Investigation of Intermolecular Interaction Between Isobutanol and Methyl Benzoate using Excess Dielectric and Thermodynamic Parameters

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Abstract— The molecular interaction between the polar systems of isobutanol and methyl benzoate for various mole fractions at different temperatures were studied by determining the frequency dependent complex dielectric permittivity by using the open-ended coaxial probe technique method in the microwave frequency range from 20MHz-20 GHz. The geometries are optimized at HF, B3LYP with 6-311G and 6-311G+ basis sets. Dipole moments of the binary mixtures are calculated from the dielectric data using Higasi's method and compared with the theoretical results. Conformational analysis of the formation of hydrogen bond between isobutanol and methyl benzoate is supported by the FT-IR, 1NMR and molecular polarizability calculations. The average relaxation times are calculated from their respective Debye and Cole-Cole plots. The activation entropy, activation enthalpy, Gibbs free energy of activation and Kirkwood correlation 'g' factor, excess permittivity (ε^E), excess inverse relaxation time $(1/\tau)^E$, Bruggeman parameter (f_B) have also been determined for isobutanol and methyl benzoate and the results were correlated.

Keywords— Complex dielectric permittivity; relaxation time; excess dielectric and thermodynamic parameters; ab-initio calculations.

1. INTRODUCTION

Dielectric spectroscopy, which is used to measure the response of the complex permittivity to time-dependent electric fields, has contributed to our understanding of the molecular dynamics in the liquid state. The phenomenon of dielectric relaxa-tion of individual liquid systems as well as binary mixtures in pure form or dissolved in non-polar solvents at microwave frequencies have been attempted by many workers [1–8]. Because such studies provide meaningful information regarding intermolecular and intramolecular association between the solutes and solvent molecules. The interactions of the microwaves (electromagnetic radiations) with polar solvents result in the microwave dielectric heating, which is rapidly becoming an established procedure in synthesis chemistry [9–11]. The measure of a real part ε ′is an indicative of dielectric material energy storing capability in the electric field, whereas the imaginary part ε ″is the absorbed electromagnetic energy by the material that converts into the thermal energy by Joule heating effect. The ε′ and ε″ of a polar solvent depends on the

strength of intermolecular hydrogen bonding and the heteromolecular H-bonded interactions in case of mixed solvents. Hydrogen bond is an important type of noncovalent interaction that is present in many chemical and biological systems [12]. A sound knowledge of hydrogen bond is fundamental to understand chemical structures, enzyme catalysis, material properties, self-assembly phenomena, and functions of molecular and biological devices and machines. Therefore, considerable amount of experimental and theoretical researches has been conducted concerning the structural, spectroscopic, and energetic issues of diverse hydrogen bonds [13–19]. The molecular parameters, the electric dipole moment (μ), dielectric relaxation time (τ) and Kirkwood 'g' factor are the helpful parameters to discuss the dielectric behavior of polar systems [19-23]. These parameters can be calculated by measuring the dielectric parameters such as static dielectric constant (ε_s), real part of dielectric permittivity (ε'), imaginary part of dielectric permittivity (ε") and high frequency dielectric constant $(\varepsilon_\infty = n^2$) of polar mixtures in pure liquid form or diluted in a non-polar solvent benzene at static, microwave and optical frequency by using different characterization techniques which are mentioned in the literature [24-28]. The values of μ, τ and Kirkwood 'g' factor gives the information regarding the structure of molecules, nature of chemical bond, charge transfer complexations, intra and intermolecular interactions, hydrogen bonding, the nature of the orientation of the polar unit etc. Dielectric relaxation studies of polar liquids such as isobutanol and methyl benzoate for various mole fractions at different temperatures in the microwave frequency range (20 MHz-20 GHz) are studied by determining the nature of interaction that exists between the molecules due to hydrogen bonding, dipole moment and the relaxation behavior phenomena Dielectric spectroscopy is sensitive to changes in bonding between different species of liquids in a liquid-liquid binary or tertiary systems-even to weak hydrogen bonding [29]. In order to have a comprehensive understanding of the nature of interactions in such systems, conformational analysis is performed using Hatree-Fock and Density Functional Theoretical methods. Such computational result gives the valid information regarding the interaction sites

between the various molecules and hence it is useful in interpreting the dielectric results [29-32]. Crossley et al. [33], Glasser et al. [34] and Garg et al. [35] studied the dielectric constant and dielectric loss of six isomeric octyl alcohols at different concentrations in a non-polar solution such as n-heptane at different microwave frequency ranges and they showed that the existence of three relaxation processes in alcohols, dominated by low frequency Debye type process - having a single relaxation time. Bao et al. [36] described the two types of relaxation process of water–methanol and water–ethanol binary mixtures at various mole fractions in the frequency range 45 MHz to 26.5 GHz. In case of most of the alcohols in dilution with nonpolar solvents, the concentration dependence of the Kirkwood correlation factor 'g' shows a minimum value at definite concentrations [37]. This means qualitatively that dilution leads to the formation of cyclic multimers with anti-parallel dipoles. Winkle Mann et al. [38] developed comprehensive relations linking the complex dielectric permittivity of binary mixtures with short range and long-range interactions as an extension of Kirkwood theory. Schwerdtfeger et al. [39] studied the relaxation behavior of monohydric alcohols with *n*alkanes and Hiejima et al. [40] in fluid phase. The theoretical approach and computer simulation studies were reported to understand the relaxation behavior and the hydrogen bonding in alcohols by Minami et al. [41] and Padro et al. [42] respectively. Yomogida et al. [43] measured the complex permittivity of 14 monohydric alcohols in the frequency range 0.2–2.5 THz, at temperatures ranging from 253 to 323 K using time domain spectroscopy. The molecular structures of these monohydric alcohols change systematically with the position of the OH group, the number of carbon atoms, and the structure of the carbon chain. Chitra et al. [44] studied the conformational and dielectric analysis of the hydrogen bonded binary system of non-associated polar liquid methyl benzoate and associated polar liquid Nmethyl aniline at discrete microwave frequencies by using the wave guide plunger method and excess dielectric, thermodynamic parameters of the binary system of isopropyl alcohol with methyl and ethyl benzoate by Madhu Mohan et al. [45]. In this paper, we measured the complex dielectric permittivity of pure liquids such as isobutanol, methyl benzoate and different molar concentration levels of methyl benzoate in isobutanol in the microwave frequency range (20MHz – 20 GHz) by using the open-ended coaxial probe method [28] at different temperatures i.e. 303K, 308K, 313K, 318K and 323K. The dipole moments of the isobutanol, methyl benzoate and its binary mixtures are calculated experimentally as well as theoretically from the HF, B3LYP calculations considering 6-311G, 6-311G+ basis sets by using Gaussian software-03. The average relaxation time is calculated from the respective Debye and Cole-Cole plots [46, 65] and molecular polarizability value obtained from the Lippincott δ function potential model [47-48]. Thermodynamical parameters such as enthalpy of activation ΔH*, entropy of activation ΔS* are calculated from the Eryings rate equation [49, 50] and effective Kirkwood 'g' factor is determined from the Kirkwood-Frohlich equation [21]. The formation of hydrogen bond between the isobutanol and methyl benzoate is confirmed from the experimental FT-

IR and theoretical IR, 1NMR and molecular polarizability calculations.

