

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

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ABSTRACT: Dielectric relaxation studies of Butyl acetate(BA) with 2-methoxyethanol(2-ME), 2-ethoxyethanol (2-EE), 2-butoxyethanol(2-BE) have been carried out for various volume fractions of Butyl acetate. The experiment was carried out by using Time domain Reflectometry(TDR) Technique over the wide range of frequencies from 10MHz to 20GHz at 308.15K. Dielectric permittivity(ϵ'), dielectric loss(ϵ'') and relaxation time(τ) were measured from the TDR instrument. From the above data the molecular interaction parameters such as Bruggeman factor(f_B), effective and corrective Kirkwood correlation factors(g_r^{eff} , g_f), Excess parameters like excess dielectric constant(ϵ^E), excess inverse relaxation time $(1/\tau)^E$ and the thermodynamic parameter, excess Helmholtz free energy of activation (ΔF^E), were also calculated and the results were discussed on the basis of the nature of molecular interactions. Further the hydrogen bonding interaction between Butyl acetate with 2-Alkoxyethanols are confirmed by FT-IR spectra.

Keywords: Dielectric permittivity, Dielectric loss, Relaxation time, Butyl acetate, 2-Alkoxyethanols, Time Domain Reflectometry, FT-IR.

1. INTRODUCTION

The importance of measuring the dielectric constant of a liquid consists in the fact that it provides valuable information about ordering of the molecules in the liquid state. Dielectric relaxation in solute-solvent mixtures gives information about the molecular interaction in the system. In the study of dielectric relaxation, the Kirkwood correlation factors of binary mixtures have considerable significance in providing valuable information about solute-solvent interaction [1]. Dielectric relaxation in esters has been reported by Saxena [2] and ester-benzene solutions has been studied by Krishnaji et al [3].

Renewable fuels and bio based fuel additives are gaining more and more attention due to their ability to cut down greenhouse gas emissions. Butyl acetate is currently considered among promising substance for bio based fuel additives. It has a good potential for improving biodiesel properties because of its very low freezing point (199.65K) and a high flash point (295K) [4 – 7]. Alkoxyethanols are used as a solvent for many purposes such as varnishes, dyes, and resins. 2-Alkoxyethanols are very interesting class of solvent have ether. Since it has both accepting and donating ability. They are aliphatic in nature [8 – 11].

This work reports a dielectric relaxation study of butyl acetate with 2-methoxyethanol, 2-ethoxyethanol and 2-butoxyethanol for different volume percentages at 308.15K. Time domain reflectometry in reflection mode is used to obtain the dielectric quantities: *viz.*, dielectric permittivity(ϵ'), dielectric loss(ϵ'') and relaxation time(τ) were measured from the TDR measurements. From the above data the molecular interaction parameters such as Bruggeman factor(f_B), effective and corrective Kirkwood correlation factors(g_r^{eff} , g_f), excess dielectric constant(ϵ^E), excess inverse relaxation time $(1/\tau)^E$ and the thermodynamic parameter like excess Helmholtz free energy of activation (ΔF^E) were calculated and the results are obtained.

2. MATERIALS

The Chemicals utilized for this work were Butyl acetate (BA), 2-methoxyethanol (2-ME), 2-ethoxyethanol (2-EE), 2-butoxyethanol (2-BE) supplied by Loba chemicals (purity >> 99%) of AR-grade and were used without further purification. The purity of chemicals were tested by comparing their densities and refractive indices of literature values. The digital electronic balance (Adventurer Ohaus AR2140) was used for the mass measurement with an accuracy of $\pm 0.0001\text{g}$.

2.1 METHODS

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

The densities of the pure compounds were determined by using a DMA 4500 M (Anton Paar) vibrating-tube digital densitometer. The sample cell was calibrated with air and double distilled water before measurements. The accuracy of the measured density and refractive index were $\pm 1 \times 10^{-2}$ kg.m⁻³ and $\pm 1 \times 10^{-5}$, respectively.

The complex dielectric spectra were measured using Time Domain Reflectometer (Agilent infinium DCA-J 86100A with sample oscilloscope HP 54754A). A repetitive fast rising time step voltage pulse of 39 picoseconds (ps) was fed through a 50 Ω impedance semi-rigid slim probe having the pin length of 0.14 mm. Reflected pulse without sample $R_1(t)$ and with sample $R_x(t)$ were recorded in a 2 ns time window and digitized into 1200 points. The frequency dependent complex spectra were obtained from reflection coefficient spectra. The detailed TDR data analysis procedure was reported previously [12, 13]. The sample cell was kept in the constant temperature water bath.

