The study of 2-Alkoxyethanols is important because they are widely used as solubilizing agents in many industries as well as in pharmaceutical and plastic products. Esters are important because they have distinctive flavor and pleasing odor due to which they are widely used in favor and fragrance industries and is also used as plasticizers to get specific thermo characteristics [1-3].

The study of mixing behavior of mixtures containing Alkoxyethanols and Esters is useful for many industrial applications. Biodiesel fuels typically contain mono alkyl, often methyl and ethyl, esters of long–chain fatty acids, derived from vegetable oils or animal fats. In general combustion performance is influenced by the chemical nature of the esters in the biodiesel fuel and their structural features, including the length of the alkyl chain and their degree of saturation and branching [4-7].

2-Alkoxyethanols are used as a solvent for many different purposes such as varnishes, dyes, and resins. 2-Alkoxyethanols are very interesting class of solvent having ether component. It has both proton accepting and donating ability. They are aliphatic in nature [8, 9]. Systematic measurements on binary liquid mixtures comprising of 2-Alkoxyethaols + Esters have been carried out in our laboratory. This study was carried out to understand the inter molecular interactions present between Alkoxyethanols and Esters for different concentrations at 308.15K, over the frequency range 10MHz to 20GHz, using time domain reflectometry.

## II. MATERIALS

The Chemicals utilized for this work were Methyl acetate (MA), 2-methoxyethanol (2-ME), 2-ethoxyethanol (2-EE), 2-butoxyethanol (2-BE) supplied by Loba chemicals (purity >> 99%) AR-grade and were used without further purification. The purity of chemicals were tested by comparing their densities and refractive indices from

the literature values. The digital electronic balance (Adventurer Ohaus AR2140) was used for the mass measurement with an accuracy of ± 0.0001g.

## 2.1 METHODS

The refractive indices for the prepared mixtures were measured by using Abbe's refractometer (SIPCON model) with sodium D line at 308.15K. Density measurement was carried out using specific gravity bottle. The water circulation bath was provisioned using a temperature controller system (ESCY IC 201 model), accuracy of 0.5 K. Perkin Elemer RXI FT-IR spectrophotometer was used to find molecular functional group and vibrational modes analysis. The complex dielectric spectra for pure and binary mixtures were determined by using TDR Instrument.

The densities of the pure compounds were determined using a DMA 4500 M (Anton Paar) vibrating-tube digital densitometer. The sample cell was calibrated with air and double distilled water before measurements. The accuracy of the measured density and temperature was $\pm 1 \times 10^{-2}$ kg.m$^{-3}$ and $\pm 0.01$ K, respectively. Refractive indices were measured with an accuracy of $\pm 1 \times 10^{-5}$. The temperature of the refractometer was controlled by a thermostat system (ESCY IC 201) with an accuracy of $\pm 0.5$ K.

The complex dielectric spectra were measured using Time Domain Reflectometry (Agilent infiniium DCA-J 86100A with sample oscilloscope HP 54754A). A repetitive fast 39 picoseconds (ps) rising time step voltage pulse was fed through a 50 $\Omega$ impedance semi-rigid slim probe having pin length 0.14 mm. Reflected pulse without sample $R_1(t)$ and with sample $R_x(t)$ were recorded in a 2 ns time window and digitized into 1200 points. The frequency dependent complex spectra were obtained from reflection coefficient spectra. The detailed TDR data analysis procedure was reported [10, 11]. The thermostat (ESCY IC 201) was used to maintain constant temperature in the sample cell with an accuracy of $\pm 0.5$ K.

## III. RESULTS

Table 1: Comparison of Experimental Densities (ρ) and Refractive Indices (n$_D$) Values of Pure compounds with Literature values at 308.15K

| | Compounds | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Methyl acetate | | 2-methoxyethanol | | 2-ethoxyethanol | | 2-butoxyethanol | |
| Properties | Exp. | Lit. | Exp. | Lit. | Exp. | Lit. | Exp. | Lit. |
| ρ (g·cm$^{-3}$) | 0.9150 | 0.9152 [12] | 0.9510 | 0.9510 [13] | 0.9160 | 0.9160 [15] | 0.8870 | 0.8889 [16] |
| n$_D$ | 1.3550 | 1.3550 [12] | 1.3960 | 1.3949 [14] | 1.4020 | 1.4017 [16] | 1.4130 | 1.4132 [16] |

Table 2: Dielectric constant (ε$_0$) and relaxation time (τ) of pure liquids at 308.15K

| Compounds | ε$_0$ | | τ (ps) | |
|---|---|---|---|---|
| | Experimental | Literature | Experimental | Literature |
| Methyl acetate | 6.19 | 6.49 [17] | 7.99 | 8.87 [17] |
| 2-Methoxyethanol | 16.06 | 15.82 [18] | 29.20 | 25.85 [18] |
| 2-Ethoxyethanol | 15.46 | 15.8(313.15K) [19] | 36.46 | 36.6(313.15K) [19] |
| 2-Butoxyethanol | 9.21 | - | 51.93 | - |

The experimentally measured values of densities (ρ) and refractive indices (n$_D$) of pure Methyl acetate (MA) and 2-Alkoxyethanol liquids at 308.15K were tabulated in Table 1. The complex permittivity spectra ε*(ω) of MA with 2-Alkoxyethanols were recorded in the TDR instrument in the frequency range of 10 MHz to 20 GHz using Tektronix model no. DSA8200 Digital Serial Analyzer at 308.15 K. The complex permittivity ε*(ω) values are fitted with Debye equation and the dielectric quantities were derived. The static dielectric constant (ε$_0$) and relaxation time (τ) values of pure liquids are listed in Table 2 and their literature values are also given and compared.

The dielectric quantities like static dielectric constant (ε$_0$), dielectric constant at high frequency (ε$_\infty$), relaxation time (τ) and activation energy for relaxation time (ΔF$_\tau$) were calculated for binary mixtures of different concentrations (0, 25, 50, 75 and 100 vol.%) of MA with 2-Alkoxyethanols (2–methoxyethanol, 2-ethoxyethanol and 2–butoxyethanol) using time domain reflectometry. The operating frequency range is from 10 MHz to 20 GHz at temperature 308.15 K and was reported in Table 3.

