Comprehensive Crew Dielectric Spectroscopy Studies on Associative and Non-Associative Dual Blends

K. Umamakeshvari[1,4*], U. Sankar[2,4], A. Moses Ezhil Raj[3,4], P. Ramesh Babu[5]

[1]Department of Physics, Wavoo Wajeeha Women's College of Arts and Science, Kayalpatnam, T.N, India

[2]Department of Physics, Sri KGS Ars College, Srivaikuntam, T.N, India

[3]Department of Physics, Scott Christian College, Nagercoil, T.N, India

[4]Manonmaniam Sundaranar University, Abishekapatti, Tirunelveli, T.N, India

[5]Department of Electronics and Communication Systems, Sri Krishna Arts and Science College, Coimbatore, T.N, India

*ram_dreams87@yahoo.com

Abstract: **In this contemporary study, the dielectric relaxation and thermodynamic performance of pure and binary mixtures of diethylene glycol and ethyl benzoate and their binary mixtures of nine concentrations were investigated. The various parameters like dielectric constant, dielectric constant at high frequency, relaxation time, effective Kirkwood correlation factor, excess dielectric constant, and excess inverse relaxation time values for different temperature were calculated. All the dielectric results have been discussed in terms of H-bond interaction and dipole orientation in binary mixture. Furthermore, the solute-solvent intermolecular interactions were confirmed by pure and equi-molar binary mixtures FT-IR spectrum.**

Keywords: **TDR, Dielectric relaxation, excess parameters, FTIR spectrum, Molecular interaction.**

I. INTRODUCTION

The confirmations of the homo or heterogeneous molecular interactions in polar binary mixtures are the central topics in liquid state molecular physics and chemistry. Thus, it is interesting to study inter and intra molecular interaction among the associative solute molecules and non-associative solvent molecules in mixture state [1]. The inter or intra molecular interactions are mainly occurs due dipole-dipole or Van der Waals or Hydrogen bond force which are generally called as non-covalent force. Among them the Hydrogen bond is the major driving non covalent interaction forces for stabilization of complex structure of organic molecules and spiral structure of deoxyribonucleic acid (DNA), ribonucleic acid (RNA) [2]. Esters are non-associative polar organic liquids with C=0 group and have technological important in different field [3]. Diethylene glycol is also scientifically and industrially important organic compound and has strongly associative nature due to presents of hydroxyl functional group in molecule [4]. It have been expected that the hydrogen bond between non associative ethyl benzoate and associative nature Diethylene glycol in mixture state. Moreover, the formation of molecular complexes in different stoichiometry ratio of binary mixtures through hydrogen bond interaction has been interesting research topic. Understandings of the nature of interaction forces that are present between diethylene glycol and molecular species have acceptor (ethyl benzoate) properties which may be useful in exploring the some other applications. The broad band dielectric relaxation study of solute-solvent mixture at microwave frequency gives information about molecular interactions in the system, formation of monomers and multiverse. Moreover, the measurement of dielectric properties at wide frequency range gives the information regarding the conduction mechanism, interfacial polarization, molecular dynamics and relaxation behavior phenomena [5]. The characterization of dielectric materials which is includes the measurement of complex permittivity as a function of frequency at a given temperature or as a function of temperature at a given frequency.

II. MATERIALS AND METHODS

2.1. Materials and sample preparation:

AR grade alcohol (≥99.5% of diethylene glycol) was purchased from Sd Fine Chemicals. AR grade esters (≥99.5% of ethyl benzoate) were supplied by Sigma Aldrich India. The chemical compounds were used without further purification. In each system nine different solute concentration binary mixtures were prepared by gravimetrically.

2.2. Measurements:

The densities of pure compounds were measured by relative density method using 10 ml specific gravity bottle. The mass measurements were performed using digital electronic balance (Adventurer OhausAR2140) with accuracy of ±0.0001 g. Abbe's refractometer (SIPCON model) with sodium D line was used to measure the refractive indices of mixture solutions at different temperatures. Constant temperature was maintained by water circulating (ESCY IC 201 model) temperature controller system with accuracy of 0.1 K. The square of refractive index value was taken as optical frequency dielectric constant ($n^2 = \varepsilon_\infty$). The uncertainties of measured density and refractive index were±0.2 kg·m−3 and 0.00005, respectively. Frequency dependent complex dielectric spectra of pure compounds and their binary mixtures were determined by (AgilentnfiniiumDCA-J86100 A with sample oscilloscope HP 54754 A model) TDR. A 39 ps rise time step voltage pulse was generated by tunnel diode and fed through 50 Ω impedance semi rigid coaxial cable having pin length 0.135 mm. Coaxial probe was dipped in the sample cell which was shielded by water circulating temperature control system with accuracy of 0.5 K. All measurements were carried out in an open load condition. The variation in step pulse was monitored after it is reflected from air and sample by sample oscilloscope and recorded in time window of 2 ns. The reflected pulses were digitized into 1200 points and used for further data analysis. The frequency dependent complex spectra were obtained from reflection coefficient spectra. The procedures for data analysis were discussed in previous reports [6-8].

