

Study of excess dielectric and thermodynamic parameters of hydrogen bonded system: Isobutanol and ethyl benzoate

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Received 20 January 2014; revised 23 April 2014; accepted 5 May 2014

The complex dielectric permittivity of polar systems of isobutanol and ethyl benzoate for various mole fractions at different temperatures has been studied by using the open-ended coaxial probe technique method in the microwave frequency range from 20 MHz to 20 GHz. The dipole moment, excess dipole moment, Bruggeman parameter, excess Helmholtz energy, excess permittivity, excess inverse relaxation time, excess thermodynamic values are calculated using experimental results. The optimized geometry, harmonic vibrational wave numbers and dipole moments of pure and equimolar binary mixtures have been calculated theoretically from HF, B3LYP with 6-311G and 6-311G+ basis sets by using Gaussian-03 software. Conformational analysis of the formation of hydrogen bond between isobutanol and ethyl benzoate is supported by the FT-IR, ¹NMR and molecular polarizability calculations. The calculated wave numbers and dipole moments agree well with the experimental values. Further, the correlations among the parameters have been discussed in detail.

Keywords: Dielectric relaxation, Thermodynamic parameters, IR spectra analysis, *ab-initio* calculations

1 Introduction

Dielectric studies on the binary mixtures are important for understanding the intermolecular interactions in the mixture due to the dipole-dipole interactions and hydrogen bonding¹⁻³. The dielectric investigations of binary polar liquid mixtures provide valuable information regarding intermolecular interactions and the subsequent structural rearrangement of molecules in solution. The homo and hetero interactions in binary systems using dielectric measurements have been studied and reported by several investigators⁴⁻¹². 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 because of dipole-dipole interaction and hydrogen bonding. Alkyl benzoates are non-associated in solution, good hydrogen bonding acceptors and important industrial chemicals that are widely used in perfumery and pesticides. “Hydrogen bonding in Biological Structures” can be used in many ways by biophysicists¹³. The study of the H-bonds of the type O-H---O=C plays a important role in the biological systems and drug synthesis¹⁴.

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 systems¹⁵⁻¹⁹. 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 ($\epsilon_\infty = n^2$) 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 literature²⁰⁻²⁴. The values of μ , τ and Kirkwood g factor gives the information regarding the structure of molecules, nature of chemical bond, intra and intermolecular interactions, the nature of the orientation of the polar unit etc. 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 bonding²⁵. 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

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hence it is useful in interpreting the dielectric results²⁵⁻²⁸. Agnieszka Chmielewska *et al.*²⁹ studied the relative permittivity of seven binary mixtures of methanol with ethanol, isomers of propanol and butanol at various mole fractions in the temperature range 288.15 K–308.15 K and observed that changes in the values of dielectric parameters are connected with the intermolecular interactions and carbon chain length. Crossley *et al.*³⁰, Glasser *et al.*³¹ and Garg *et al.*³² studied the dielectric relaxation spectra 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. Jian-Zhong Bao *et al.*³³ 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. Winkle Mann *et al.*³⁴ developed comprehensive relations linking the complex dielectric permittivity of binary mixtures with short range and long-range interactions as an extension of Kirkwood theory. The theoretical approach and computer simulation studies were reported to understand the relaxation behavior and the hydrogen bonding in alcohols by Minami *et al.*³⁵ and Padro *et al.*³⁶, respectively. Yomogida *et al.*³⁷ measured the complex permittivity of 14 monohydric alcohols in the frequency range 0.2–2.5 THz, at temperatures ranging from 253 K to 323 K using time domain spectroscopy. Chitra *et al.*³⁸ studied the conformational and dielectric analysis of the hydrogen bonded binary system of non-associated polar liquid ethyl benzoate and associated polar liquid *N*-methyl 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 ethyl and ethyl benzoate by Madhu Mohan *et al.*³⁹.

In this paper, the complex dielectric permittivity of pure liquids such as isobutanol, ethyl benzoate and different molar concentration levels of ethyl benzoate in isobutanol in the microwave frequency range (20 MHz – 20 GHz) have been measured by using the open-ended coaxial probe method²⁴ at different temperatures, i.e., 303 K, 308 K, 313 K, 318 K and 323 K. The dipole moments of the isobutanol, ethyl 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^{40,58} and molecular polarizability value obtained from the Lippincott δ function potential model⁴¹⁻⁴². Thermodynamical parameters such as enthalpy of activation ΔH^* , entropy of activation ΔS^* are calculated from the Eyrings rate equation⁴³⁻⁴⁴ and effective Kirkwood g factor is determined from the Kirkwood-Frohlich equation¹⁷. The formation of hydrogen bond between the isobutanol and ethyl benzoate is confirmed from the experimental FT-IR and theoretical IR, ¹NMR and molecular polarizability calculations.

2 Experimental Details

2.1 Materials

The compounds of isobutanol, ethyl benzoate and benzene of AR grade with purity 99 % procured from Merck, Germany. All the liquids used were further purified by standard procedure⁴⁵. The mid fraction of the distillate stored over 4 Å 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 Procedure

The static dielectric constant values of the above dilute systems, i.e., isobutanol, and ethyl benzoate in benzene and equimolar binary mixtures of the isobutanol and ethyl benzoate are measured at 820 Hz by using digital capacitance meter and high frequency dielectric constant ($\epsilon_\infty = n^2$) 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 303 K, 308 K, 313 K, 318 K and 323 K with a variation of ± 0.1 K. The error estimated in the calculation of static dielectric constant and optical refractive indexes (n) are 1%, respectively. The complex dielectric permittivity ($\epsilon^* = \epsilon' - j\epsilon''$) of pure liquids isobutanol, ethyl benzoate and the different molar concentration levels of ethyl benzoate in isobutanol is measured in the microwave frequency range (20 MHz – 20 GHz) by using the open-ended coaxial probe method in the different frequency intervals of 0.5 GHz at different temperatures from 303 K to 323 K. The procedure involves with one end of the coaxial probe is connected to the PNA-L Network analyzer (N5230C)

and other end is inserted into 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 5 K 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 303 K. The first measurement was made when the temperature reading was stable. The water controlled bath was then increased to 5 K 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 5 K. Thus, the temperature gradient in the sample is from the stated temperature to 5 K 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 ethyl benzoate in isobutanol were measured from 20 MHz–20 GHz with varying temperature from 303 K to 323 K. All the measurements were repeated at least two times and were reproducible in the range $\pm 2\%$. 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 ^1NMR spectra by Bruker spectrometer with CDCl_3 as solvent medium.