The frequency dependent values of permittivity ($\varepsilon'$) and dielectric loss ($\varepsilon''$) of Methyl acetate (MA) with 2–Alkoxyethanols mixtures at 308.15K are shown in Fig. 1 and Fig. 2. The static dielectric constant ($\varepsilon_o$), static permittivity at high frequency ($\varepsilon_\infty$) and relaxation time ($\tau$) were obtained by using the non–linear least–square fit method [20]. The general form of the relaxation model is given by Havriliak–Negami equation [21].

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

where $\varepsilon^*(\omega)$ is the complex reflection coefficient, ($\varepsilon_0$) is the static dielectric constant, ($\varepsilon_\infty$) is the static permittivity at high frequency, ($\tau$) is the relaxation time, $\alpha$ and $\beta$ are empirical parameters for the distribution of relaxation times with values between 0 and 1. The Havriliak–Negami equation includes three relaxation modes as limiting forms. The Debye mode ($\alpha = 0$ and $\beta = 1$) implies a single relaxation time while Cole–Cole ($\alpha = 1$ and $\beta = 1$) and Cole Davidson ($\alpha = 0$ and $\beta = 1$) both suggest a distribution of relaxation times. But the polar–polar binary mixtures volume percentage of all concentration of Methyl acetate with 2-Alkoxyethanols could fit Debye type dispersion. Therefore, here ($\alpha = 0$ and $\beta = 1$) and experimental values of $\varepsilon^*(\omega)$ were fitted to the Debye equation as,

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{(\varepsilon_0 - \varepsilon_\infty)}{\left[1 + (j\omega\tau)\right]^\beta} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(2)$$

The values of ($\varepsilon_0$), ($\tau$) and ($\varepsilon_\infty$) are fitting parameters. The parameters like effective Kirkwood correlation factor ($g^{eff}$), corrective Kirkwood correlation factor ($g_f$), Bruggeman factor ($f_B$), excess dielectric constant ($\varepsilon^E$) and excess inverse relaxation time $(1/\tau)^E$ values of MA with 2-Alkoxyethanol binary mixtures were reported in Table 4. The excess Helmholtz free energy values are also reported in Table 5 with their volume fractions of methyl acetate.

## IV. DISCUSSION

The binary liquid systems taken for the study are

1) Methyl acetate + 2-methoxyethanol
2) Methyl acetate + 2-ethoxyethanol
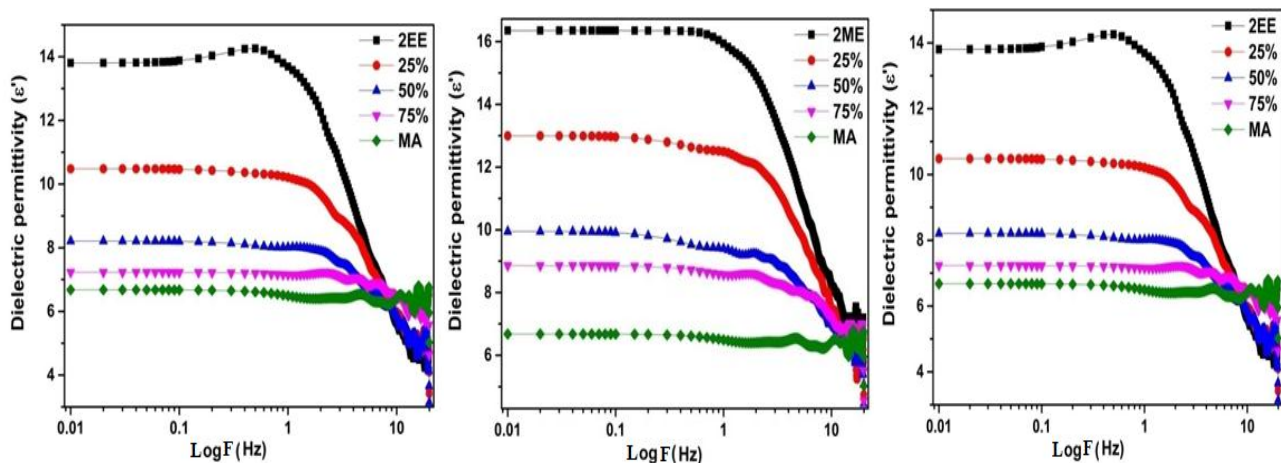3) Methyl acetate + 2-butoxyethanol



Fig. 1: Dielectric permittivity spectra vs. Log F ($H_Z$) of Methyl acetate (MA) with 2-methoxyethanol (2-ME), 2-ethoxyethanol (2-EE) and 2-butoxyethanol (2-BE).
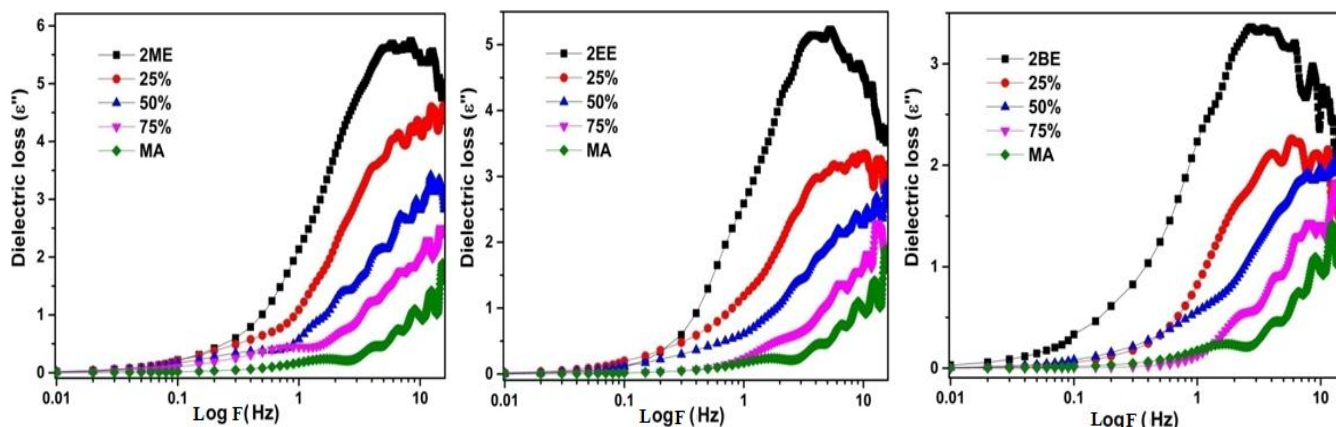
Fig. 2: Dielectric loss spectra vs. Log F ($H_Z$) of Methyl acetate (MA) with 2-methoxyethanol (2-ME), 2-ethoxyethanol (2-EE) and 2-butoxyethanol (2-BE).