III. RESULTS AND DISCUSSION

The values of dielectric constant (ε_0) of pure DEG, BBZ and different volume fraction of DEG in BBZ binary mixtures dielectric constant (ε_{0m}) at four different temperatures were presented in Table 1. To find the uncertainty of measured dielectric values, the pure liquids were experimentally measured more three times and the calculated uncertainty value has been given blow the table 1. The ε_0 value increased with rise of DEG volume concentration. These values have deviated from the linear variation with respect to volume concentration of solute (the plot is not shown here). This nonlinearity of dielectric constant variation attributes that the presents of H-bond interaction in between solute and solvent molecules. The formation of heterogeneous H-bond interaction leads to form complex molecular cluster structures and enhanced electronic polarization in mixtures of entire concentration range of DEG. Similar type of change was observed in most of polar binary mixtures. The temperature dependent ε_0 value for binary mixture systems also carried out for study the H-bond stability. It was observed that the rising of temperature effectively disassociated the H-bond strength and number of H-bond in the mixture solution.

To determine the dipole alignment and strength of hetero H-bond interaction in mixture, we have calculated the excess dielectric constant for binary mixture solution. The excess dielectric constant is also a one of the parameter to evaluate the intermolecular interaction. The calculated excess dielectric constant values for DEG+BBZ binary mixtures were plotted in fig 1. From the fig. 1, it has been seen that the non-zero value for entire concentration of DEG in mixtures, which confirms the formation of H-bond complex and change in H-bond strength of mixture molecular connectivity.
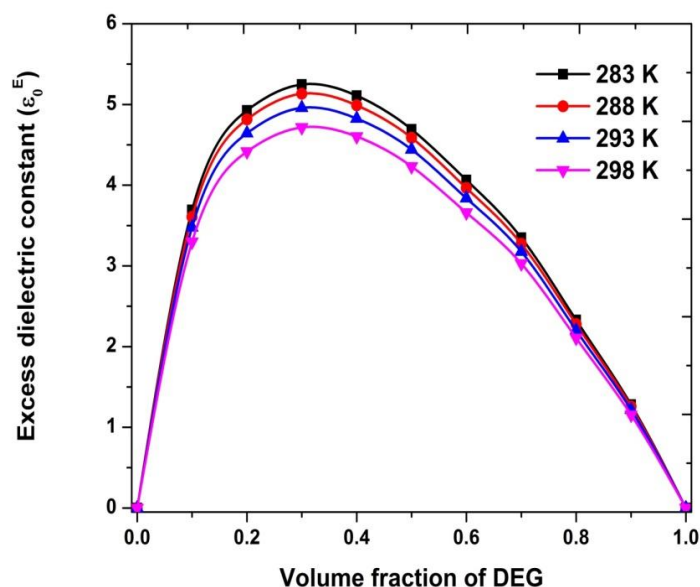

Fig 1: Excess dielectric constant (ε_0^E) versus mole fraction of DEG at different temperatures.

The excess dielectric values are falls in very positive for DEG concentration range, which owing that the mixture complex formed with increase of parallel dipole aliment in mixtures. The maximum magnitude has been falls in the range of 0.3 volume fraction of DEG, which attribute that the stable complex is formed in 1:2 molar ratio in binary mixture. Moreover, it has been seen that as rising of temperature leads to decrease in excess dielectric constant magnitude, this is confirms the decrease of H-bond strength in mixtures with rising of temperature.

The dielectric relaxation time values of DEG+BBZ binary mixture for four different temperatures were reported in Table 1. The DEG has high relaxation time value compare to solute BBZ molecule. Because, involvement of intermolecular interaction between neighboring like molecules, which hinders the molecules alignment in alternative applied field direction. Other hand, BBZ molecule has low relaxation time value as a result; the BBZ molecule rotates very faster. For the binary mixtures, it observes that the dielectric relaxation time is decreasing with increasing of solute concentration in solvent.