3 Computational Details

The minimum energy based geometry optimization of the monomers of isobutanol, ethyl benzoate and their binary system were carried out at different levels of theory, namely at Hatree-Fock (HF) level⁴⁶⁻⁴⁸, at DFT level⁴⁹ 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)⁵⁰⁻⁵¹. The calculations were performed on a Pentium IV workstation, at 3.0 GHz, running the Gaussian 03 package⁵².

4 Determinations of the Parameters

The dipole moment of the isobutanol, ethyl benzoate and its equimolar binary mixture of ethyl

benzoate in isobutanol in benzene are determined by using the Higasi's method as given by Koga *et al.*⁵³:

$$\epsilon_2 = \frac{27kTM_2(a_o - a_\infty)}{4Nd_1(\epsilon_1 + 2)^2} \dots (1)$$

where a_o and a_∞ are the slopes obtained from the linear plots of ϵ_0 and ϵ_∞ versus the weight fraction of solutes isobutanol, ethyl benzoate and binary system isobutanol + ethyl benzoate diluted in benzene, respectively, 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, ethyl 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 Huyskens⁵⁴:

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

where μ_a is the dipole moment of the isobutanol and μ_b is the dipole moment of ethyl benzoate and μ_{ab} is the dipole moment of the equimolar binary system of isobutanol + ethyl 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 mixture⁵⁵ can be computed as:

$$\epsilon^E = (\epsilon_m - \epsilon_{\infty m}) - [(\epsilon_1 - \epsilon_{\infty 1})\chi_1 + (\epsilon_2 - \epsilon_{\infty 2})\chi_2] \dots (3)$$

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 permittivity⁵⁶ about the mixture indicates:

- (i) $\epsilon^E=0$ indicates that there is no interaction between the components in the mixture.
- (ii) $\epsilon^E<0$ 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.
- (iii) $\epsilon^E>0$ 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 equations⁵⁷. The Bruggeman factor (f_B) is given by:

$$f_B = \left(\frac{m-2}{1-2} \right) \left(\frac{-1}{2} \right)^{\frac{1}{3}} = (1-2) \quad \dots (4)$$

where 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 2 , but if there are interactions between the components then f_B varies non-linearly with 2 .

The dielectric data obtained, i.e., low frequency dielectric permittivity (ϵ_0) 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 plot⁵⁸ using the relation:

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

where α is the distribution parameter and this value is zero for Debye and non zero for Cole-Cole Plot. The values of v and u are determined from their respective Cole-Cole and Debye plots.

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 spectra⁵⁹, and it can be defined as:

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

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 unimolecular chemical reactions, Eyring⁴³⁻⁴⁴ identified a relation with Gibbs free energy of activation ΔG^* . His theory leads to an expression for τ as:

$$= \frac{h}{kT} \exp\left(\frac{\Delta G^*}{RT} \right) \quad \dots (7)$$

i.e.,

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

with $\Delta G^* = \Delta H^* - T\Delta S^*$ one can write from Eq. (7):

$$\begin{aligned} \ln(\tau) &= \ln\left(\frac{h}{k} \right) + (\Delta H^* - T\Delta S^*)/RT \\ &= \left[\ln\left(\frac{h}{k} \right) - \left(\frac{\Delta S^*}{R} \right) \right] + \left[\frac{\Delta H^*}{RT} \right] \quad \dots (9) \end{aligned}$$

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:

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

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:

$$\frac{4 N_A^2}{9kTM} g = \frac{(\epsilon_\infty - \epsilon_0)(2 + \epsilon_\infty)}{(\epsilon_\infty + 2)^2} \quad \dots (11)$$

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:

$$\frac{4 N_A}{9kT} \left(\frac{\mu_1^2}{M_1} x_1 + \frac{\mu_2^2}{M_2} x_2 \right) g^{eff} = \frac{(\epsilon_m - \epsilon_\infty)(2\epsilon_m + \epsilon_\infty)}{m(\epsilon_\infty + 2)^2} \dots (12)$$

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 $\epsilon_{\infty m}$ is the square of the refractive index of the mixture and g^{eff} is an index of solute solvent interactions.

Assuming that the dipole moments of both the liquids are affected by the same amount g_f the Kirkwood equation for the mixtures is modified as:

$$\frac{4 N_A}{9kT} \left(\frac{\mu_1^2}{M_1} g_1 x_1 + \frac{\mu_2^2}{M_2} g_2 x_2 \right) g_f = \frac{(\epsilon_m - \epsilon_\infty)(2\epsilon_m + \epsilon_\infty)}{m(\epsilon_\infty + 2)^2} \dots (13)$$

where g_1 and g_2 and g_f represent Kirkwood correlation factor for liquid 1, liquid 2 and corrective Kirkwood correlation factor, respectively

Here the value of g^{eff} in Eq. (12), varies from g_1 to g_2 , in the case of associate and non-associate mixtures as the concentration of liquid 2 increases from 0 to 1 and the value of g_f in Eq. (3) is unity for pure liquids and close to unity if there is no interaction. The deviation of g_f from unity indicates interaction between liquids 1 and 2.

The excess Helmholtz energy (ΔF^E) is a dielectric parameter to evaluate the interaction between the components in the mixture through breaking mechanism of hydrogen bond⁶⁰ and is expressed as:

$$\Delta F^E = \Delta F^{E_{or}} + \Delta F^{E_{rr}} + \Delta F^{E_{12}} \dots (14)$$

where $\Delta F^{E_{or}}$ represents the excess dipolar energy due to long range electrostatic interaction, $\Delta F^{E_{rr}}$ represents the excess dipolar energy due to the short range interaction between identical molecules, $\Delta F^{E_{12}}$ represents the excess free energy due to the short range interaction between the dissimilar molecules.