Table 3: Values of static dielectric constant ($\varepsilon_o$), dielectric constant at an optical frequency ($\varepsilon_\infty$), relaxation time ($\tau$) and activation energy of relaxation time ($\Delta F_\tau$) with volume fraction of Methyl acetate ($\varphi_2$)

| $\varphi_2$ | $\varepsilon_o$ | $\varepsilon_\infty$ | $\tau$ ps | $\Delta F_\tau$ |
|---|---|---|---|---|
| **System-I: Methyl acetate + 2-methoxyethanol** | | | | |
| 0 | 16.06 | 1.9488 | 29.20 | 125.5138 |
| 0.25 | 11.98 | 1.9516 | 21.59 | 124.7401 |
| 0.50 | 9.25 | 1.9530 | 14.30 | 123.6845 |
| 0.75 | 8.08 | 1.9155 | 10.34 | 122.8532 |
| 1.0 | 6.19 | 1.8360 | 7.99 | 122.1929 |
| **System-II Methyl acetate + 2-ethoxyethanol** | | | | |
| 0 | 15.46 | 1.9656 | 36.46 | 126.0828 |
| 0.25 | 9.74 | 1.9605 | 23.5 | 124.9573 |
| 0.50 | 7.61 | 1.9516 | 15.7 | 123.9238 |
| 0.75 | 6.78 | 1.9238 | 9.97 | 122.7599 |
| 1.0 | 6.19 | 1.8360 | 7.99 | 122.1929 |
| **System-III: Methyl acetate + 2-butoxyethanol** | | | | |
| 0 | 9.21 | 1.9966 | 51.93 | 126.9890 |
| 0.25 | 8.47 | 1.9952 | 30.52 | 125.6271 |
| 0.50 | 7.06 | 1.9980 | 15.94 | 123.9627 |
| 0.75 | 6.95 | 1.9572 | 10.29 | 122.8414 |
| 1.0 | 6.19 | 1.8360 | 7.99 | 122.1929 |

Table 4: Values of kirkood correlation factors ($g^{eff}$, $g_f$), Bruggeman factor ($f_B$), Excess dielectric constant ($\varepsilon^E$) and excess inverse relaxation time $(1/\tau)^E$ with volume fraction of Methyl acetate ($\varphi_2$)

| $\varphi_2$ | $g^{eff}$ | $g_f$ | $f_B$ | $\varepsilon^E$ | $(1/\tau)^E$ Ps |
|---|---|---|---|---|---|
| **System-I: Methyl acetate + 2-methoxyethanol** | | | | | |
| 0 | 1.3954 | 1.0000 | 1.0000 | 0.0000 | 0.0000 |
| 0.25 | 1.1463 | 0.8629 | 0.6468 | -1.6435 | -0.0107 |
| 0.50 | 0.9854 | 0.7945 | 0.3726 | -1.9356 | -0.0098 |
| 0.75 | 1.0177 | 0.9090 | 0.2408 | -0.6287 | -0.0057 |
| 1.0 | 0.9439 | 1.0000 | 0.0000 | 0.0000 | 0.0000 |
| **System-II Methyl acetate + 2-ethoxyethanol** | | | | | |
| 0 | 2.1000 | 1.0000 | 1.0000 | 0.0000 | 0.0000 |

| 0.25 | 1.3124 | 0.7095 | 0.4467 | -3.4298 | -0.0093 |
|------|--------|--------|--------|---------|---------|
| 0.50 | 1.0291 | 0.6529 | 0.1940 | -3.2658 | -0.0126 |
| 0.75 | 0.9513 | 0.7457 | 0.0838 | -1.7829 | -0.0004 |
| 1.0 | 0.9439 | 1.0000 | 0.0000 | 0.0000 | 0.0000 |
| **System-III: Methyl acetate + 2-butoxyethanol** | | | | | |
| 0 | 1.5633 | 1.0000 | 1.0000 | 0.0000 | 0.0000 |
| 0.25 | 1.3735 | 0.9850 | 0.7763 | -0.0237 | -0.0130 |
| 0.50 | 1.0630 | 0.8604 | 0.3148 | -0.7217 | -0.0095 |
| 0.75 | 1.0392 | 0.9573 | 0.2764 | -0.0760 | -0.0015 |
| 1.0 | 0.9439 | 1.0000 | 0.0000 | 0.0000 | 0.0000 |

### 4.1 Dielectric permittivity (ε')

The complex permittivity spectra of two pure liquids as well as the three binary mixtures of Methyl acetate (MA) with 2–methoxyethanol (2–ME), 2–ethoxyethanol (2–EE) and 2–butoxyethanol (2–BE) are shown in Fig 1. In the case of MA with 2–Alkoxyethanols systems, a graph is drawn between dielectric permittivity (ε') on the Y–axis and Log F on the X–axis. From the graph it is inferred that the dielectric permittivity (ε') is comparatively low for MA and is high for 2–Alkoxyethanols. As the MA concentration increases, the dielectric permittivity (ε') values gets decreases. In other words as the concentration of 2–Alkoxyethanols increases the dielectric permittivity (ε') values gets increases. Hence (ε') values are directly proportional to the 2–Alkoxyethanols concentrations and inversely proportional to the MA concentration.

### 4.2 Dielectric loss (ε")

A graph is drawn between dielectric loss (ε") on Y–axis and Log F on X–axis and is shown in fig. 2. The position of the peak of the curves shifts towards higher side (right) of Log F. As the Log F increases, the dielectric loss (ε") also gets increases. It is found that when comparing all the three alcohols with Methyl acetate, the dielectric loss is in the order of 2-ME > 2-EE > 2-BE.