Table 1: Excess dielectric constant (ε_0^E) with respect to mole fraction of DEG at different temperatures

Volume Fraction of DEG		ε_0						τ_0	
	283K	288 K	293 K	298 K	283K	288 K	293 K	298 K
0.00	5.15	5.02	4.96	4.88	24.34	21.61	20.19	15.47
0.10	11.67	11.39	11.12	10.75	115.90	87.62	75.91	64.52
0.20	15.73	15.36	14.97	14.44	162.59	122.39	105.76	90.20
0.30	18.88	18.44	17.97	17.31	198.04	148.85	128.51	109.73
0.40	21.57	21.06	20.52	19.77	227.89	171.16	147.71	126.20
0.50	23.98	23.42	22.82	21.97	254.56	191.11	164.87	140.92
0.60	26.18	25.56	24.90	23.97	278.71	209.18	180.43	154.26
0.70	28.29	27.63	26.92	25.91	301.95	226.57	195.4	167.09
0.80	30.10	29.40	28.63	27.56	321.72	241.36	208.14	178.00
0.90	31.88	31.14	30.33	29.18	341.21	255.96	220.71	188.77
1.00	33.43	32.65	31.80	30.60	358.10	268.60	231.60	198.10
	$\varepsilon\infty$							
0.00	2.54023	2.51609	2.48210	2.45169				
0.10	2.49441	2.47250	2.44178	2.41423				
0.20	2.44802	2.42836	2.40096	2.37630				
0.30	2.40242	2.38497	2.36083	2.33902				
0.40	2.35706	2.34182	2.32092	2.30195				
0.50	2.31115	2.29815	2.28052	2.26440				
0.60	2.26519	2.25441	2.24008	2.22682				
0.70	2.21705	2.20861	2.19772	2.18746				
0.80	2.17307	2.16677	2.15902	2.15150				
0.90	2.12697	2.12291	2.11845	2.11380				
1.00	2.08484	2.08282	2.08138	2.07933				

It suggested that the addition of DEG molecule forms solute-solvent association and possible bond formation between DEG molecule of hydroxyl (H-O) and BBZ molecule of carboxyl (O-C) functional groups. Moreover, this increasing trend of relaxation time suggests that the size, shape of complex structures is increasing in binary mixtures [8]. When the temperature increases, the relaxation time distinctly decreases due to the weakening of intermolecular H-bond interaction. As a result, the effective dipole length of molecule increases and absorbs less electromagnetic energy which causes molecules to relax very fast. From Table 1, it can be observed that the relaxation time increases with solute concentration in binary system, which indicates the structural making effect in this system.

The Fig. 2 shows the plot of $(1/\tau)^E$ versus volume fraction of DEG for all four different temperature. From Fig. 2, it can be seen that, the $(1/\tau)^E$ value is positive for low (0.1) DEG concentration and negative for remaining entire TEG volume fraction in binary system. The binary mixture solution with addition of small amount TEG has positive value of $(1/\tau)^E$, which indicates that the solute DEG and solvent BBZ molecular interaction produce a electric field such that the effective dipole rotates faster due to the field which co-operates dipole rotation. Whereas, the remaining entire DEG concentrations have negative value due to formation linear structure through intermolecular H-bonding in mixtures, thus the effective dipoles are rotate slowly.

The g factor is a macroscopic parameter which used for qualitative interpretation the molecular association and dipole orientation. The binary mixture g values for four different temperatures are plotted in fig 3. The g values are more than unite for DEG, it means the dipoles are align in parallel direction than it could be form alfa clusters in pure DEG. Whereas the g value is less than unity for BBZ, which indicates the dipoles align in opposite direction which form beta clusters. From Fig. 4, it can be seen that the binary mixture g values increased nonlinearly from g value of BBZ to DEG when increase of solute concentration, which confirms that dipole interaction takes place between the mixture constituents in solution.
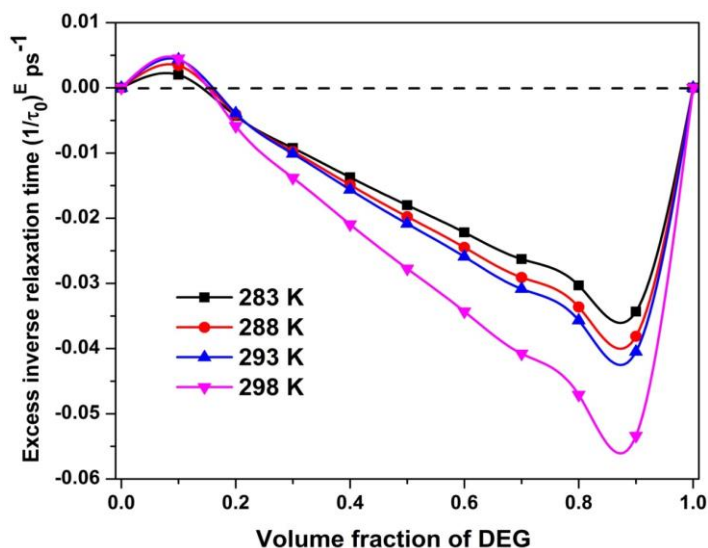

Fig 2: The excess relaxation time $(1/\tau)^E$ versus mole fraction DEG at different temperatures.