The above terms are given in detail in below equation:

$$\begin{aligned} \Delta F^E = & \frac{-N_A}{2} \left\{ \sum_{r=1,2} \frac{\mu_r^2}{V_r} \left[R_{fr} - R_{fr}^o \right. \right. \\ & + \sum_{r=1,2} \frac{\mu_r^2}{V_r} \left[g_{rr} - 1 \right] \left[R_{fr} - R_{fr}^o \right] \\ & + \left. \left. \mu_1 \mu_2 \left[R_{f1} + R_{f2} - R_{f1}^o - R_{f2}^o \right] \right\} \dots (15) \end{aligned}$$

Where

$$R_{fr}^o = \left(\frac{8 N_A}{9V_r} \right) \frac{(\epsilon_r - 1)(\epsilon_\infty + 2)}{(2\epsilon_r + \epsilon_\infty)}$$

$$R_{fr} = \left(\frac{8 N_A}{9V_r} \right) \frac{(\epsilon_m - 1)(\epsilon_\infty + 2)}{(2\epsilon_m + \epsilon_\infty)}$$

$$g_{12} = g_f$$

and V_r is the molar volume of the components. ϵ_r , and $\epsilon_{\infty r}$ are the dielectric permittivity values at static and optic frequencies of the pure liquids, respectively.

5 Results and Discussion

The low frequency dielectric permittivity value (ϵ_o) which is measured at 20 MHz and high frequency dielectric constant ($\epsilon_\infty = n^2$) of various mole fractions of ethyl benzoate in isobutanol at different temperatures are shown in Figs 1 and 2. The frequency dependent

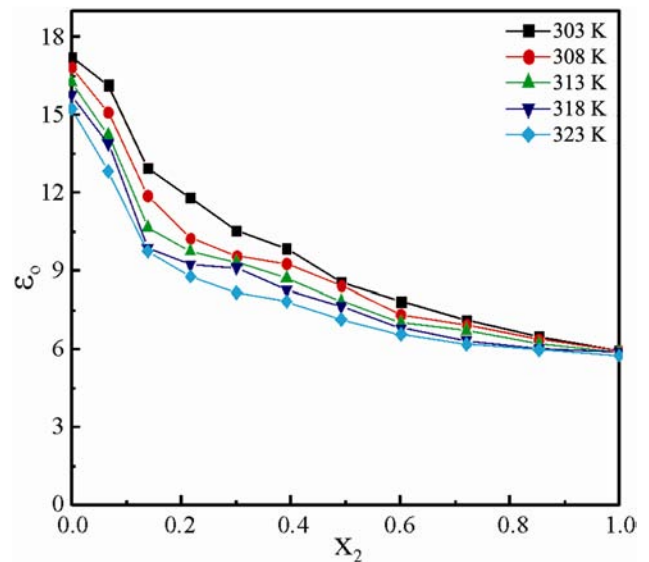


Fig. 1 – Plot of low frequency dielectric permittivity (ϵ_o) with respective mole fraction of ethyl benzoate in isobutanol (X_2) at different temperatures

complex dielectric permittivity ($\epsilon^* = \epsilon' - j\epsilon''$) of pure systems of isobutanol, ethyl benzoate and equimolar concentrations levels of isobutanol and ethyl benzoate at different temperatures are shown in Figs. 3, 4 and 5, respectively. From the Figs. 1 and 2 it is observed that there is non-linear variation of low frequency dielectric permittivity (ϵ_0), and high frequency dielectric constant with mole fraction at all temperatures confirms that the formation of heteromolecular interaction in the binary system. Similar results were reported by Kroeger⁶¹ for the mixture of alcohols and polar liquids.

The experimentally determined values of low frequency dielectric permittivity, relaxation times of pure liquids are tabulated in Table 1 and compared with available literature data. The dipole moment (μ) values of the pure and equimolar binary systems of isobutanol and ethyl benzoate are determined by using the Higasi's method at different temperatures and compared the room temperature dipole moments (298 K) of the above systems with the theoretical HF, B3LYP calculations which are tabulated in Table 2 and 3, respectively. The dipole moments of these systems are measured experimentally by diluting them in non-polar solvent benzene. From the Tables 2 and 3, 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 ethyl benzoate. The theoretical dipole moment values are in good

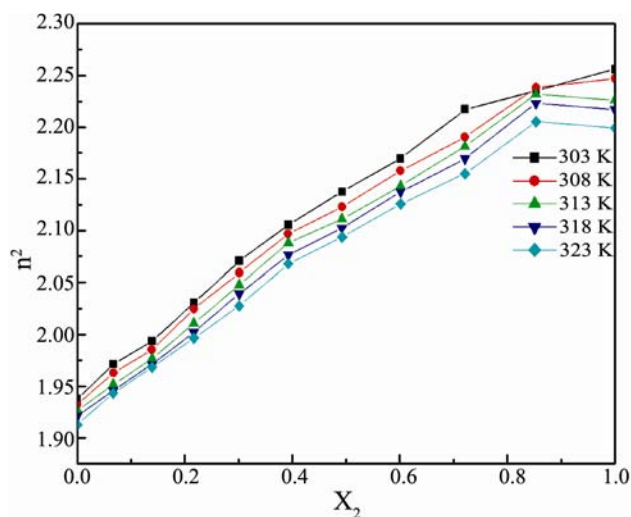


Fig. 2 – Plot of high frequency dielectric constant ($\epsilon_\infty = n^2$) with respective mole fraction of ethyl benzoate in isobutanol (X_2) at different temperatures

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

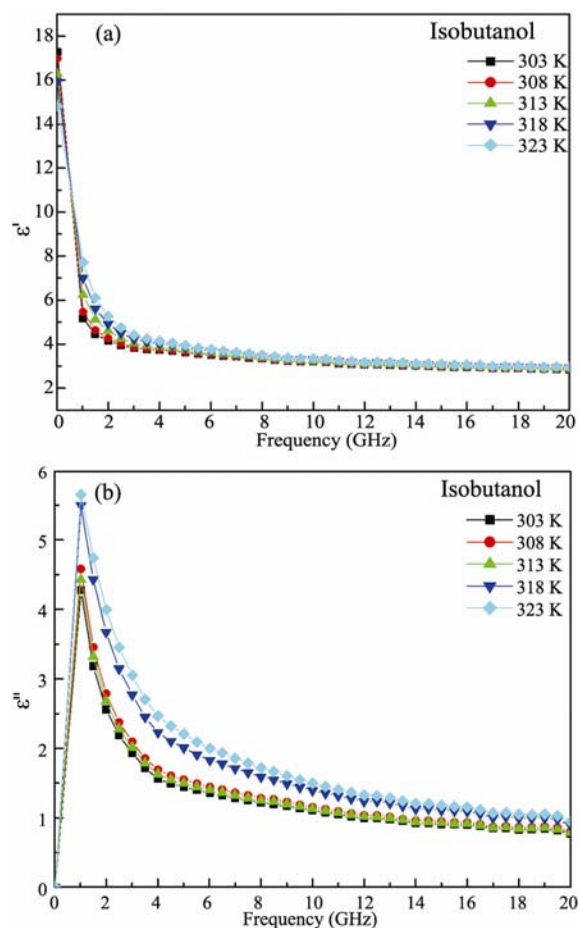


Fig. 3 – Plot of (a) real (ϵ') and (b) imaginary part of dielectric permittivity (ϵ'') of isobutanol with respective frequency (X_3) at different temperatures

leads to a decrease in the cancelling of the side-group dipole moments and a consequential increase in the mean dipole moment value.