II. EXPERIMENTAL DETAILS

2.1. Materials

The compounds of isobutanol, methyl benzoate and benzene of AR grade with purity 99 % were procured from Merck, Germany. All the liquids used were further purified by standard procedure [51]. The mid fraction of the distillate stored over 4Å molecular sieves is used for the experiments. At first step dilute solutions of polar solutes are prepared over a concentration range of 0 to 1 ml in 10 ml of non-polar solvent benzene in order to determine the dipole moments by using the Higasi's method.

2.2. Computational Details

A full geometry optimization of isobutanol, methyl benzoate and their binary system were carried out at different levels of theory, namely at Hartree–Fock (HF) level [52–54], at second-order Møller–Plesset (MP2) perturbation theory level [55], and at the DFT level [56] using 6-311G, 6-311G+ basis sets. DFT results were obtained using Becke's three parameter exchange functional along with the Lee, Yang, and Parr correlation functional (B3LYP) [57,58]. The calculations were performed on a Pentium IV workstation, at 3.0 GHz, running the Gaussian 03 [59] package.

2.3. Procedure

The low frequency dielectric permittivity values of the above dilute systems i.e., isobutanol, and methyl benzoate in benzene and equimolar binary mixtures of the isobutanol and methyl benzoate are measured at 820Hz by using digital capacitance meter and high frequency dielectric constant ($\varepsilon_\infty = n^2$) for the pure and diluted systems were measured by using the Carl-Zeiss Abbe refracto-meter with sodium D light as a source at different temperatures of 303K, 308K, 313K, 318K and 323K with a variation of ± 0.1K. The error estimated in the calculation of low frequency dielectric permittivity and optical refractive indices (n) are 1% respectively. The complex dielectric permittivity ($\varepsilon^*=\varepsilon'-j\varepsilon''$) of pure liquids isobutanol, methyl benzoate and the different molar concentration levels of methyl benzoate in isobutanol is measured in the microwave frequency range (20MHz – 20 GHz) by using the open-ended coaxial probe method at different temperatures from 303K to 323K. The procedure involves with one end of the coaxial probe is connected to the PNA-L Network analyzer (N5230C) and other end is inserted in to the sample holder jacketed and attached to a temperature controlled unit. The probe and the cable were fixed so they could not be moved during the sample measurement. Temperature of the system can be varied in a regular interval of 5K by using programmed controller temperature set up. A calibration was done using a short, air, acetone and water before each set of experiments and compared with the standard result and the error is to be found in the measurement of real part of dielectric permittivity is 2% and

imaginary part of dielectric permittivity is 2 to 3%. The sample and the jacketed sample holder were adjusted initially to 303K. The first measurement was made when the temperature reading was stable. The water controlled bath was then increased to 5K above the temperature of the measurement. When the sample reached the desired temperature the dielectric properties were measured and the water controlled temperature was increased another 5K. Thus, the temperature gradient in the sample is from the stated temperature to 5K warmer. The sample holder was sealed to prevent any moisture loss as steam. The complex dielectric properties of the pure and different molar concentration levels of methyl benzoate in isobutanol were measured from 20 MHz-20 GHz with varying temperature from 303K to 323K. All the measurements were repeated at least two times and were reproducible in the range ±2%. The formation of hydrogen bonds in the binary mixtures was studied in the 450-4000 cm-1 region with a Perkin Elmer FT-IR spectrometer and ^{1}NMR spectra by Bruker spectrometer with CDCl3 as solvent medium.

III. DETERMINATION OF THE PARAMETERS

The dipole moment of the isobutanol, methyl benzoate and its equimolar binary mixture of methyl benzoate in isobutanol in benzene are determined by using the Higasi's method as given by Koga et al. [60]

$$\mu^2 = \frac{27kTM_2\left(a_0 - a_\infty\right)}{4\pi Nd_1\left(\varepsilon_1 + 2\right)^2}$$ (1)

where a_o and a_∞ are respectively the slopes obtained from the linear plots of ε_0 and ε_∞ versus the weight fraction of solutes isobutanol, methyl benzoate and binary system isobutanol + methyl benzoate diluted in benzene and M_2 is the molecular weight of the solute, d_1 and ε^1 indicate the density and static dielectric constant of the solvent respectively. These dipole moments of the above pure systems isobutanol, methyl benzoate are compatible with the HF, B3LYP calculations. These quantum mechanical calculations were carried out using the Gaussian-03 software and the excess dipole moment ($\Delta\mu$) of the system as given by Debecker and Huyskens [61].

$$\Delta\mu = \mu_{ab} - \mu_a - \mu_b$$ (2)

Where μ_a is the dipole moment of the isobutanol and μ_b is the dipole moment of methyl benzoate and μ_{ab} is the dipole moment of the equimolar binary system of isobutanol + methyl benzoate.

The contribution of hydrogen bonds to the dielectric properties of the mixtures can be studied in terms of the excess permittivity (ε^E). The excess permittivity (ε^E) which provides qualitative information about the formation of multimers in the mixture [62] can be computed as

$$\varepsilon^E = \left(\varepsilon_m - \varepsilon_{\infty m}\right) - \left[\left(\varepsilon_1 - \varepsilon_{\infty m}\right)x_1 + \left(\varepsilon_2 - \varepsilon_{\infty m}\right)x_2\right]$$ (3)

Where χ is the mole fraction and suffixes 1, 2, and m represent liquid 1, liquid 2 and mixture respectively.