The g values are less than unity for low solute concentration due to the large amount of BBZ dipoles are surrounded on solute dipole, thus the solvent-solvent dipoles are aligned in anti-parallel direction. When the DEG concentration increased more than 0.4, the g values become higher than unity, indicating the dominance of parallel dipole structures over the anti-parallel aligned dipole structures, which implies that the strong hydrogen bond interaction in DEG rich region. A similar trend in g value is observed at all studied temperatures. The (g^f) values of DEG+BBZ binary mixture system are plotted in fig.4. From the fig. 4, it has been seen that the g^f values are deviated from unity, this deviation of g^f values from unity indicates the presence of dipole interaction between solute and solvent dipole. The magnitude of deviation is maximum in 0.1-0.2 DEG concentration range, it concludes that the strength of interaction is high in low concentration of DEG.
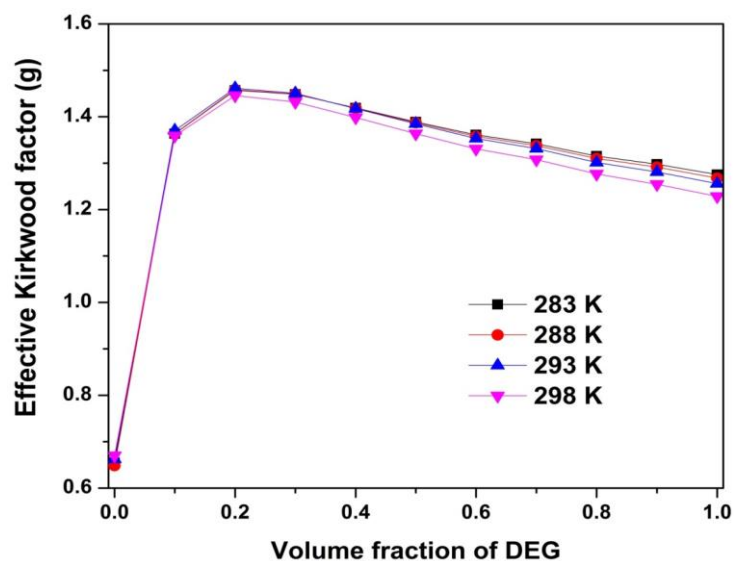

Fig 3: Effective Kirkwood correlation factor for DEG+BBZ binary mixture at different temperatures.

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In the present case, as rising of temperature, the g^f value is being almost same, which indicates that the independents of dipole strength with rising of temperature. The deviation of linear behavior of Bruggeman factor with mole fraction shows hetero interaction in binary mixture solution. The Bruggeman factor for DEG+BBZ binary mixtures is calculated and those values are plotted in fig. 5. From this plot, it can be seen that the values are deviates from linearity, it may be due to hydrogen bonding of the-OH group of DEG with C=O of BBZ. The value of suggest that the effective volume fraction of DEG in BBZ solution is reduced considerably, indicating significant interaction between DEG and BBZ in the mixtures.
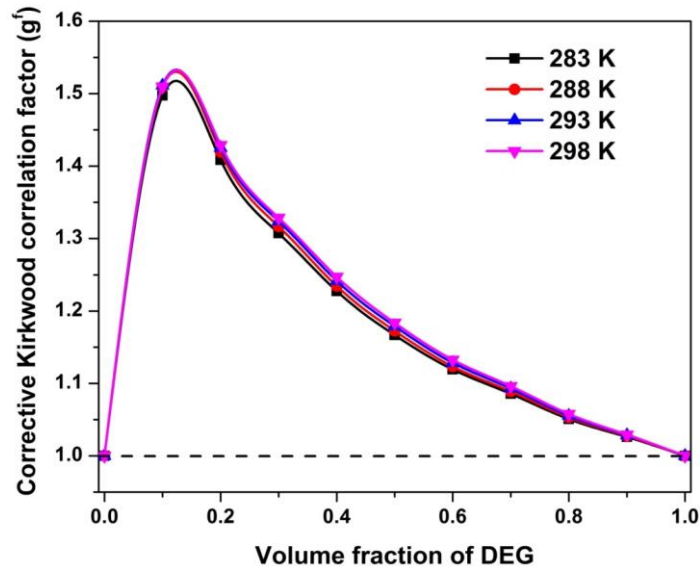

Fig 4: Corrective Kirkwood correlation factor for DEG+BBZ binary mixtures at different temperatures.