Table 5: Values of excess Helmholtz free energy ($\Delta F^E$) and its components with volume fraction of Methyl acetate ($\varphi_2$)

| $\varphi_2$ | $\Delta F_{0r}^{E}$ J/mol | $\Delta F_{rr}^{E}$ J/mol | $\Delta F_{12}^{E}$ J/mol | $\Delta F^{E}$ J/mol |
|------|------|------|------|------|
| **System-I: Methyl acetate + 2-methoxyethanol** | | | | |
| 0 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| 0.25 | 83.3704 | 57.9874 | -11.0806 | 130.2772 |
| 0.50 | 124.9438 | 57.1200 | 0.0143 | 182.0780 |
| 0.75 | 27.3371 | 23.8875 | 0.8026 | 52.0271 |
| 1.0 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| **System-II Methyl acetate + 2-ethoxyethanol** | | | | |
| 0 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| 0.25 | 133.4999 | 176.8102 | -8.8210 | 301.4891 |
| 0.50 | 163.6883 | 135.9551 | 1.5191 | 301.1625 |
| 0.75 | 93.9439 | 43.2267 | -3.6792 | 133.4914 |
| 1.0 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| **System-III: Methyl acetate + 2-butoxyethanol** | | | | |
| 0 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| 0.25 | -20.3300 | 16.7025 | -16.7606 | -20.3881 |
| 0.50 | 33.5534 | 25.5652 | 0.2404 | 59.3590 |
| 0.75 | -23.5248 | 9.3315 | 0.2864 | -13.9070 |
| 1.0 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |

### 4.3 Static dielectric constant (ε₀)

     The static dielectric constant values of Methyl acetate (MA) is 6.19, 2–methoxyethanol (2-ME) is 16.06, 2–ethoxyethanol (2-EE) is 15.46 and 2–butoxyethanol (2–BE) is 9.21. In the case of MA with 2–ME, 2-EE and

2–BE systems, as the volume percent of MA increases the static dielectric constant ($\varepsilon_0$) values gets decreases and approaching towards the 2-Alkoxyethanols dielectric constant values.

### 4.4 Dielectric constant at an optical frequency ($\varepsilon_\infty$)

As the volume percent of the Methyl acetate molecule increases, the dielectric constant at an optical frequency ($\varepsilon_\infty$) values gets increases at the initial concentration and then decreases at higher concentration of Methyl acetate (MA) with 2–ME, 2–EE and the 2–BE systems.

### 4.5 Relaxation time ($\tau$)

The relaxation time depends on the nature of participating functional groups and volume of molecule. Functional groups are those able to form the hydrogen bonding which have a strong influence on relaxation times. In the pure state the experimental relaxation time values of Methyl acetate is 7.99 ps, 2–methoxyethanol is 29.20 ps, 2-ethoxyethanol is 36.46 ps and 2–butoxyethanol is 51.93 ps at 308.15 K. The 2–methoxyethanol relaxation time is low when compared to 2-ethoxyethanol and 2–butoxyethanol. The relaxation time value is high for 2-butoxy ethanol due to the higher chain length of alkyl group.

Alcohols play a vital role in the structural dynamics and relaxation mechanism of the individual components. This is due to the formation of intra molecular hydrogen bonding between one alcohol molecule and another alcohol molecule (R–O–H···OH–R) and leads to the formation of self associated groups. There is an increment in the number of self associated groups which causes the alcohol molecules to absorb more electromagnetic energy. Due to this reason molecule rotate slowly leading to higher relaxation times. Further, it is observed that the relaxation times of pure 2–BE is greater than that of pure 2–ME, 2-EE due to larger effective radius of the rotating unit [22].

From the relaxation time values of three binary liquid systems, it is observed that the relaxation time is higher for MA + 2–BE system. The relaxation time is in the order of MA + 2–BE > MA + 2–EE > MA + 2–ME.

The dielectric parameters like the static dielectric constant ($\varepsilon_0$), dielectric constant at an optical frequency ($\varepsilon_\infty$) and relaxation time ($\tau$) values calculated are found to be non linear behaviour and can be attributed to the appearance of aggregates in solutions.

### 4.6 Free energy of activation for relaxation time ($\Delta F_\tau$)

$$\Delta F_\tau = RT\ 2.303\ \log_{10}\ [\frac{\tau_0 KT}{h}]\ldots\ldots\ldots(3)$$

T is absolute temperature, K – Boltzman constant, h is a Plank's constant, $\tau_0$ is relaxation time, $\Delta F_\tau$ is Free energy activation for relaxation time. The study of thermodynamic properties like free energy of activation for dielectric relaxation $\Delta F_\tau$ for polar compounds may be useful in accordance with the states of dipoles under the influence of applied field. The measurement of free energy of activation for dielectric relaxation ($\Delta F_\tau$) is calculated for all the systems studied. It is clear from the data that the dielectric relaxation time ($\Delta F_\tau$) involves rotational motion only and not due to translational motion, which is pertaining to the free energy of activation for viscous flow ($\Delta F_\eta$). Free energy of activation for relaxation time is in the order of MA + 2–BE > MA + 2–EE > MA + 2–ME. The values are given in the Table 3.

### 4.7 Effective Kirkwood correlation factor ($g^{eff}$)

The structural information about the molecules of the liquids by dielectric relaxation parameter can be obtained by Kirkwood correlation factor 'g' [23]. The Kirkwood correlation factor provides useful information regarding the orientation of dipoles in polar liquids. The 'g' factor for the pure liquid may be obtained from the expression,

$$\frac{4\pi N_A \mu^2 \rho}{9kTM}\ g = \frac{(\varepsilon_0 - \varepsilon_\infty)(2\varepsilon_0 + \varepsilon_\infty)}{\varepsilon_0(\varepsilon_\infty + 2)^2}\ \ldots\ldots\ldots(4)$$

where $N_A$ is Avogadro's number, $\mu$ is the dipole moment in the gas phase, $\rho$ is the density, K is the Boltzmann constant, T is the temperature in Kelvin, M is the molecular weight, $\varepsilon_0$ is the static dielectric constant and $\varepsilon_\infty$ is the dielectric constant at optical frequency which is the square of the refractive index. Modified forms of this equation have been used to

study the orientation of electric dipoles in binary mixture of Methyl acetate with 2–Alkoxyethanols. Equation (4) is modified and is called as ($g^{eff}$) the effective Kirkwood correlation factor [24],

$$\frac{4\pi N_A}{9kT}\left(\frac{\mu_1^2 \rho_1}{M_1}\phi_1 + \frac{\mu_2^2 \rho_2}{M_2}\phi_2\right)g^{eff} = \frac{(\varepsilon_{0m}-\varepsilon_{\infty m})(2\varepsilon_{0m}+\varepsilon_{\infty m})}{\varepsilon_{0m}(\varepsilon_{\infty m}+2)^2} \quad \text{..........(5)}$$

The effective Kirkwood correlation factor ($g^{eff}$) calculated using equation (5) is given in Table 4. If the ($g^{eff}$) values are greater than unity which indicates the parallel orientation of dipoles and if less than unity it indicates the anti–parallel orientation of dipoles. In the pure state the ($g^{eff}$) values of 2–methoxyethanol is (1.3954), 2-ethoxyethanol is (2.1000) and 2–butoxyethanol is (1.5633) are greater than unity having parallel orientation of electric dipoles. The ($g^{eff}$) values calculated for pure Methyl acetate is less than unity, indicating anti–parallel orientation of dipoles or no dipole correlation of electric dipoles. As the volume percentage of solute increases, the ($g^{eff}$) values get decreases for all the systems studied.