The qualitative information provided by excess permittivity [63] about the mixture indicates ε^E=0 indicates that there is no interaction between the components in the mixture. ε^E<0 indicates that the components in the mixture interact in such a way that the effective dipolar polarization gets reduced and the components may form multimers leading to less effective dipoles. ε^E>0 indicates that the components in the mixture interact in such a way that the effective dipolar polarization gets increased and the components may form multimers leading to more effective dipoles. The hetero interaction between the components of a mixture can also be obtained from Bruggeman equations [64]. The Bruggeman factor (f_B) is given by

$$f_B = \left(\frac{\varepsilon_m - \varepsilon_2}{\varepsilon_1 - \varepsilon_2}\right)\left(\frac{\varepsilon_1}{\varepsilon_m}\right)^{\frac{1}{3}} = \left(1 - \phi_2\right)$$ (4)

where φ_2 is the volume fraction of liquid 2 in liquid 1. If there is no interaction between the components in the mixture then the Bruggeman factor (f_B) should vary linearly with volume fraction φ_2 ,but if there are interactions between the components then f_B varies non-linearly with φ_2 The dielectric data obtained i.e., low frequency dielectric permittivity (ε_o), real part of dielectric permittivity (ε'), imaginary part of dielectric permittivity (ε'') and high frequency dielectric constant (ε_∞) are used to fit on Argand diagram to calculate the relaxation time (τ). The distribution of relaxation times is calculated from the Debye and Cole-Cole arc plot [65] using the relation

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

where α is the distribution parameter and this value is zero for Debye and non zero for Cole-Cole Plot. The values of ν and u are determined from their respective Cole-Cole and Debye plots. The comparison table of low frequency dielectric constant which is measured at 20MHz and relaxation time of pure liquids samples are tabulated in Table 1.

The excess inverse relaxation time $(1/\tau)^E$, gives the information regarding the dynamics of solute-solvent interaction and represents the average broadening of the dielectric spectra [66],

$$\left(\frac{1}{\tau}\right)^E = \left(\frac{1}{\tau}\right)_m - \left[\left(\frac{1}{\tau}\right)_1 x_1 + \left(\frac{1}{\tau}\right)_2 x_2\right]$$ (6)

and it can be defined as The phenomenon of dielectric relaxation can be viewed as the dipole actually rotating between two positions of the equilibrium, separated by a potential barrier. The dielectric relaxation time τ depends on this height of the potential barrier, a temperature dependent constant, and the average time required by an excited molecule to rotate from one equilibrium position to the other. Postulating on the analogy between the process of the dipole rotation and uni-molecular chemical reactions, Erying [49,

50] identified a relation with Gibbs free energy of activation ΔG^*. His theory leads to an expression for τ as

$$\tau = \frac{h}{kT} \exp\left[\frac{\Delta G^*}{RT}\right] \qquad (7)$$

$$\Delta G^* = 2.303 RT \log\left(\frac{\tau kT}{h}\right) \ldots\ldots(8)$$

ie.,

$$\ln(\tau T) = [\ln(h/k) - (\Delta S^*/R)] + [\Delta H^*/RT]\ldots\ldots(9)$$

Thus, the slope of the linear plot between $\ln(\tau T)$ and $(1/T)$ gives $(\Delta H^*)/2.303R$, With obtained value of ΔH^* and ΔS^*, ΔG^* can be calculated with the following relation

$$\Delta G^* = \Delta H^* - T\Delta S^* \ldots\ldots(10)$$

where h is the Planck's constant, k is the Boltzmann constant and T is the temperature in Kelvin and R is the universal gas constant.

The molecular interaction between a polar solute and a non-polar solvent can be described by the modified Kirkwood-Frohlich correlation factor. The Kirkwood-Frohlich theory takes into account the short range interactions through the introduction of the dimensionless factor 'g',

which gives the information regarding the orientation of the electric dipoles in polar liquids. The Kirkwood correlation factor (g) for the pure liquids is given by the expression,

$$\frac{4\pi N_A \mu^2 \rho}{9kTM} g = \frac{(\varepsilon - \varepsilon_\infty)(2\varepsilon + \varepsilon_\infty)}{\varepsilon(\varepsilon_\infty + 2)^2} \qquad (11)$$

where N_A is Avogadro's number, μ is the dipole moment in the gaseous phase, ρ is the density, k is the Boltzmann constant, T is the temperature in Kelvin, M is the molecular weight, ε is the low frequency dielectric permittivity and ε_∞ is the permittivity at optical frequency which is the square of the refractive index

Assuming that g^{eff} is the effective correlation factor for the mixture, the Kirkwood equation for the mixture can be expressed as:

$$\frac{4\pi N_A}{9kT}\left(\frac{\mu_1^2 \rho_1}{M_1}x_1 + \frac{\mu_2^2 \rho_2}{M_2}x_2\right)g^{eff} = \frac{(\varepsilon_m - \varepsilon_{\infty m})(2\varepsilon_m + \varepsilon_{\infty m})}{\varepsilon_m(\varepsilon_{\infty m} + 2)^2} \qquad (12)$$

where x_1 and x_2 are the mole fractions of liquid 1 and 2 in the mixture respectively, and μ_1 and μ_2 are the gaseous phase dipole moments of the liquids 1 and 2 respectively. The suffixes m, 1, and 2 represent mixture, liquid 1 and liquid 2 respectively and $\varepsilon_{\infty m}$ is the square of the refractive index of the mixture and g^{eff} is an index of solute solvent interactions To determine the theoretical values of the dipole moments, the minimum energy structure of the monomers of isobutanol, methyl benzoate and equimolar binary mixture of isobutanol and methyl benzoate are obtained from the *ab-intio* quantum mechanical calculations from Gaussian-03 and molecular polarizability value is calculated for the above systems by using Lippincott δ function potential model. In order to calculate the molecular polarizability values of the above systems we have considered the bond lengths from the optimized structure obtained from the theoretical quantum mechanical calculations.