The study of excess Helmholtz free energy (ΔF^E) can provide the evidence of involvement of interaction between the long and short range dipole mixture and breaking mechanism of H-bond in binary mixtures [28]. And it can be expressed as follows,

$$\Delta F^E = \Delta F_{0r}^E + \Delta F_{rr}^E + \Delta F_{12}^E \qquad \dots\dots\dots\dots (1)$$

where ΔF_{0r}^E is represents the excess dipolar energy due to long range electrostatic interaction, , ΔF_{rr}^E is represents the excess dipolar energy due to short range interaction between identical molecules, and ΔF_{12}^E is represents the free energy due to short range interaction between dissimilar molecules. The ΔF^E also denotes as follows,
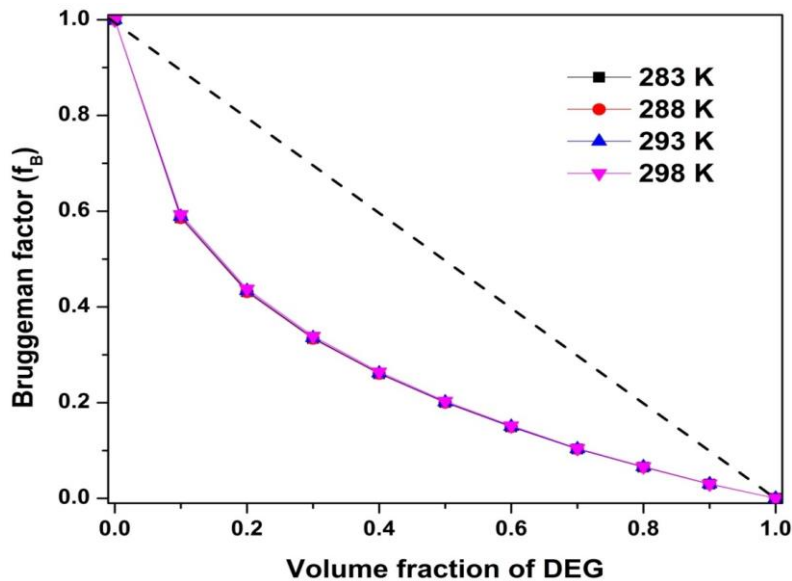

Fig 5: Bruggeman dielectric factor (f_B) versus mole fraction of DEG at different temperatures.

$$\Delta F^E = -\frac{N}{2}\left\{ \begin{array}{l} \left[\sum_{r=1,2} X_r \mu_r^2 (R_{fr} - R_{fr}^0) \right] \\ + \left[\sum_{r=1,2} X_r^2 \mu_r^2 (g_{rr} - 1) \times (R_{fr} - R_{fr}^0) \right] \\ + \left[X_1 X_2 \mu_1 \mu_2 (g_m - 1) \times (R_{f_1} + R_{f_2} - R_{f_1}^0 - R_{f_2}^0) \right] \end{array} \right\} \qquad \ldots\ldots\ldots\ldots (2)$$

where $R_{fr}^0 = \left(\dfrac{8\pi N}{9V_r} \right) \dfrac{(\varepsilon_r - 1)(\varepsilon_{\infty r} + 2)}{(2\varepsilon_r + \varepsilon_{\infty r})}$, $R_{fr} = \left(\dfrac{8\pi N}{9V_r} \right) \dfrac{(\varepsilon_m - 1)(\varepsilon_{\infty r} + 2)}{(2\varepsilon_m + \varepsilon_{\infty r})}$

where R^0_{fr} - reaction field parameter of pure liquids,

R_{fr} - reaction field parameter of mixtures,

V_r - molar volume of compounds and g is mutual correlation factor of solutions.