From Figs 3(a), 4(a), and 5(a) it is observed that real part of dielectric permittivity (ϵ') decreases with increase in frequency and molar concentration of ethyl benzoate in isobutanol with temperature. From the Fig. 3(b) 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 ethyl benzoate and equimolar binary mixture which is as shown in Figs. 4(b) and 5(b), respectively. It is due to the formation of inter molecular hydrogen bonding between one alcohol molecule and another (R-OH---OH-R) which 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

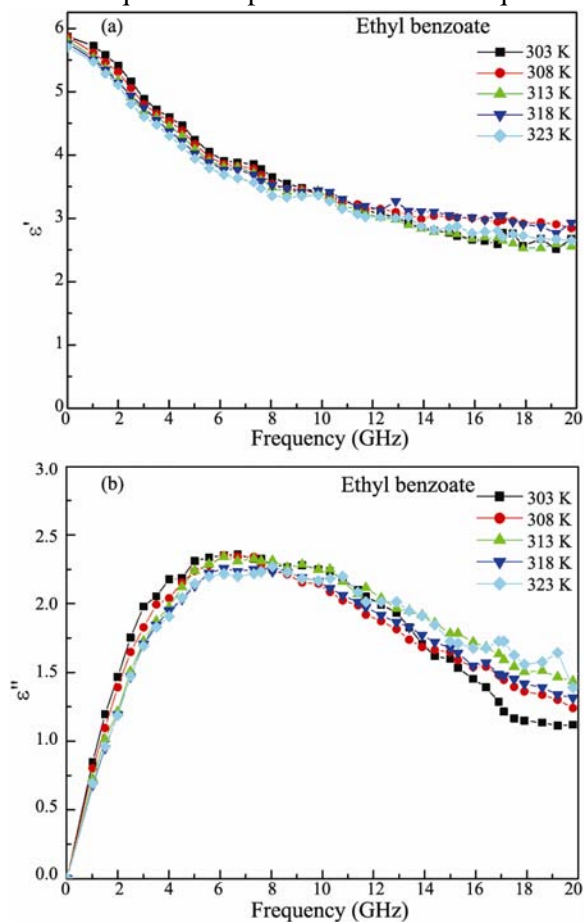


Fig 4. – Plot of (a) real (ϵ') and (b) imaginary part of dielectric permittivity (ϵ'') of ethyl benzoate with respective frequency (X_3) at different temperatures

position causing increase in the relaxation time values which are calculated by using the Cole-Cole plots whereas non associated liquid ethyl benzoate is exhibiting the single relaxation time which is calculated from the Debye plot⁶². The relaxation time value of ethyl benzoate is smaller compared to the isobutanol due to the non existence of self associated groups which is as shown in Fig. 6, and it is observed that the relaxation time value decreases with increase in the molar concentration of ethyl benzoate in isobutanol and temperature. The increase in temperature results in the increase of hydrogen bonds which is due to break up of 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

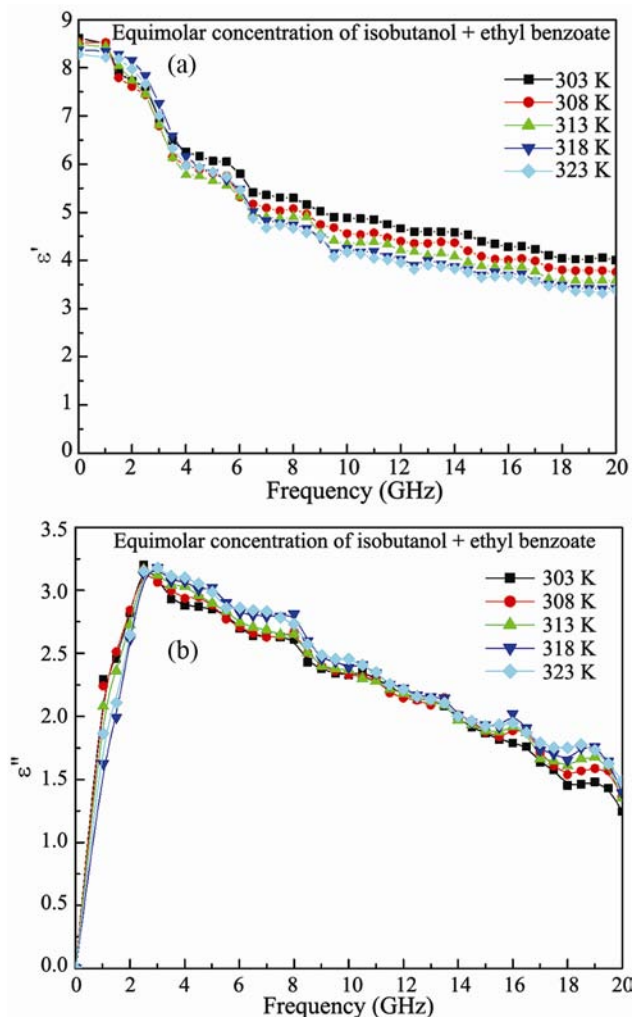


Fig 5 – Plot of (a) real (ϵ') and (b) imaginary part of dielectric permittivity (ϵ'') of equimolar binary system of isobutanol and ethyl benzoate with respective frequency (X_3) at different temperatures

Table 1 – Comparison of low frequency dielectric permittivity (ϵ_0) and relaxation time (τ) values of the pure compounds

Liquid	ϵ_0 at 298 K		τ (ps)	
	Present work	Literature†	Present work	Literature†
Isobutanol (A)	17.20	17.70	496.60	---
Ethyl benzoate (B)	5.98	6.46 ⁶²	38.71	42.03
Equimolar binary mixtures of A+B	9.12	---	211.35	---