### 4.8 Corrective Kirkwood correlation factor ($g_f$)

The structural information on the interacting species is obtained by another correlation factor named as corrective Kirkwood correlation factor ($g_f$). It is a dielectric parameter which supplies essential information regarding interaction of the participating molecules in the mixture. For an ideal mixture, ($g_f$) must be unity and the deviation of ($g_f$) from unity indicates the magnitude of interaction between the compounds i.e., If there is a greater deviation from unity means a larger the strength of interactions [25].

$$\frac{4\pi N_A}{9kT}\left(\frac{\mu_1^2 \rho_1 g_1}{M_1}\phi_1 + \frac{\mu_2^2 \rho_2 g_2}{M_2}\phi_2\right)g_f = \frac{(\varepsilon_{0m}-\varepsilon_{\infty m})(2\varepsilon_{0m}+\varepsilon_{\infty m})}{\varepsilon_{0m}(\varepsilon_{\infty m}+2)^2} \quad \text{..........(6)}$$

where $N_A$ is Avogadro's number, $\mu$ is the dipole moment in the gas phase, $\rho$ is the density, K is the Boltzmann constant, T is the temperature in Kelvin, M is the molecular weight, $\varepsilon_{0m}$ is the static dielectric constant of mixture and ($\varepsilon_\infty$) is the dielectric constant at optical frequency which is the square of the refractive index of the mixture. The corrective Kirkwood correlation factor ($g_f$) was calculated by using equation (6).

If ($g_f$) values will remain close to unity then there is no interaction between the molecules. In the present study, the values of ($g_f$) are close to unity for all the systems. But ($g_f$) values are found to be deviate more from unity for MA + 2–EE system. This indicates that effective dipoles in the mixture are greater than the average of those in the pure compounds. The values of ($g_f$) are found to be depending more on the concentration than the temperature, as reported by Balamurugan et al., [26].

### 4.9 Bruggeman factor ($f_B$)

The information about the solute–solvent interaction is given by the Bruggeman factor ($f_B$). The effective volume of the solute gets modified by solute – solvent interactions and is best illustrated by the non – linearity of the Bruggeman formula [27].

$$f_B = \left(\frac{(\varepsilon_{0m}-\varepsilon_{02})}{(\varepsilon_{01}-\varepsilon_{02})}\right)\left(\frac{\varepsilon_{01}}{\varepsilon_{0m}}\right)^{1/3} = (1-\phi_2) \quad \text{..........(7)}$$

According to equation (7), a non linear relationship is expected between ($f_B$) and Volume fraction of Methyl acetate.

The non linear relation of ($f_B$) of Methyl acetate with 2-ME, 2-EE and 2-BE suggest that there is an intermolecular interaction between the mixed components. A graph is drawn between Bruggeman factor ($f_B$) and volume fraction ($\varphi_2$) of Methyl acetate which is shown in Fig. 3.
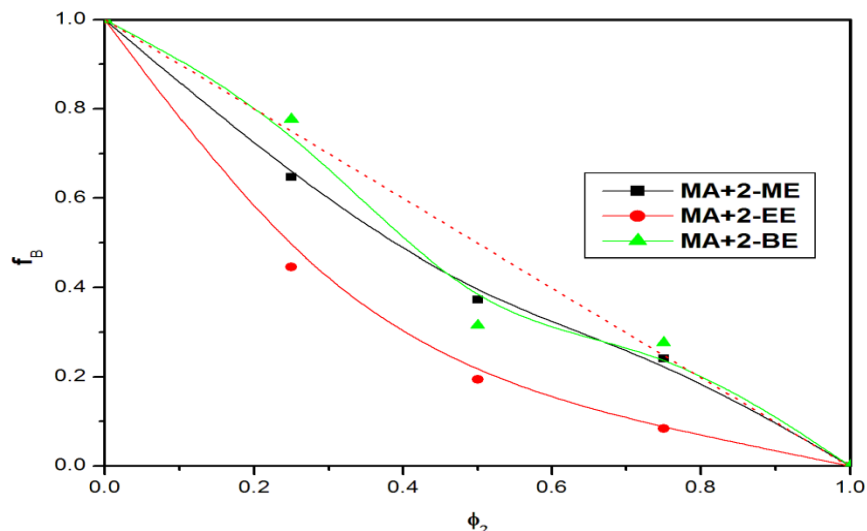
Fig. 3. Bruggeman factor ($f_B$) vs. volume fraction of Methyl acetate ($\varphi_2$)

In our studied systems, it is observed that there are deviations from the ideal linearity of Bruggeman line (dotted line). It means that there exists some sort of interactions prevailing among the participating liquids. The non linearity of the ($f_B$) behavior indicates that the hetero interaction, which may be due to hydrogen bonding of the –OH group of alcohol with C=O group of Ester [28; 26].

### 4.10  Excess dielectric constant ($\varepsilon^E$)

The excess permittivity is defined as [29],

$$\varepsilon^E = (\varepsilon_0 - \varepsilon_\infty)_m - \left\{ (\varepsilon_0 - \varepsilon_\infty)_1 \phi_1 + (\varepsilon_0 - \varepsilon_\infty)_2 \phi_2 \right\} \ldots\ldots\ldots(8)$$

Where $\phi_1$ and $\phi_2$ represents the volume fractions of liquid 1 (2-Alkoxyethanols) and liquid 2 (Methyl acetate). The excess dielectric constant ($\varepsilon^E$) provides information about the formation of multimers in the mixture as follows:

1.  If $\varepsilon^E = 0$ which indicates that there is no interaction between the components in the mixture.
2.  If $\varepsilon^E < 0$ which reveals that components in the mixture may form closed multimers leading to the less effective dipoles due to the interaction between the components in such a way that the effective dipole moment gets reduced.
3.  If $\varepsilon^E > 0$ which denotes that components in the mixture interact in such a way that the effective dipole moment is increased. There is a probability for the formation of linear multimers. In an ideal mixture of polar liquids if the molecules are interacting, a non linear variation in dielectric constant and relaxation time occurs. This confirms that the intermolecular association is taking place in these systems.