Table 2: Bruggeman dielectric factor (f_B) versus with respect to mole fraction of DEG at different temperatures

DEG	ΔF^E	ΔF_{0r}^E	ΔF_{rr}^E	ΔF_{12}^E		ΔF^E	ΔF_{0r}^E	ΔF_{rr}^E	ΔF_{12}^E
		T=283 K					T=288 K		
0.00	0.00	0.00	0.00	0.00		0.00	0.00	0.00	0.00
0.10	-127.46	-262.34	133.78	1.10		-130.77	-268.53	137.32	0.44
0.20	-166.27	-267.13	136.91	-36.05		-171.67	-274.37	140.13	-37.43
0.30	-189.32	-240.64	122.32	-71.00		-195.78	-247.84	124.71	-72.65
0.40	-196.58	-207.08	103.02	-92.52		-202.77	-213.49	104.54	-93.82
0.50	-190.50	-172.26	82.66	-100.91		-196.54	-178.04	83.41	-101.91
0.60	-172.35	-137.41	62.77	-97.71		-177.03	-141.97	62.94	-98.01
0.70	-147.60	-105.11	43.74	-86.22		-151.49	-108.81	43.50	-86.18
0.80	-105.23	-68.98	27.13	-63.38		-107.89	-71.57	26.71	-63.03
0.90	-58.80	-35.89	12.05	-34.96		-60.07	-37.21	11.71	-34.57
1.00	0.00	0.00	0.00	0.00		0.00	0.00	0.00	0.00
		T=293 K					T=298 K		
0.00	0.00	0.00	0.00	0.00		0.00	0.00	0.00	0.00
0.10	-127.91	-258.86	129.59	1.36		-121.01	-247.60	124.16	2.44
0.20	-167.33	-264.23	132.79	-35.89		-158.02	-252.91	127.54	-32.66
0.30	-190.91	-238.56	118.52	-70.88		-179.64	-227.66	113.76	-65.74
0.40	-197.35	-205.19	99.61	-91.77		-186.06	-195.83	95.40	-85.63
0.50	-190.93	-171.01	79.67	-99.59		-179.08	-162.66	76.06	-92.47
0.60	-171.22	-136.14	60.29	-95.37		-160.12	-129.34	57.30	-88.08
0.70	-146.30	-104.56	41.76	-83.51		-136.49	-99.40	39.50	-76.58
0.80	-103.09	-68.35	25.79	-60.53		-95.89	-65.04	24.18	-55.03
0.90	-57.38	-35.73	11.34	-32.99		-52.77	-33.76	10.61	-29.60
1.00	0.000	0.00	0.00	0.00		0.00	0.00	0.00	0.000

The long range and short range dipole-dipole interaction information such as ΔF_{or}^E, ΔF_{rr}^E and free energy ΔF^E values of binary mixture at different temperatures were given in Table 2.

The negative value of ΔF_{0r}^E is indicated that the repulsive force of interaction exists in between unlike long range dipoles. For all studied temperatures range, the ΔF_{0r}^E values were negative for entire concentration of DEG and which decreased with rising of temperatures, confirms that the existence of long range repulsive dipole-dipole interaction decreased as increase of temperature. The maximum value was found in middle of DEG concentration for all studied temperature range and those values were decreased with rising of temperature in binary mixture system. These changes suggest that the long range dipole interaction depends on the DEG concentration and temperature.

The (ΔF_{rr}^{E}) values are positive for binary mixture of entire DEG concentration range at different temperature. The positive values are suggested that the strength of short range dipole interaction increased as increase of DEG concentration. The ΔF_{12}^{E} values negative for entire DEG concentration and temperature. This change suggests that the short range force between unlike heterogeneous interaction in mixture.