† CRC Handbook of Chemistry and Physics (1969-1970,) Weast Rc (ed) (1983-84) Hand Book of Chemistry and Physics. 64th edn, CRC Press, Aparicio *et al*⁶²

Table 2 – Experimental dipole moment (μ) and excess dipole moment ($\Delta\mu$) values for the pure system isobutanol, ethyl benzoate and equimolar binary systems- isobutanol and ethyl benzoate

T (K)	Isobutanol μ (D)	Ethyl benzoate μ (D)	Equimolar binary mixture of isobutanol + ethyl benzoate μ (D)	$\Delta\mu$ (D)
303	1.76	1.93	3.19	-0.50
308	1.74	1.94	3.21	-0.47
313	1.75	1.95	3.21	-0.49
318	1.77	1.96	3.22	-0.51
323	1.78	1.96	3.23	-0.51

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 mixture⁵⁷. Mehrotra *et al.*⁶³ 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. 7. 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 reduced¹⁹.

The calculated values of excess inverse relaxation time $(1/\tau)^E$ shows a negative value as shown in Fig. 8. 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 rotation⁶⁴⁻⁶⁵. 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 ethyl benzoate indicates the anti-parallel orientation of the electric dipoles or non associative nature. But for the mixture of isobutanol and ethyl benzoate, the parameter g^{eff} exhibits a steady decrease as the concentration of ethyl benzoate increases which is as shown in Fig. 9. 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 ethyl benzoate leads to the formation of multimers with anti-parallel orientation of the electric dipoles¹⁸. 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 ethyl benzoate in isobutanol at all temperatures that indicates an interaction is taking place in the mixtures as shown in Fig. 10. The temperature dependence of $\ln(T\tau)$ vs $1/T$ of different molar concentrations of ethyl benzoate in isobutanol as shown in Fig. 11 and obtained the thermodynamic parameters by using Eyring's rate equation and which are tabulated in Table 4, respectively. From Fig. 11 it is observed that $\ln(T\tau)$ varies linearly with increase in molar concentration of ethyl benzoate in isobutanol attributes formation of multimeric structure in the solution. From Table 4 it can be observed that the value of free energy of activation ΔG^* is least value for ethyl benzoate and increases with increase in concentration of isobutanol at all temperatures. This indicates that the isobutanol molecules in the mixture dominate over ethyl benzoate molecules. This dominance of isobutanol over ethyl 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, ethyl benzoate and their mixtures increases. This can

Table 3 – Experimental and theoretical dipole moment (μ) and excess dipole moment ($\Delta\mu$) values of pure system isobutanol, ethyl benzoate and equimolar binary systems- isobutanol and ethyl benzoate at 298 K

System	Experimental (298 K)				Theoretical calculations						
	M (D)	Literature*	$\Delta\mu$ (D)	6-311G	Hartree-Fock (HF)			Density Functional theory (DFT-B3LYP)			
					$\Delta\mu$ (D)	6-311G+	$\Delta\mu$ (D)	6-311G	$\Delta\mu$ (D)	6-311G+	$\Delta\mu$ (D)
Isobutanol (A)	1.76	1.64		1.89		1.94		1.77		1.84	
Ethyl benzoate (B)	1.93	1.95		2.37		2.43		2.09		2.12	
A+B	3.19	–	-0.50	2.56	-1.70	2.64	-1.73	3.04	-0.82	3.09	-0.87

*CRC Handbook of Chemistry and Physics(1969-1970)

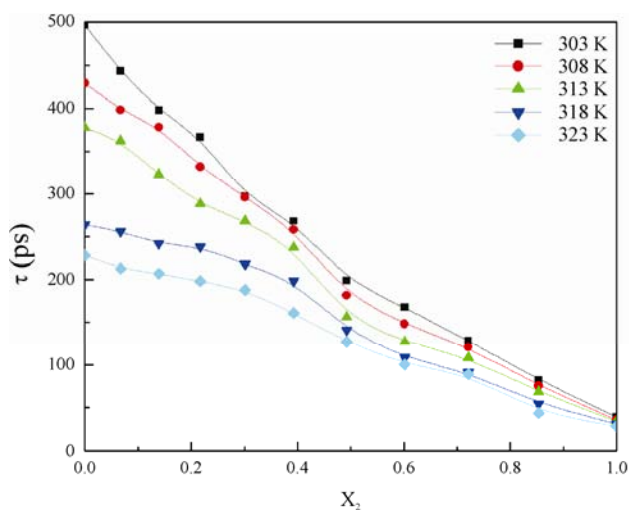


Fig. 6 – Plot of relaxation time (τ /ps) with respective mole fraction of ethyl benzoate in isobutanol (X_2) at different temperatures

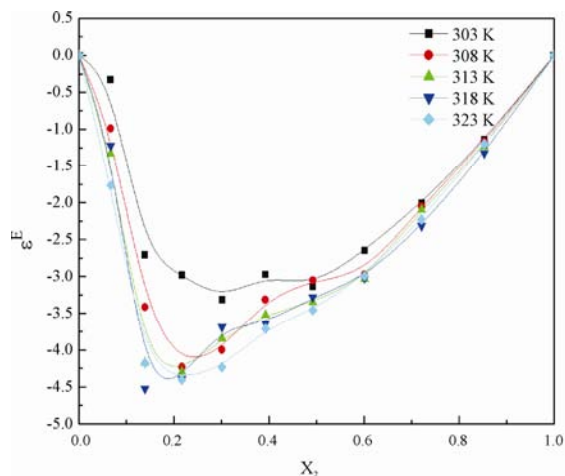


Fig. 7 – Plot of excessive dielectric permittivity (ϵ^E) with respective mole fraction of ethyl benzoate in isobutanol (X_2) at different temperatures

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

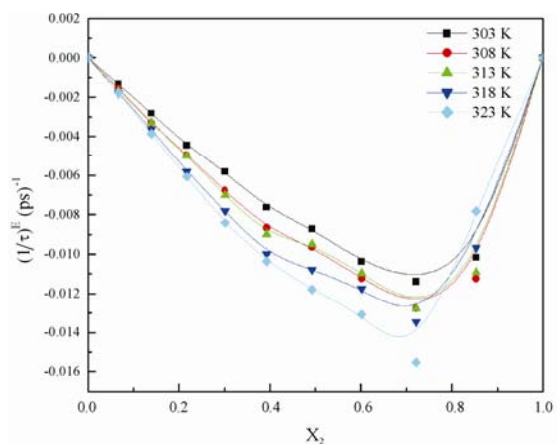


Fig. 8 – Plot of excessive relaxation time ($(1/\tau)^E$) with respective mole fraction of ethyl benzoate in isobutanol (X_2) at different temperatures

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 mixtures⁶⁶. Enthalpy of activation ΔH^* depends upon the local environment of the molecules. From Table 4, it is observed that the ΔH^* value is maximum for isobutanol and its value decreases with increase in the concentration of ethyl benzoate. It indicates that the interaction between the molecules by hydrogen bonding decreases as the concentration of ethyl benzoate increases results to an increase in the freedom of rotation of non associated molecules.