The values of excess dielectric constant ($\varepsilon^E$) of Methyl acetate with 2–alkoxyethanols (2–methoxyethanol, 2-ethoxyethanol and 2–butoxyethanol) are listed in Table 4. In an ideal mixture of polar liquids, if the molecules are interacting, a non linear variation in excess dielectric constant ($\varepsilon^E$) occurs. This confirms that the intermolecular association is taking place in the systems.

In the present study excess dielectric constant ($\varepsilon^E$) values are negative for all the systems selected (i.e) Methyl acetate with 2–ME, 2-EE and 2–BE systems. The negative value of ($\varepsilon^E$) indicates that molecules of the mixtures may form closed multimers structures via hydrogen bonding in such a way that the effective dipoles get reduced. The excess property related to static dielectric constant and relaxation time provides significant information regarding interaction between the polar–polar liquid mixtures [30, 31].

### 4.11  Excess inverse relaxation time $(1/\tau)^E$

The excess inverse relaxation time is defined as,

$$\left(\frac{1}{\tau}\right)^E = \left(\frac{1}{\tau}\right)_m - \left\{ \left(\frac{1}{\tau}\right)_1 \phi_1 + \left(\frac{1}{\tau}\right)_2 \phi_2 \right\} \ldots\ldots\ldots(9)$$

where $(1/\tau)^E$ is excess inverse relaxation time which represents the average broadening of dielectric spectra. The inverse relaxation time analogy is taken from spectral line broadening in the resonant spectroscopy [32]. The information regarding the dynamic of the molecules of liquids 1 and 2 is as follows:

(i)   If $(1/\tau)^E = 0$: then there is no change in the dynamics of liquids 1 and 2 interaction.

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

(iii) If $(1/\tau)^E > 0$: then the liquids 1 and 2 interaction produces a field such that the effective dipoles rotate fastly i.e. the fields will co–operate in the rotation of dipoles.

The excess inverse relaxation time $(1/\tau)^E$ is calculated for Methyl acetate with 2-Alkoxyethanols systems and is shown in Table 4. From the data it reveals that all the $(1/\tau)^E$ values are negative. It means that the interaction between the molecules of liquid 1 and liquid 2 produces a field such that the effective dipoles rotate slowly due to the formation of H – bonded structures [25, 26].

## 4.12  Excess Helmholtz free energy ($\Delta F^E$)

The study of Excess Helmholtz free energy gives information on the interaction between the components in the mixture through the breaking mechanism of the H–bonds. The excess free energy due to mixing is given as [33];

$$(\Delta F^E) = (\Delta F_{0r}{}^E) + (\Delta F_{rr}{}^E) + (\Delta F_{12}{}^E)\dots\dots\dots\dots\dots\dots\dots (10)$$

where, $(\Delta F_{0r}{}^E)$ represents the excess dipolar energy due to long range electrostatic interaction. $(\Delta F_{rr}{}^E)$ represents the excess dipolar energy due to short range interaction between identical molecules and $(\Delta F_{12}{}^E)$ represents the excess free energy due to short range interaction between dissimilar molecules. The above terms are given in detail in equation (11):

$$\Delta F^E = -\left[\frac{N_A}{2}\right]\left\{\left[\sum_{r=1,2} X_r^2 \mu_r^2 (R_{fr} - R_{fr}^0)\right] + \left[\sum_{r=1,2} X_r^2 \mu_r^2 (g_{rr} - 1)(R_{fr} - R_{fr}^0)\right] + \left[X_1 X_2 \mu_1 \mu_2 (g_{12} - 1)(R_{f1} + R_{f2} - R_{f1}^0 - R_{f2}^0\right]\right\}\dots\dots\dots(11)$$

$$R_{fr}^0 = \left(\frac{8\pi N_A}{9V_r}\right)\frac{(\varepsilon_r - 1)(\varepsilon_{\infty r} + 2)}{(2\varepsilon_r + \varepsilon_{\infty r})}$$

$$R_{fr} = \left(\frac{8\pi N_A}{9V_r}\right)\frac{(\varepsilon_m - 1)(\varepsilon_{\infty r} + 2)}{(2\varepsilon_m + \varepsilon_{\infty r})}$$

$V_r$ is the molar volume of the components. $(\varepsilon_r)$ and $(\varepsilon_{\infty r})$ are the static dielectric constant and static dielectric constant at optical frequencies, of the pure liquids, respectively.

The long range and short range interaction between dipoles can be studied from the thermodynamic parameter, excess Helmholtz free energy ($\Delta F^E$). The different components of $\Delta F^E$ such as $\Delta F_{0r}{}^E$, $\Delta F_{rr}{}^E$ and $\Delta F_{12}{}^E$ are given in Table 5. The first term $\Delta F_{0r}{}^E$ represents the excess dipolar energy due to the long range electrostatic interaction between similar molecules. The second term $\Delta F_{rr}{}^E$ represents the excess dipolar energy due to the short range interaction between the similar molecules. The third term $\Delta F_{12}{}^E$ represents the excess free energy due to short range interaction between dissimilar molecules. The long range interaction between the dipoles in the mixture can be identified from the values of $\Delta F_{0r}{}^E$ [34].

In the present study, MA+2-ME and MA+2-EE systems have positive values of $\Delta F_{0r}{}^E$ which indicates the existence of attractive forces between the dipoles. Where as in the MA+2-BE system $\Delta F_{0r}{}^E$ have negative values which indicates the repulsive forces between the dipoles.