IV. RESULTS AND DISCUSSION

The low frequency dielectric permittivity value (ε_o) which is measured at 20 MHz and high frequency dielectric constant ($\varepsilon_\infty = n^2$) of various mole fractions of methyl benzoate in isobutanol at different temperatures are shown in Figs. 1 and 2 and also the frequency dependent complex dielectric permittivity ($\varepsilon^* = \varepsilon' - j\varepsilon''$) of pure systems of isobutanol, methyl benzoate and equimolar concentrations levels of isobutanol and methyl benzoate at different temperatures are shown in Figures 3, 4 and 5 respectively.
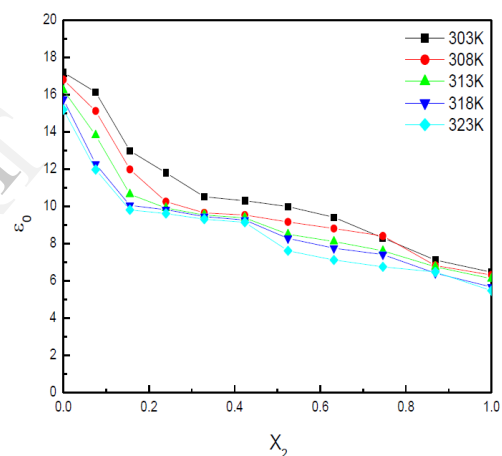

Fig 1. Plot of low frequency dielectric permittivity (ε_0) with respective mole fraction of methyl benzoate in isobutanol (X_2) at different temperatures
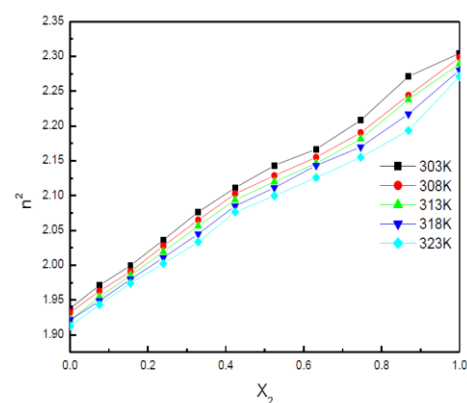

Fig.2. Plot of high frequency dielectric constant ($\varepsilon_\infty = n^2$) with respective mole fraction of methyl benzoate in isobutanol (X_2) at different temperatures
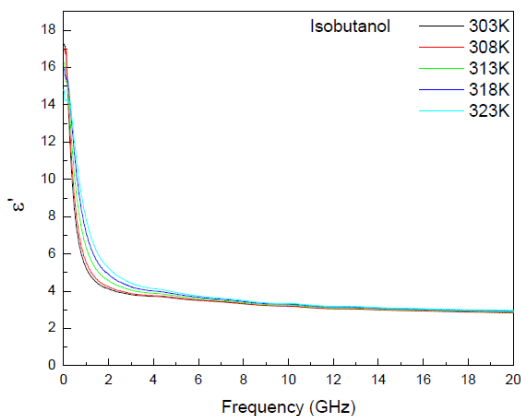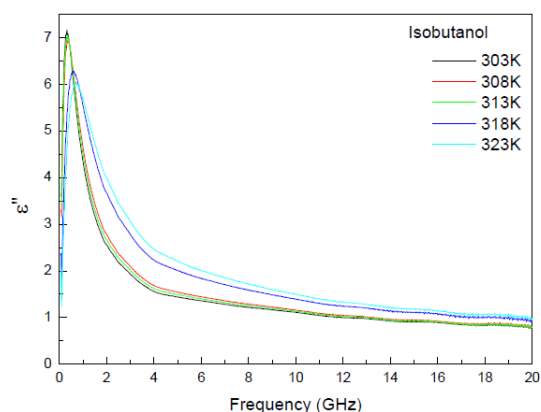
Fig. 3(a)

Fig.3(b)

Fig. 3 (a) & 3(b)Plot of real (ε) and imaginary part of dielectric permittivity (ε'') of isobutanol with respective frequency (X_3) at different temperatures

From the Fig. 1 and 2 it is observed that there is non-linear variation of low frequency dielectric permittivity (εo) and high frequency dielectric constant with mole fraction at all temperatures confirms that the formation of hetero-molecular interaction in the binary system. Similar results were reported by Kroeger [67] for the mixture of alcohols and polar liquids. The dipole moment (μ) values of the pure and equimolar binary systems of isobutanol and methyl benzoate are determined by using the Higasi's method at different temperatures and compared the room temperature dipole moments (298K) of the above systems with the theoretical HF, B3LYP calculations which are tabulated in Table 2 and Table 3 respectively. The dipole moments of these systems are measured experimentally by diluting them in nonpolar solvent benzene. From the Table 2 and 3,

TABLE I. Comparison of low frequency dielectric permittivity and relaxation time values of the pure compounds

Liquid	ε_0 at 25 (^{o}C)		τ (ps)	
	This work	Literature†	This work	Literature†
Methanol	32.07(2)	32.63	50.32(10)	51.98
Propan-1-ol	20.02(2)	20.1	272.05(15)	274.60
Isobutanol(A)	17.20(2)	17.70	496.60(25)	---
Methyl benzoate (B)	6.47 (2)	6.59	35.21(10)	---
A+B	10.31(3)	----	241.20(16)	---

† crc handbook of chemistry and physics (1969-1970,) weast rc (ed) (1983-84) hand book of chemistry and physics. 64th edn, crc press, fl

TABLE II. Experimental dipole moment (μ/D) and excess dipole moment ($\Delta\mu/D$) values for the pure systemisobutanol, methyl benzoate and equimolar binary systems- isobutanol and methyl benzoate

T (K)	isobutanol μ (D) (a)	methyl benzoate μ (D) (b)	(a)+(b)	$\Delta\mu$ (D)
303	1.76(1)	1.85(1)	3.12(1)	-0.49
308	1.74(1)	1.87(1)	3.13(1)	-0.48
313	1.75(1)	1.88(1)	3.13(1)	-0.50
318	1.77(1)	1.90(1)	3.14(1)	-0.53
323	1.78(1)	1.91(1)	3.15(1)	-0.54

TABLE III. . Experimental and theoretical dipole moment (μ/D) and excess dipole moment values of pure system isobutanol, methyl benzoate and equimolarbinary systems- isobutanol and methyl benzoate at 298 K

System	Experimental (298K)		
	μ (D)	Lit*	$\Delta\mu$ (D)
Isobutanol (A)	1.76(1)	1.64	
Methyl benzoate (B)	1.85(1)	1.86	
A+B	3.12(1)	---	-0.49

System	Theoretical calculations							
	Hatree-Fock (HF)				Density Functional theory (DFT-B3LYP)			
	6-311G	$\Delta\mu$ (D)	6-311G+	$\Delta\mu$ (D)	6-311G	$\Delta\mu$ (D)	6-311G+	$\Delta\mu$ (D)
Isobutanol (A)	1.89		1.94		1.77		1.84	
Methyl benzoate (B)	2.24		2.29		1.96		2.06	
A+B	2.53	-1.60	2.83	-1.40	3.13	-0.60	3.29	-0.61