The ΔF^{E} values are negative for entire concentration of DEG at different temperatures which indicates that the formation β-cluster with anti-parallel dipole alignment and destruction of angular correlation between dislike molecules and decrease of internal energy. The high negative values of ΔF^{E}, in case of DEG+BBZ system at middle concentration indicate the formation of β-cluster is high in middle range. At this state the molecules attain an ordered state and dipoles are aligned in a head to tail arrangements, thus spontaneous polarization becomes maximum, as the temperature increases, the spontaneous polarization increase, so ΔF^{E} values of mixing increases in binary systems.
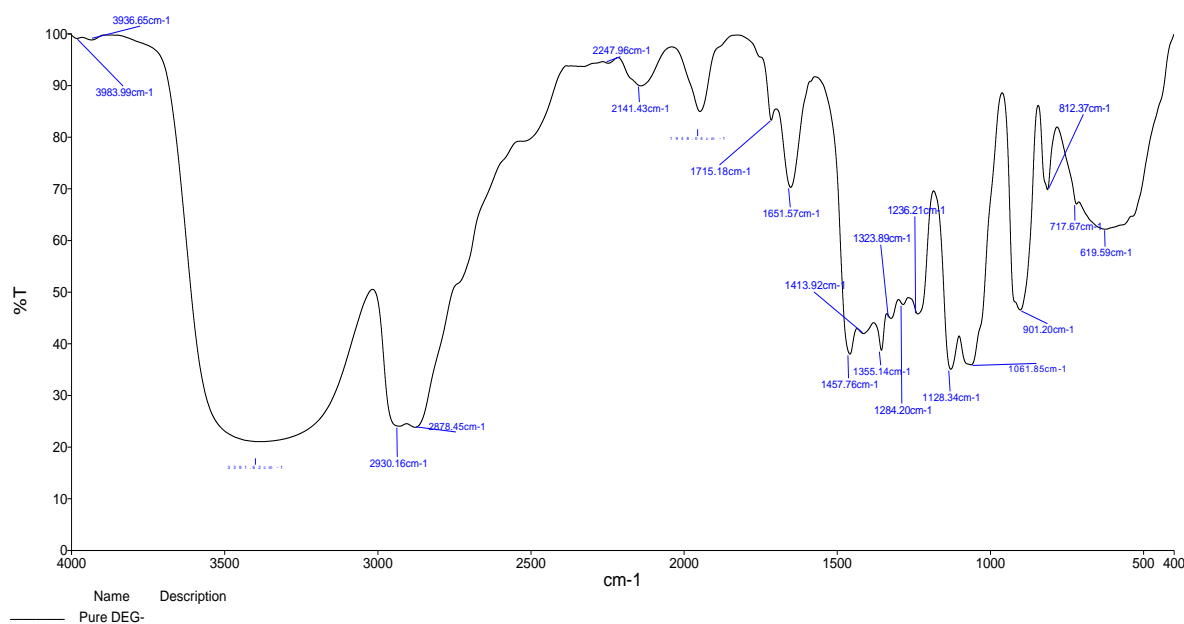

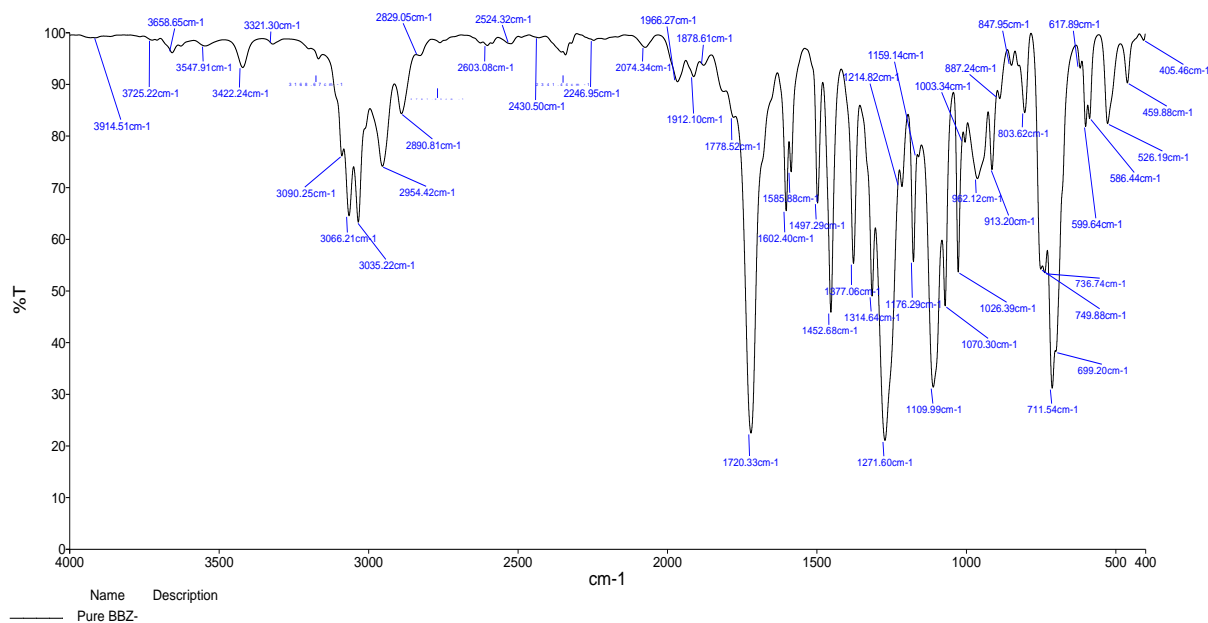**Fig 5a: FTIR spectrum of pure DEG at room temperature**