The long range and short range interactions between dipoles can be studied from the thermodynamic parameter excess Helmholtz energy (ΔF^E) and its constituent parameters $\Delta F^{E_{or}}$, $\Delta F^{E_{rr}}$ and $\Delta F^{E_{12}}$ ⁶⁷ which are given in Table 5. The value of $\Delta F^{E_{or}}$ represents the long range interaction between the dipoles in the mixture. In the present chosen system

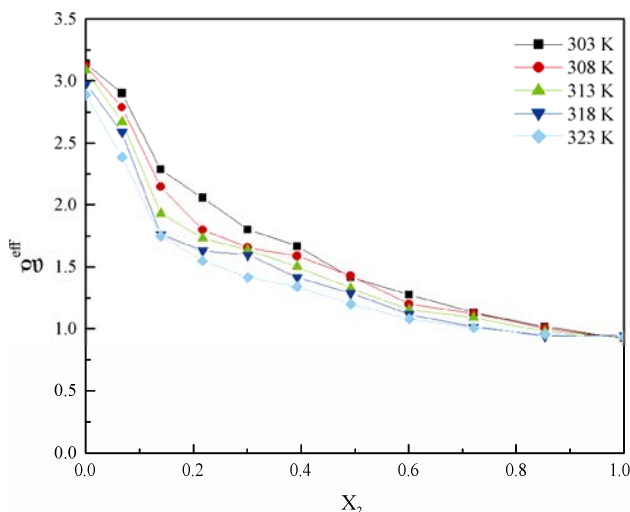


Fig. 9 – Plot of Kirkwood effective (g^{eff}) correlation factor with respective mole fraction of ethyl benzoate in isobutanol (X_2) at different temperatures

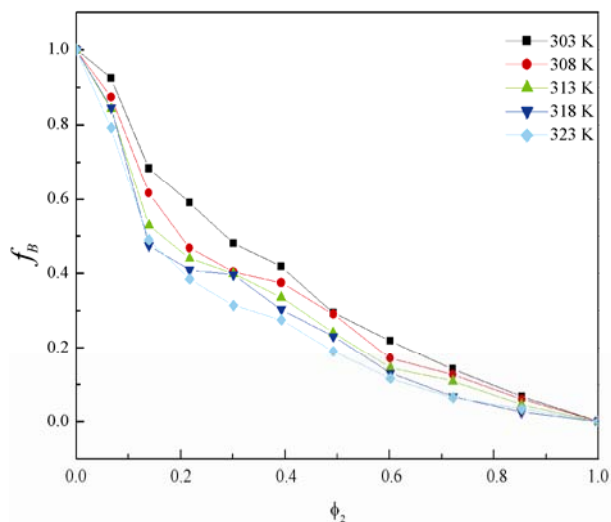


Fig. 10 – Plot of Bruggeman parameter (f_B) with volume fraction (ϕ_2) of ethyl benzoate in isobutanol at different temperatures

the positive values of $\Delta F^{E_{or}}$ indicate the repulsive force between the dipoles. From the Table 5 it is observed that the values $\Delta F^{E_{or}}$ are positive up to equimolar concentration and negative for remaining concentrations and this value decreases with increase in temperature and mole fractions. The strength of the dipole-dipole interaction depends on the concentration and temperature. The value of $\Delta F^{E_{rr}}$ gives the information regarding the short range interaction between the similar molecules, i.e., through hydrogen bonding. This interaction is strongest at high level of concentration of ethyl benzoate in isobutanol and decreases with increase in temperature which is

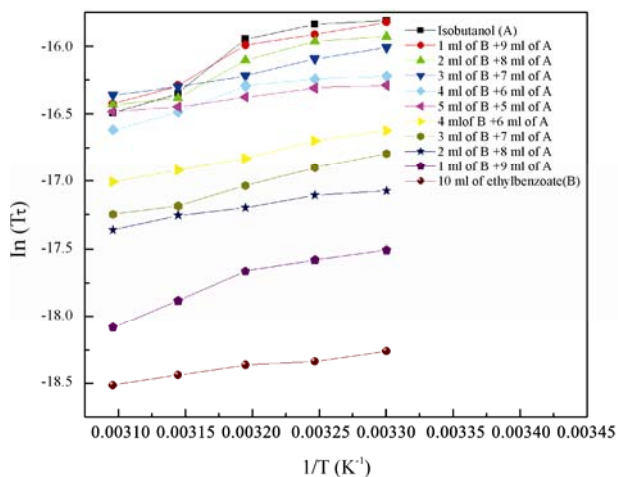


Fig. 11 – Plot of temperature dependence of $\ln(\tau_r)$ vs $1/T$ at different molar concentrations of ethyl benzoate in isobutanol (X_2) at different temperatures

observed from the values tabulated in Table 5 and it may due to breakage of hydrogen bond network between the molecules. The magnitude of $\Delta F^{E_{12}}$ reveals the information on the strength of interactions between the unlike molecules. The values of $\Delta F^{E_{12}}$ in the system ethyl benzoate + isobutanol indicate that it is hetero interaction between the compounds which is varying with concentration and temperature. The high positive values of ΔF^E indicates the formation of β clusters with anti parallel alignment in system. The formation of β clusters decreases the effective dipole moment of the system when compared to the sum of the dipole moments of the individual systems and thereby decreasing the internal energy⁶⁸. The decrement in the internal energy of a molecule leads to an increase in the excess Helmholtz value. From the high positive values of ΔF^E (from Table 5) indicates the formation of β clusters in the binary system and negative values of ΔF^E indicates the formation of α clusters. The formation of α clusters increases the effective dipole moment which in turn increases the internal energy.