*crc handbook of chemistry and physics (1969-1970)

it is observed that there is an increase in the dipole moment of equimolar binary mixture when compared to the individual pure systems. This may be due to the formation of hydrogen bond between the isobutanol and methyl benzoate. The theoretical dipole moment values are in good agreement with the experimental values. The small deviation between the experimental and theoretical values may be due to the π electron cloud of non polar solvent benzene affecting the dipole moment values of the solute systems. It is also

observed that the variation in temperature significantly affects the dipole moment values of the pure compounds and equimolar binary systems. At low temperatures, the bond lengths between the atoms are very much restricted in their movement, and hence maintain their minimum energy stable conformational structure. This conformational structure enables the cancellation of dipole moments to some extent, resulting in lower dipole moments at low temperatures. As the temperature increases, there is more thermal energy and hence rotation of the individual groups and chain movement between the atoms also increases, resulting in some disruption of the stable structure. This change in the stable structure leads to a decrease in the cancelling of the side-group dipole moments and a consequential increase in the mean dipole moment value.
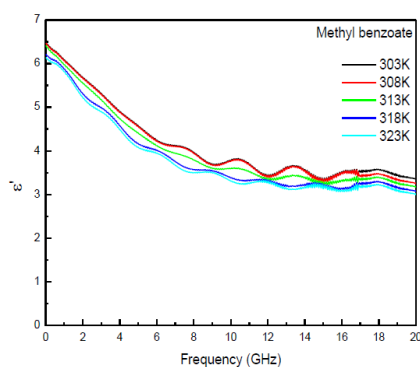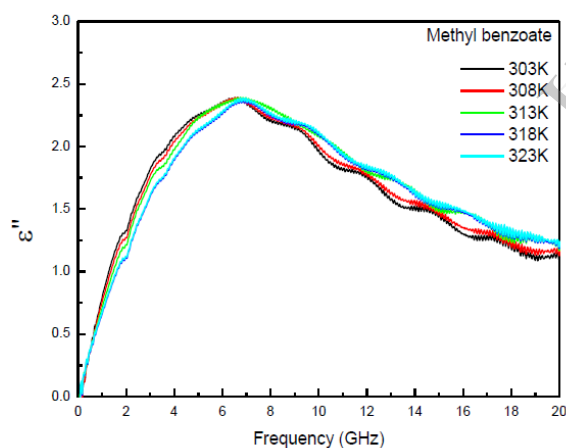
From the Fig. 3a, 4a, and 5a it is observed that real part of dielectric permittivity (ε') decreases with increase in frequency and molar concentration of methyl benzoate in isobutanol with temperature and also from the Fig. 3b it is observed that the imaginary part of the dielectric permittivity i.e., dielectric loss (ε'') is so high for isobutanol when compared to the methyl benzoate and equimolar binary mixture which is as shown in Fig. 4b and 5b respectively. It is due to the formation of inter
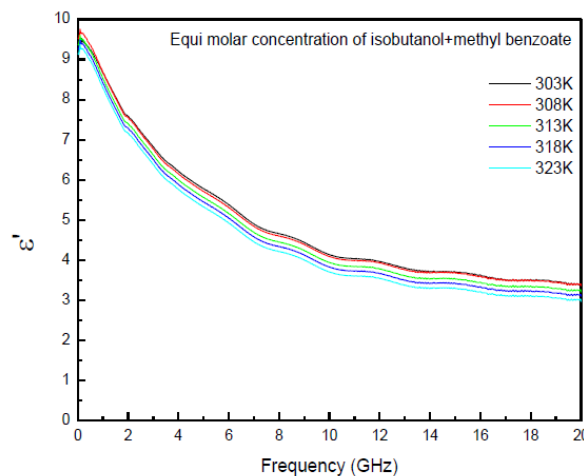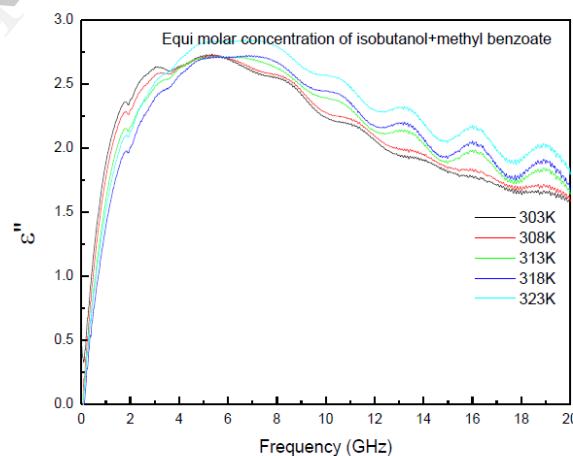

Fig.4. (a)

Fig.5. (a)

Fig.4. (b)

Fig.4. (a) and (b) Plot of real (ε) and imaginary part of dielectric permittivity (ε'') of methylbenzoate ctive frequency (X_3) at different temperatures

Fig.5. (b)

Fig.5. (a) and (b) Plot of real (ε) and imaginary part of dielectric permittivity (ε'') of equimolar binary system of isobutanol and methyl benzoate with respective frequency (X_3) at different temperatures

The excess dipole moment ($\Delta\mu$) values obtained experimentally and theoretically are given in Tables 2 and 3 respectively. The negative $\Delta\mu$ values indicate the absence of ionic structure in the binary system because the presence of ionic bonding in the system resembles high positive values of $\Delta\mu$ [61, 68]. The excess dipole moment value is a qualitative index for the presence of hydrogen bonding between and methyl benzoate or excessive dipole moment is attributed to the proton transfer in the bond.

molecular hydrogen bonding between one alcohol molecule and another (R-OH---OH-R) leads to the formation of self associated groups. The increment in the number of self associated groups causes the alcohol molecules absorb more electromagnetic energy. Due to this reason self associated molecules take longer time to attain one equilibrium position to another equilibrium position causing increase in the relaxation time values which is calculated by using the Cole-Cole plots whereas non associated liquid methyl benzoate is exhibiting the single relaxation time which is calculated from the Debye plot [69].
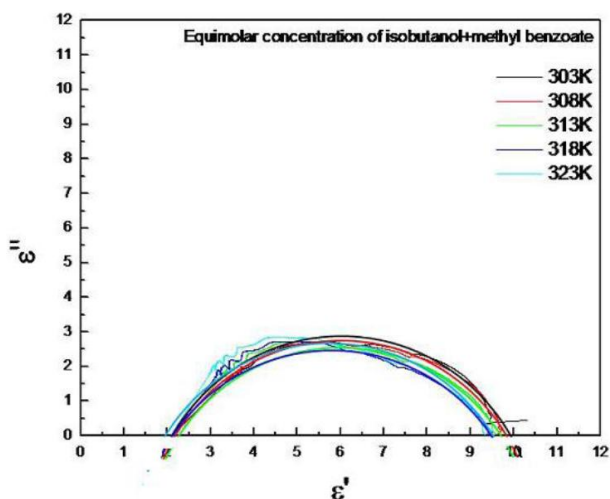
Fig.6. Cole-Cole plot of equimolar concentration of methyl benzoate and isobutanol at different temperatures