The second term $(\Delta F_{rr}{}^E)$ gives the excess free energy due to short range interaction between the like molecules. (i.e) $(\Delta F_{rr}{}^E)$ indicates rupture of H – bonds between the acid (ester) molecules formed by short range interaction. As the concentration of the solute molecules increases, the $(\Delta F_{rr}{}^E)$ values are positive and indicate the strong short range interaction through H–bonding. The $(\Delta F_{rr}{}^E)$ values gradually increases first and attains maximum at equimolar concentrations and then gradually decreases in all the studied systems. The magnitude of $\Delta F_{12}{}^E$ gives information on the strength of interactions between unlike molecules. The values of $\Delta F_{12}{}^E$ calculated in the systems of Methyl acetate with 2–Alkoxyethanols are both the positive and negative values, which indicate that the hetero interaction between the compounds which are varying with concentration and temperature.

The excess Helmholtz free energy values are completely positive for MA+ 2-ME and MA+2-EE system. Whereas it is found to be positive and negative for MA+2-BE system. Which indicates the formation of β–clusters to α-clusters (i.e) anti–parallel to parallel alignment of dipoles takes place [25, 35]. From the results of the studied systems, intermolecular interaction depends on the molecular size, volume and the functional group.

## V.  FTIR STUDIES

The FTIR spectra of Methyl acetate with 2-Alkoxyethanols are shown in Figure 4. The Table 6 shows the O-H stretching vibrations are observed for 2-methoxyethanol at (3411cm$^{-1}$), for 2-ethoxyethanol at (3420 cm$^{-1}$) and 2-butoxyethanol at (3422 cm$^{-1}$), respectively. The transmittance spectra of broad band appeared for MA+2-ME system at (3412 cm$^{-1}$), for MA+2-EE system at (3422 cm$^{-1}$) and for MA+2-BE system at (3425 cm$^{-1}$), which is attributed to the stretching frequency of O-H bond in binary system. The CH$_2$ asymmetric stretching were observed at 2932 cm$^{-1}$, 2935 cm$^{-1}$, 2935 cm$^{-1}$ for MA+2-ME, MA+2-EE and MA+2-BE systems respectively. The C=O stretching for pure MA is observed at frequency 1777 cm$^{-1}$. The C=O vibrations are observed at 1778 cm$^{-1}$ for MA+2-ME, MA+2-EE and MA+2-BE systems respectively. These vibrations are nearly coinciding with literature value [36]. We also observed the O-H and C=O shifted to the higher frequency with increase in mole fraction of Methyl acetate with 2-Alkoxyethanols binary mixtures. The formation of complexes is may be due to the hydrogen bonding between the oxygen of carbonyl group (C=O) of methyl acetate with the hydroxyl group (OH) of 2-Alkoxyethanols (Figs. 5, 6 and 7). The formation of inter-molecular hydrogen bonding between the components of liquid mixtures in the present study has been confirmed by recording of IR spectra of pure liquids and their liquid mixtures.
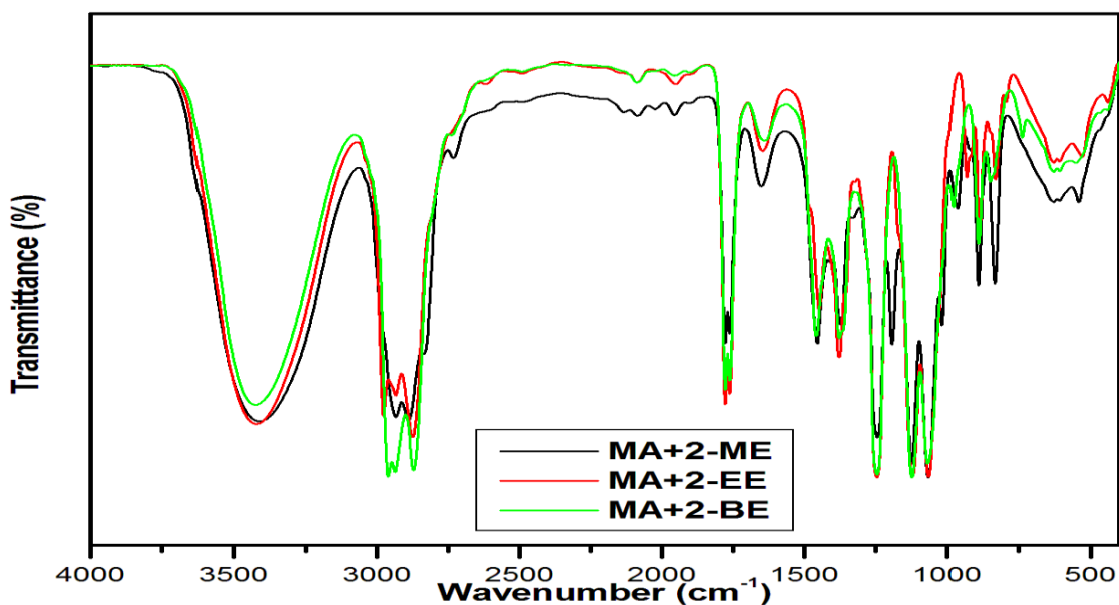


Fig. 4. FTIR spectra of equimolar ratio of Methyl acetate (MA) with 2-Alkoxyethanols
(2–methoxyethanol (2-ME), 2-ethoxyethonal (2-EE) and 2–butoxyethanol (2-BE)) corresponding peaks shift in binary mixtures.

Table 6 FT-IR Spectral band assignments for pure Methyl acetate, 2-Alkoxyethanols and their equimolar binary solutions

| Compounds | Vibration modes | Frequency cm$^{-1}$ | |
|---|---|---|---|
| | | $\upsilon$ cm$^{-1}$ | $\Delta\upsilon$ cm$^{-1}$ |
| 2–Methoxyethanol | O–H | 3411 | - |
| 2–Ethoxyethanol | O–H | 3420 | - |
| 2–Butoxyethanol | O–H | 3422 | - |
| Methyl acetate | CH$_3$ asymmetric stretch | 3002 | - |
| | CH$_2$ asymmetric stretch | 2961 | - |
| | C=O stretch | 1777 | - |
| | C-C-O stretch | 1247 | - |
| | O-CH$_2$-C asymmetric stretch | 1060 | - |
| Methyl acetate +2–Methoxyethanol | O–H | 3412 | 01 |