By observing the pure FT-IR spectra of equimolar binary mixture of the isobutanol and the ethyl benzoate, there is a shift of 12 cm^{-1} in the position of $-\text{OH}$ for the mixture compared with the IR spectrum of pure isobutanol and a shift of 5 cm^{-1} in the position of $-\text{CO}$ for the mixture compared with the spectrum of pure ethyl benzoate which is as shown in Fig. 12. These shifts are caused by the weak interaction that exist between the hydrogen of alcoholic group ($-\text{OH}$) and oxygen of $-\text{CO}$ group, respectively. Thus IR

Table 4 – Variation of thermodynamical parameters, i.e, Gibbs free energy of activation (ΔG^*), enthalpy of activation (ΔH^*) and entropy of activation (ΔS^*) with respective volume fraction of ethyl benzoate in isobutanol at different temperatures

Variation of volume fraction of ethyl benzoate per ml in isobutanol	T (K)	ΔH^* (kcal/mole)	ΔG^* (kcal/mole)	ΔS^* (Cal/mole/K)
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	59.000	19.996	128.73
	308		20.094	126.32
	313		20.215	123.91
	318		20.285	121.74
	323		20.345	119.67
0.2	303	52.750	19.726	108.99
	308		19.966	106.44
	313		19.919	104.89
	318		19.928	103.21
	323		19.971	101.48
0.3	303	52.271	19.523	108.08
	308		19.630	105.98
	313		19.620	104.32
	318		19.724	102.35
	323		19.874	100.30
0.4	303	38.275	18.989	63.65
	308		19.248	61.77
	313		19.432	60.20
	318		19.538	58.92
	323		19.685	57.55
0.5	303	37.222	18.566	61.57
	308		19.082	58.90
	313		19.220	57.51
	318		19.334	56.25
	323		19.469	54.96
0.6	303	35.326	17.981	57.24
	308		18.086	55.97
	313		18.029	55.26
	318		18.086	54.21
	323		18.131	53.23
0.7	303	33.201	17.550	51.65
	308		17.562	50.77
	313		17.582	49.90
	318		17.681	48.80
	323		17.789	47.71
0.8	303	31.133	16.769	47.40
	308		17.115	45.51
	313		17.071	44.93
	318		16.932	44.66
	323		17.176	43.21
0.9	303	27.303	15.749	38.13
	308		15.825	37.27
	313		15.867	36.54
	318		15.873	35.94
	323		15.887	35.34
1.0	303	22.670	13.854	29.09
	308		13.887	28.52
	313		14.044	27.56
	318		14.068	27.05
	323	14.092	26.56	

Table 5 – Variation of ΔF_{Or}^E , ΔF_{rr}^E , ΔF_{12}^E and ΔF^E with volume fraction of ethyl benzoate in isobutanol

Volume fraction of ethyl benzoate per ml in isobutanol	ΔF_{Or}^E (J.mol ⁻¹)	ΔF_{rr}^E (J.mol ⁻¹)	ΔF_{12}^E (J.mol ⁻¹)	ΔF^E (J.mol ⁻¹)
<i>T</i> = 303 K				
0.0	0.0000	0.0000	0.0000	0.0000
0.1	17.5280	-0.7827	1.2031	17.9483
0.2	74.0678	-15.7503	6.6905	65.0080
0.3	75.8564	-19.2880	7.8744	64.4428
0.4	72.3377	-22.1129	4.7646	54.9894
0.5	44.2243	-13.5577	0.4176	31.0842
0.6	29.0120	-10.2542	-13.3025	5.4552
0.7	-3.1550	1.0864	-21.5293	-23.5979
0.8	-28.3501	9.0231	-24.5473	-43.8744
0.9	-32.5352	7.5264	-14.9968	-40.0056
1.0	0.0000	0.0000	0.0000	0.0000
<i>T</i> = 308 K				
0.0	0.0000	0.0000	0.0000	0.0000
0.1	31.6264	-2.9058	2.2592	30.9798
0.2	95.8761	-25.7606	6.4116	76.5271
0.3	115.8490	-40.9832	3.3945	78.2603
0.4	96.2715	-35.2515	-1.1789	59.8411
0.5	56.9171	-19.5164	-4.0872	33.3134
0.6	29.3036	-10.2966	-13.8255	5.1815
0.7	14.8664	-5.7338	-30.9289	-21.7963
0.8	-20.7256	6.7260	-26.6584	-40.6580
0.9	-27.8045	6.7496	-15.9817	-37.0366
1.0	0.0000	0.0000	0.0000	0.0000
<i>T</i> = 313 K				
0.0	0.0000	0.0000	0.0000	0.0000
0.1	41.3702	-4.9799	2.7475	39.1378
0.2	127.8506	-42.8222	4.4553	89.4837
0.3	126.4205	-46.9024	1.1749	80.6930
0.4	98.2011	-35.9762	-2.1474	60.0775
0.5	70.0515	-26.1210	-9.2730	34.6574
0.6	47.0488	-18.3965	-22.6266	6.0257
0.7	25.5530	-10.2913	-36.3703	-21.1086
0.8	-11.7042	3.9716	-29.8581	-37.5906
0.9	-17.7758	4.6466	-17.9979	-31.1271
1.0	0.0000	0.0000	0.0000	0.0000
<i>T</i> = 318 K				
0.0	0.0000	0.0000	0.0000	0.0000
0.1	41.3945	-4.3736	2.4329	39.4537
0.2	153.2010	-55.7289	2.2675	99.7396
0.3	141.4800	-53.9487	-1.2954	86.2359
0.4	101.7690	-36.1559	-2.5976	63.0155
0.5	83.3793	-32.1086	-13.7811	37.4895
0.6	52.4737	-20.2769	-24.1631	8.0337
0.7	32.8046	-13.2591	-39.2068	-19.6612
0.8	9.2644	-3.4185	-38.0993	-32.2535
0.9	-5.0803	1.4012	-20.3705	-24.0496
1.0	0.0000	0.0000	0.0000	0.0000

(Contd.)