The Cole-Cole plot of the equimolar concentration of isobutanol and methyl benzoate binary mixture at different temperatures is shown in Fig.6. The relaxation time value of methyl benzoate is smaller compared to the isobutanol due to the non existence of self associated groups which is as shown in Fig.7, and it is observed that the relaxation time value decreases with increase in the molar concentration of methyl benzoate in isobutanol and temperature. The increase in temperature results increase of hydrogen bonds break up due to the thermal vibrations in solute and solvent molecules. As a result, the weakened intermolecular forces lead to a decrease in internal pressure, cohesive energy and relaxation time. At higher temperature the hydrogen bonds become weak due to the thermal vibrations and structure breaking effect predominates over the formation of stable internal structure through hydrogen bonding.

The excess permittivity ε^E is a dielectric parameter which gives information about the interaction between the compounds of the mixture [63]. Mehrotra et al. [70] had pointed out that the change in the values of ε^E with concentration is due to the interaction between dissimilar molecules which may produce structural changes. In the preset chosen system, the majority negative values of ε^E are obtained for all concentrations at different temperatures which are shown in Fig. 8. This negative value indicates that the molecules in the mixture form multimers through hydrogen bonding in such a way that the effective dipole moment value gets reduced [23].

The calculated values of excess inverse relaxation time $(1/\tau)^E$ shows a negative value as shown in Fig.9. The negative values of relaxation time $(1/\tau)^E$ indicate the slower rotation of dipoles due to the formation of hydrogen bonded structures producing a field which hinders the effective dipole rotation [71,72]. The high values of g^{eff} for the pure isobutanol system suggest that the molecular dipoles have parallel orientation among themselves and the low value of g^{eff} for the pure methyl benzoate indicates the anti-parallel orientation of the

electric dipoles or non associative nature. But for the mixture of
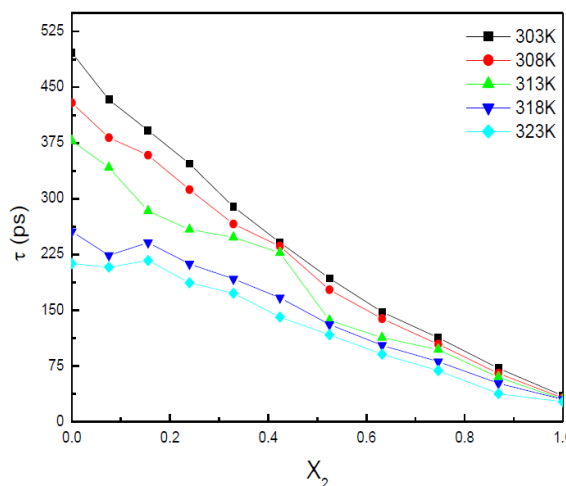

Fig.7. Plot of relaxation time (τ ps) with respective mole fraction of methyl benzoate in isobutanol (X_2) at different temperatures

isobutnaol and methyl benzoate, the parameter g^{eff} exhibits a steady decrease as the concentration of methyl benzoate increases which is as shown in Fig.10. This tendency leads to the conclusion that heterogeneous interaction between the compounds i.e., hydrogen bond between the –OH group of alcohol and –CO group of methyl benzoate leads to the formation of multimers with anti-parallel orientation of the electric dipoles [22]. The strength of this heterogeneous interaction is found to depend on the temperature and concentration of the mixture which shows that the change in temperature and concentration have some impact on the structural properties. The other dielectric parameter is the Bruggeman parameter (f_B) which is found to vary non-linearly with volume fraction of methyl benzoate in isobutanol at all temperatures that indicates an interaction is taking place in the mixtures as shown in Fig.11.
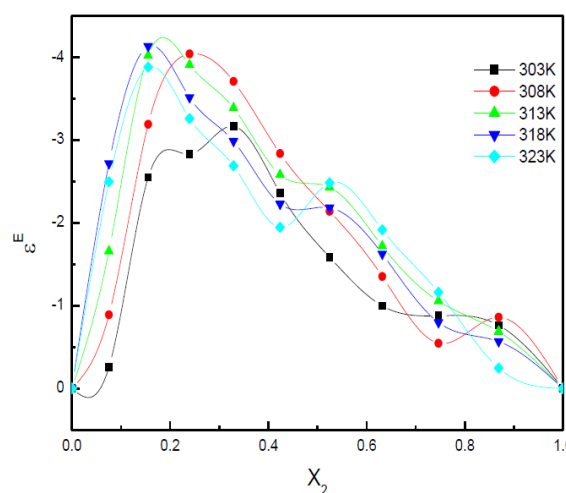

Fig.8. Plot of excessive dielectric permittivity (ε^E) with respective mole fraction of methyl benzoate in isobutanol (X_2) at different temperatures
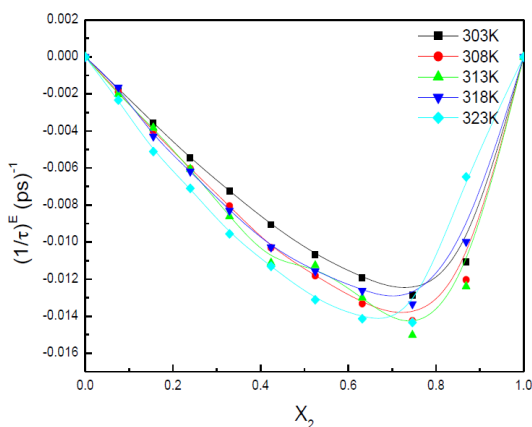
Fig.9.Plot of excessive relaxation time ($(1/\tau)^E$, ps^{-1}) with respective mole fraction of methyl benzoate in isobutanol (X_2) at different temperatures .
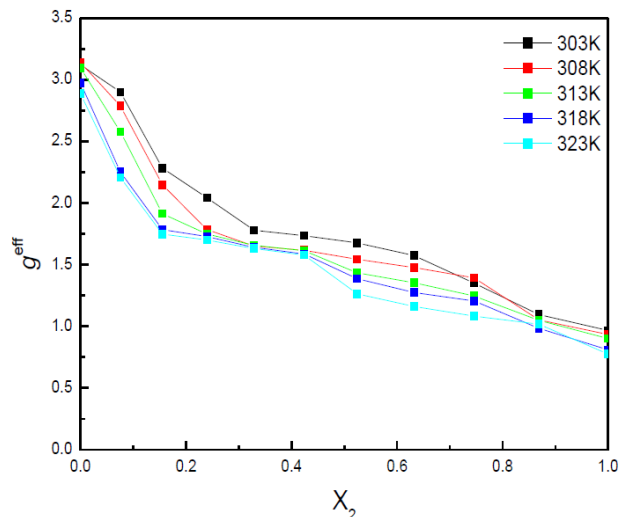