| | | | |
|---|---|---|---|
| | $CH_3$ asymmetric stretch | 2974 | 28 |
| | $CH_2$ asymmetric stretch | 2932 | 29 |
| | C=O stretch | 1778 | 01 |
| | C-C-O stretch | 1245 | 02 |
| | O-$CH_2$-C asymmetric stretch | 1066 | 06 |
| Methyl acetate + 2–Ethoxyethanol | O–H | 3422 | 02 |
| | $CH_3$ asymmetric stretch | 2976 | 26 |
| | $CH_2$ asymmetric stretch | 2935 | 26 |
| | C=O stretch | 1778 | 01 |
| | C-C-O stretch | 1246 | 01 |
| | O-$CH_2$-C asymmetric stretch | 1065 | 05 |
| Methyl acetate + 2–Butoxyethanol | O–H | 3425 | 03 |
| | $CH_3$ asymmetric stretch | 2959 | 43 |
| | $CH_2$ asymmetric stretch | 2935 | 26 |
| | C=O stretch | 1778 | 01 |
| | C-C-O stretch | 1246 | 01 |
| | O-$CH_2$-C asymmetric stretch | 1069 | 09 |
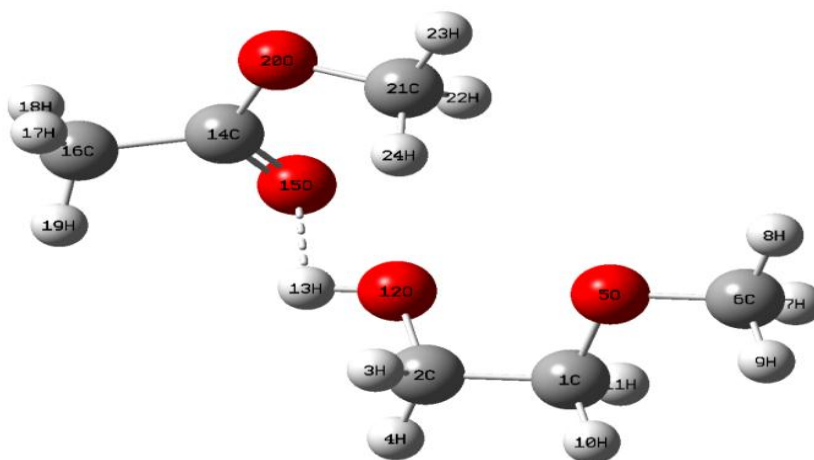


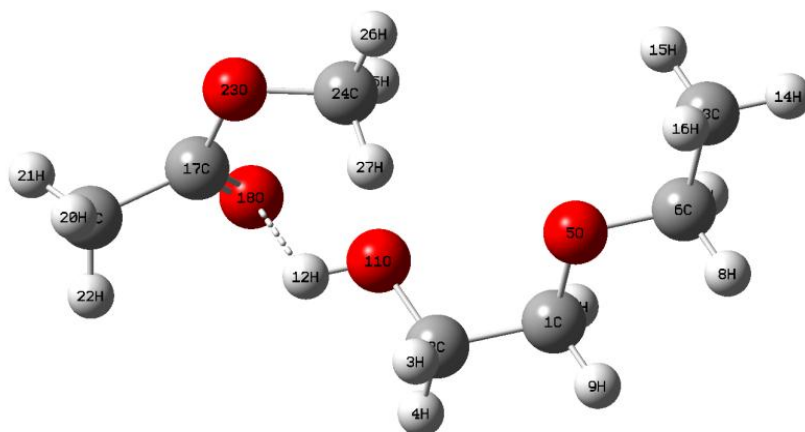Fig. 5: Hydrogen bond formation of Methyl acetate with 2-methoxyethanol.



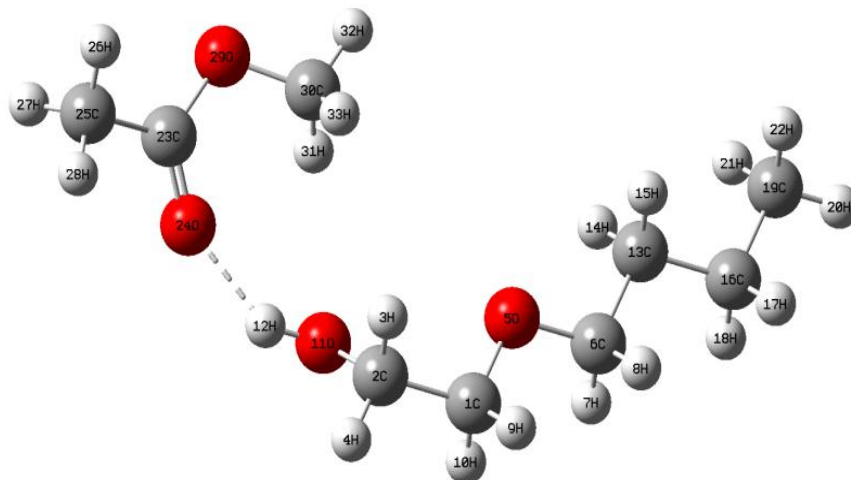Fig. 6: Hydrogen bond formation of Methyl acetate with 2-ethoxyethanol.

Fig. 7: Hydrogen bond formation of Methyl acetate with 2-butoxyethanol.

## VI. CONCLUSION

The study is concerned with the molecular interaction of Methyl acetate with 2–Alkoxyethanols. The conclusion from the above three systems of molecular interaction with 2–methoxyethanol, 2-ethoxyethonal and 2–butoxyethanol are as follows:

1. Pertaining to the relaxation time, the relaxation time of Pure 2-Alkoxyethanols gets increases with increase of chain length of alcohol molecules (i.e) Methyl acetate with 2–butoxyethanol have more relaxation time than that of 2–methoxyethanol and 2-ethoxyethanol. This conclusion was supported by Sivagurunathan *et al.,* [37] in the case of methyl methacrylate with alcohol systems. In our study, Methyl acetate with 2–butoxyethanol is having more chain length when compared to 2–ethoxyethanol and 2-methoxyethanol. The relaxation time is in the order of MA + 2–BE > MA + 2–EE > MA + 2–ME.

2. The dielectric constants, the relaxation times, the Kirkwood correlation factors, Bruggeman factor, excess dielectric constant, excess inverse relaxation times, excess Helmholtz free energies of activation, adjustable parameter and standard deviations for esters + alcohols mixtures of various concentrations have been reported. The dielectric parameters show that there are systematic changes with concentration of alkyl chain length of 2-Alkoxyethanols.

3. FT-IR spectra analysis confirms that there exists the H-bond interaction between the participating molecules of the liquids.

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