Table 5 – Variation of ΔF_{Or}^E , ΔF_{rr}^E , ΔF_{12}^E and ΔF^E with volume fraction of ethyl benzoate in isobutanol (*Contd.*)

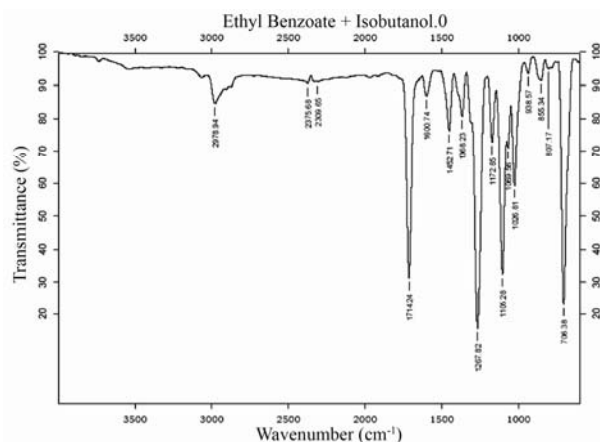
Volume fraction of ethyl benzoate per ml in isobutanol	Volume fraction of ethyl benzoate per ml in isobutanol	Volume fraction of ethyl benzoate per ml in isobutanol	Volume fraction of ethyl benzoate per ml in isobutanol	Volume fraction of ethyl benzoate per ml in isobutanol
$T = 323 \text{ K}$				
0.0	0.0000	0.0000	0.0000	0.0000
0.1	60.0428	-9.1032	3.1039	54.0434
0.2	149.8901	-52.7132	2.6289	99.8057
0.3	154.1189	-61.1757	-3.6421	89.3010
0.4	134.7763	-55.8872	-12.4080	66.4811
0.5	95.9689	-38.8797	-18.7577	38.3315
0.6	69.6824	-29.1601	-33.0988	7.4235
0.7	40.7981	-16.9163	-43.1705	-19.2887
0.8	12.2445	-4.5234	-38.8759	-31.1549
0.9	-9.8975	2.6266	-19.1524	-26.4232
1.0	0.0000	0.0000	0.0000	0.0000

Table 6 – FI-IR analysis for the pure and binary mixture of isobutanol and ethyl benzoate

System	Bond lengths (Theoretical) (Å)		Frequency band	Experimental		Theoretical			
	(DFT-B3LYP) 6-311G basis set	(DFT-B3LYP) 6-311G+ basis set		ν (cm^{-1})	$\Delta\nu$ (cm^{-1})	(DFT-B3LYP) 6-311G basis set		(DFT-B3LYP) 6-311G+basis set	
						ν (cm^{-1})	$\Delta\nu$ (cm^{-1})	N (cm^{-1})	$\Delta\nu$ (cm^{-1})
Isobutanol+ Ethyl benzoate	1.8831	1.9299	OH-CO	3316	12	3553.12	130.06	3567.73	115.04
	1.3901	1.3843	CO	1267	5	1271.00	35.21	1281.03	49.22
Isobutanol	0.9721	0.9728	OH	3328		3683.18		3682.77	
Ethyl benzoate	1.3858	1.3826	CO	1262		1235.79		1231.81	

spectrum gives an evidence of presence of intermolecular hydrogen bonding between isobutanol and ethyl 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 6. 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 ethyl 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 weak interaction exists between the high electro negativity - CO group of ethyl benzoate and the positive charge of hydrogen of -OH group of isobutanol and is conformed from the quantum mechanical calculations.

The formation of hydrogen bond between the binary system, i.e., isobutanol + ethyl benzoate causes increase in the mean molecular polarizability value compared to the mean molecular polarizability values of the individual systems of isobutanol, ethyl


 Fig. 12 – FT-IR spectra of the binary mixtures of isobutanol and ethyl benzoate in the region of 450-4000 cm^{-1}

benzoate and which are tabulated in Table 7. In this molecular polarizability calculation the contribution of hydrogen bond (A-H...B) between the two individual systems isobutanol and ethyl benzoate is

Sample	Mean molecular polarizability (ϵ_M) (cm ⁻³)
Isobutanol	94.84×10^{-25}
Ethyl benzoate	128.21×10^{-25}
Isobutanol + Ethyl benzoate	227.55×10^{-25}

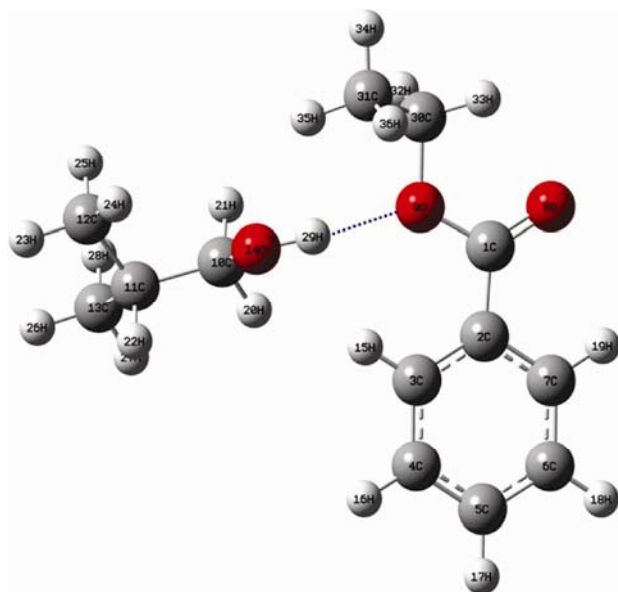


Fig. 13 – Optimized converged geometrical structure of hydrogen bonded system of isobutanol and ethyl benzoate from DFT 6-311G basis set using Gaussian-03 programming software

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 ethyl 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. 13.

6 Conclusions

The dipole moment, excess dipole moment, Bruggeman parameter, excess Helmholtz energy, excess permittivity, excess inverse relaxation time,

excess thermodynamic values of pure and binary mixtures of isobutanol and ethyl benzoate are calculated for various mole fractions at different temperatures. The formation of hydrogen bond between the isobutanol and ethyl 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 FT-IR, ¹NMR and the theoretical IR and molecular polarizability 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 values of term $(1/\tau)^E$ are negative at all the temperatures and it confirms that dipoles rotate slowly in the binary mixture of isobutanol and ethyl benzoate. The Bruggeman parameter (f_B) shows a deviation for all the concentrations in the temperature range of 303-323 K and confirms the strong interaction between the molecules isobutanol and ethyl benzoate in the mixture. The effective g^{eff} factor value is high for isobutanol and decreases with increase in the concentration of ethyl benzoate in the binary system.

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