Fig.10. Plot of Kirkwood effective (g^{eff}) correlation factor with respective mole fraction of methyl benzoate in isobutanol (X_2) at different temperatures

The temperature dependence of $\ln(T\tau)$ vs $1/T$ of different molar concentrations of methyl benzoate in isobutanol as shown in Fig.12 and obtained the thermodynamic parameters by using Eyring's rate equation and which are tabulated in Table 4 respectively. From the Fig.12 it is observed that ln ($T\tau$) varies linearly with increase in molar concentration of methyl benzoate in isobutanol attributes formation of multimeric structure in the solution. From the Table 4 it can be observed that the value of free energy of activation ΔG^* is least value for methyl benzoate and increases with increase in concentration of isobutanol at all temperatures. This indicates that the isobutanol molecules in the mixture dominate over methyl benzoate molecules. This dominance of isobutanol over methyl benzoate is primarily due to its more interaction between the self associated groups. Furthermore, it can be seen that as the temperature increases the molar free energy of activation for dipole relaxation process for isobutanol, methyl benzoate and their mixtures increases. This can be attributed to the fact that as the temperature increases; thermal agitation increases and the molecules require more energy to overcome the energy barrier separating the two mean equilibrium positions and also Gibbs free energy of activation ΔG^* shows a positive value which indicates the presence of interaction between the molecules in the system. The magnitude of ΔG^* is an excellent indicator of the strength of interaction between unlike molecules in liquid mixtures [73]. Enthalpy of activation ΔH^* depends upon the local environment of the molecules. From the Table 4 it is observed that the ΔH^* value is maximum for isobutanol and its value decreases with increase in the concentration of methyl benzoate. It indicates that the interaction between the molecules by hydrogen bonding decreases as the concentration of methyl benzoate increases results to an increase in the freedom of rotation of non associated molecules.

TABLE IV. . Variation of thermodynamical parameters ΔG^*, ΔH^* and ΔS^* with respective volume fraction of methyl benzoate in isobutanol at different temperatures(K)

Variation of volume fraction of methyl benzoate per ml in isobutanol	Temperature (K)	ΔH^* (kcal/mole)	ΔG^* (kcal/mole)	ΔS^* (Cal/mole/K)Literature†
0.0	303	77.769	20.279	189.74
	308		20.285	186.63
	313		20.295	183.62
	318		20.308	180.69
	323		20.317	177.87
0.1	303	69.26	19.973	162.76
	308		19.981	159.97
	313		19.991	157.4
	318		19.99	154.93
	323		20.043	152.37
0.2	303	57.747	19.686	125.61
	308		19.822	123.13
	313		19.983	120.65
	318		19.989	118.73
	323		20.17	116.33
0.3	303	54.818	19.382	116.95
	308		19.47	114.77
	313		19.533	112.73
	318		19.564	110.85

|	323		19.571	109.12
	303		18.924	84.66
	308		19.061	82.83
0.4	313	44.574	19.23	18.97
	318		19.302	79.74
	323		19.762	76.81
	303		18.464	81.18
	308		18.755	78.91
0.5	313	43.061	18.93	77.09
	318		18.934	75.87
	323		18.942	74.67
	303		17.604	83.63
	308		17.648	82.13
0.6	313	42.947	17.666	80.77
	318		17.892	78.79
	323		17.911	77.51
	303		17.23	78.93
	308		17.38	77.16
0.7	313	41.147	17.384	75.91
	318		17.356	74.81
	323		17.392	73.54
	303		16.556	78.19
	308		16.656	76.59
0.8	313	40.247	16.787	74.95
	318		16.79	73.76
	323		16.793	72.61
	303		15.422	52.04
	308		15.463	51.06
0.9	313	31.19	15.537	50.01
	318		15.543	49.2
	323		15.891	47.36
	303		13.615	33.04
	308		13.647	32.4
1.0	313	23.627	13.732	31.61
	318		13.926	30.51
	323		13.973	29.89
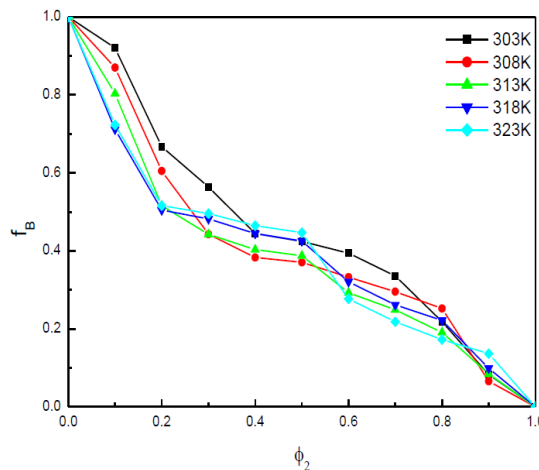
Fig.11. Plot of Bruggeman parameter (f_B) with volume fraction (ϕ_2) of methyl benzoate in isobutanol at different temperatures

From observing the pure FT-IR spectra of equimolar binary mixture of the isobutanol and the methyl benzoate, there is a shift of 42 cm-1 in the position of –OH for the mixture compared with the IR spectrum of pure isobutanol and a shift of 8 cm-1 in the position of –CO for the mixture compared with the spectrum of pure methyl benzoate which is as shown in Fig. 13.