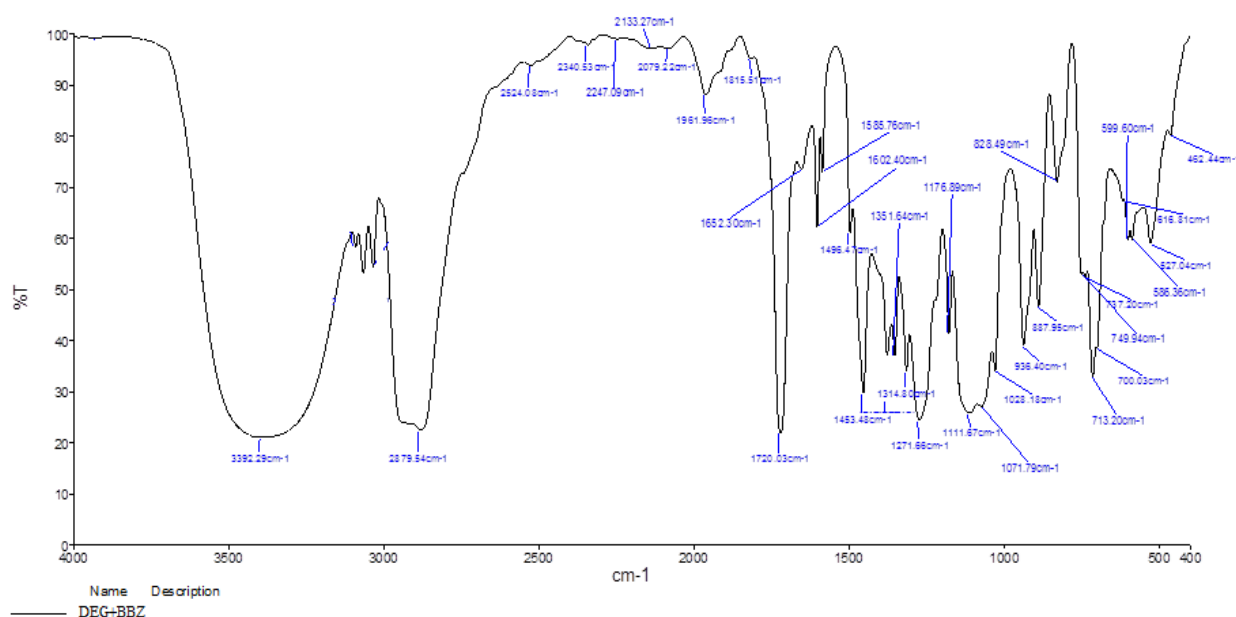**Fig 5b: FTIR spectrum of pure BBZ at room temperature.**

Fig 5c: FTIR spectrum of equi-molar binary mixture of DEG+BBZ at room temperature.

The molecule functional group vibrations of pure solute, solvent and binary mixtures are studied by using of FT-IR method. The experimental analyzed FT-IR spectra are as showed in Fig.8 a,b,c. From fig. 8a, the DEG molecule hydroxyl (O-H) symmetric stretching vibration is appeared in the range of 3800-3900 cm^{-1} and , the sharp vibration peck appear around 2900 cm^{-1}, which is due C-H vibration of DEG molecule. In fig.8b, the symmetric vibration mode is appears in 1700 cm^{-1} which is due BBZ molecule carboxyl functional group. From fig. 8c, it has been clearly observed that the considerable shift in hydroxyl, carboxyl functional group and intensity of vibrations in equi-molar binary mixtures. The shift hydroxyl and carboxyl group strongly suggests that the H-band connection take place between DEG molecule and BBZ molecule in mixtures. Moreover, the two functional group blue and red shift is indicates that the hydrogen bonding formed between oxygen atom of BBZ and hydrogen atom of DEG in binary mixture solutions.

IV.   CONCLUSIONS

The formation of heterogeneous complex structure between DEG and BBZ were confirmed by studying their dielectric parameters of pure and binary mixtures in entire concentration. The non-linear variation of dielectric parameters were confirms the complex structure in mixtures. The mixture dipoles are aligned in parallel direction and addition of DEG molecules is effectively formed cluster structures, this result was confirmed by positive excess permittivity analysis. Stable complex structure was formed in 2:1 solute solvent concentration regions. Excess Helmholtz free energy values were positive for binary mixtures which indicate β-cluster structure formed in DEG+BBZ mixtures. The mixture FT-IR spectra analyze was also supported the H-bond interactions between solute-solvent molecular functional group.

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