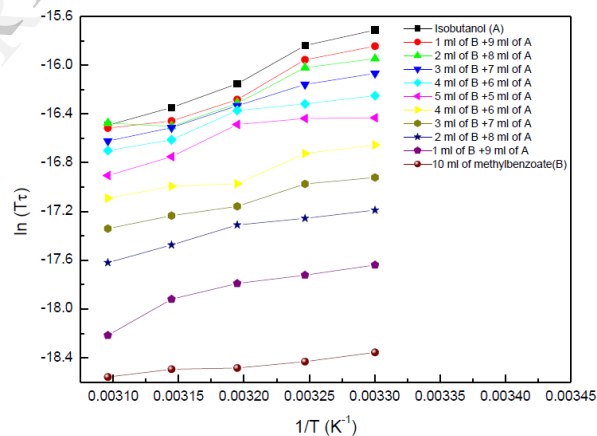

Fig.12. Plot of temperature dependence of ln(Tτ) vs 1/T (K^{-1}) of different molar concentrations of methyl benzoate in isobutanol (X$_2$) at different temperatures
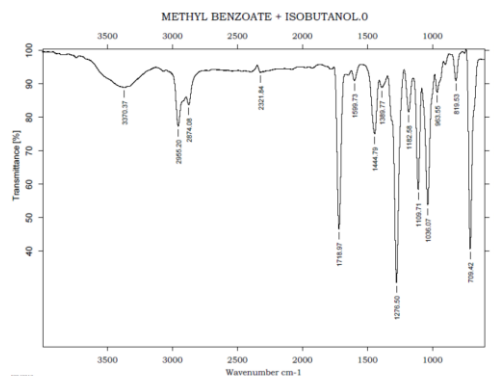

Fig.13. FT-IR sp-1ectra of the binary mixtures of Isobutanol and Methyl benzoate in the region of 450-4000cm^{-1}
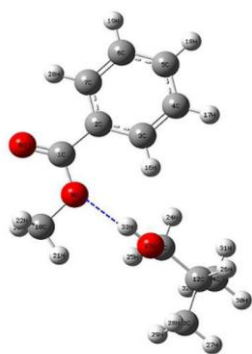
Fig.14. Optimized converged geometrical structure of hydrogen bonded system of isobutanol and methyl benzoate from DFT 6-311G basis set using Gaussian-03 programming software

These shifts are caused by the strong interaction that exist between the hydrogen of alcoholic group (-OH) and oxygen of -CO group respectively. Thus IR spectrum gives an evidence of presence of intermolecular hydrogen bonding between isobutanol and methyl benzoate. The comparison of experimental FT-IR and theoretical IR frequency values as well as the bond lengths of OH-CO of binary system and individual bond lengths OH and CO are tabulated in Table 5. From the proton NMR analysis, there is a up field chemical shift in the binary system when compared to the pure system of isobutanol and methyl benzoate and it is due to fact that hydrogen atom of- OH group is shielded with the lone pair of electrons. This reveals that a strong interaction exists between the high electro negativity - CO group of methyl benzoate and the positive charge of hydrogen of –OH group of isobutanol and is conformed from the quantum mechanical calculations.

TABLE V. FI-IR analysis for the pure and binary mixture of Isobutanol and Methyl benzoate

System	Bond lengths Theoretical (Å)		Frequency band)	Density Functional theory (DFT-B3LYP)	
	(DFT-B3LYP) 6-311G basis set	(DFT-B3LYP) 6-311G+ basis set		ν (cm-1)	$\Delta\nu$ (cm-1)
Isobutanol+ Methyl benzoate	1.9024	1.8603	OH-CO	3370	42
	1.3949	1.3925	CO	1276	8
Isobutanol	0.9721	0.9728	OH	3328	
Methyl benzoate	1.3799	1.3784	CO	1268	

System	Theoretical			
	(DFT-B3LYP) 6-311G basis set		(DFT-B3LYP) 6-311G+ basis set	
	ν (cm-1)	$\Delta\nu$ (cm-1)	ν (cm-1)	$\Delta\nu$ (cm-1)
Isobutanol+	3571.82	111.36	3561.82	120.95

System	Theoretical			
	(DFT-B3LYP) 6-311G basis set		(DFT-B3LYP) 6-311G+ basis set	
Methyl benzoate	1263.00	23	1281.04	0.27
Isobutanol	3683.18		3682.77	
Methyl benzoate	1286.00		1281.31	

TABLE VI. Mean Molecular polarizability values of the binary system of isobutanol, methyl benzoate and their binary mixtures of isobutanoland methyl benzoate

Sample	Mean molecular polarizabilty (αM), (cm-3)
Isobutanol	94.84×10^{-25}
Methyl benzoate	123.36×10^{-25}
Isobutanol + Methyl benzoate	255.65×10^{-25}

The formation of hydrogen bond between the binary system i.e. isobutanol + methyl benzoate causes increase in the mean molecular polarizability value compared to the mean molecular polarizability values of the individual systems of isobutanol, methyl benzoate and which are tabulated in Table 6. In this molecular polarizability calculation the contribution of hydrogen bond (A-H…B) between the two individual systems isobutanol and methyl benzoate is considered as half of the polarizability due to the weak interaction. The contribution of this weak interaction (i.e. O--H bond) towards the polarizability is very small. Therefore the total mean polarizability of the binary system is given by sum of two individual polarizabilities and half of the polarizability of the hydrogen bond term. The increase in the molecular polarizability of the binary system provides information about the existence of hydrogen bond between the two individual systems The optimized geometrical structure representing the formation of hydrogen bond between the isobutanol and methyl benzoate is obtained from the B3LYP with 6-311G as basis set using Gaussian-03 chemical molecular modeling software which is as shown in Fig.14.

V. CONCLUSIONS

The formation of hydrogen bond between the isobutanol and methyl benzoate causing the increase in the dipole moment values and also considerable change in the relaxation time values compared to the individual systems and it is also confirmed from the experimental FTIR, [1]NMR and the theoretical IR calculations. The experimental dipole moment values are well in agreement with the theoretical quantum mechanical calculations. The absence of ionic contribution to the structure is seen from the excess dipole moment values. The term $(1/\tau)^E$ values are negative at all the temperatures and it confirms that dipoles rotates slowly in the binary mixture of isobutanol and methyl benzoate. The Bruggeman parameter

(f_B) shows a deviation for all the concentrations in the temperature range of 298K-318K and confirms the strong interaction between the molecules isobutanol and methyl benzoate in the mixture. The effective g^{eff} factor value is high for isobutanol and decreases with increase in the concentration of methyl benzoate in the binary system.

VI. ACKNOWLEDGEMENTS

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