3. RESULTS

The experimentally measured values of densities (ρ) and refractive indices (n_D) of pure Butyl acetate (BA) and 2-Alkoxyethanol liquids at 308.15K were given in Table 1 along with literature values. The complex permittivity spectra $\epsilon^*(\omega)$ of BA with 2-Alkoxyethanols were recorded with the help of Time domain reflectometry instrument in the frequency range of 10 MHz to 20 GHz. The complex permittivity $\epsilon^*(\omega)$ values are fitted with Debye equation and the dielectric quantities were derived. The static dielectric constant (ϵ_0) and relaxation time (τ) values of pure liquids are listed in Table 2 along with their literature values.

Table 1: Experimental Densities (ρ) and Refractive Indices (n_D) values of pure liquids with literature values at 308.15K

Properties	Liquids							
	Butyl acetate		2-methoxyethanol		2-ethoxyethanol		2-butoxyethanol	
	Exp.	Lit.	Exp.	Lit.	Exp.	Lit.	Exp.	Lit.
ρ (g·cm ⁻³)	0.8654	0.8654 ¹⁴	0.9510	0.9510 ¹⁵	0.9160	0.9160 ¹⁷	0.8870	0.8889 ¹⁸
n_D	1.3880	1.3882 ¹⁴	1.3960	1.3949 ¹⁶	1.4020	1.4017 ¹⁸	1.4130	1.4132 ¹⁸

Dielectric constant (ϵ_0) and relaxation time (τ) values of pure liquids at 308.15K

Liquids	ϵ_0		τ (ps)	
	Experimental	Literature	Experimental	Literature
Butyl acetate	4.56	4.65 ¹⁹	6.52	5.01 (293.15K) ²⁰
2-Methoxy ethanol	16.06	15.82 ²¹	29.20	25.85 ²¹
2-Ethoxy ethanol	15.46	15.8 (313.15K) ²²	36.46	36.6 (313.15K) ²²
2-Butoxy ethanol	9.21	8.39 ²³	51.93	47.78 (298.15K) ²⁴

Table 3: Values of static dielectric constant (ϵ_0), dielectric constant at an optical frequency (ϵ_∞), relaxation time (τ) and activation energy for relaxation time (ΔF_τ) with volume fraction of Butyl acetate (ϕ_2) + 2-Alkoxyethanols

ϕ_2	ϵ_0	ϵ_∞	τ ps	ΔF_τ (KJ/mol)
System-I: Butyl acetate + 2-methoxyethanol				
0	16.06	1.9488	29.20	125.5138
0.25	13.31	1.9572	27.94	125.4008
0.50	9.03	1.9516	15.60	123.9074
0.75	6.53	1.9474	11.90	123.2137
1.0	4.56	1.9279	6.52	121.6719
System-II Butyl acetate + 2-ethoxyethanol				
0	15.46	1.9656	36.46	126.0828
0.25	10.45	1.9712	28.69	125.4687

0.50	8.78	1.9642	19.53	124.4832
0.75	7.05	1.9586	10.35	122.8561
1.0	4.56	1.9279	6.52	121.6719
System-III: Butyl acetate + 2-butoxyethanol				
0	9.21	1.9966	51.93	127.2692
0.25	7.27	1.9952	30.52	125.6271
0.50	6.72	1.9867	24.34	125.0473
0.75	5.15	1.9754	24.77	125.0922
1.0	4.56	1.9279	6.52	121.6719

The dielectric quantities like static dielectric constant (ϵ_0), dielectric constant at high frequency (ϵ_∞) and relaxation time (τ) and activation energy for relaxation time (ΔF_τ) were obtained for binary mixtures of different volume percentages (0, 25, 50, 75 and 100 vol.%) of BA with 2-Alkoxyethanols (2-methoxyethanol, 2-ethoxyethanol and 2-butoxyethanol) using time domain reflectometry and were reported in Table 3.

The static dielectric constant (ϵ_0), static permittivity at high frequency (ϵ_∞) and relaxation time (τ) were obtained by using the non-linear least-square fit method [25]. The general form of the relaxation model is given by Havriliak–Negami equation [26]

$$\epsilon^*(\omega) = \epsilon_\infty + \frac{(\epsilon_0 - \epsilon_\infty)}{[1 + (j\omega\tau)^{(1-\alpha)}]^\beta} \dots\dots\dots(1)$$

where $\epsilon^*(\omega)$ is the complex reflection coefficient, α and β are empirical parameters for the distribution of relaxation times with values between 0 and 1. The Havriliak–Negami equation includes three relaxation modes as limiting forms. The Debye mode ($\alpha = 0$ and $\beta = 1$) implies a single relaxation time while Cole–Cole ($\alpha = 1$ and $\beta = 1$) and Cole Davidson ($\alpha = 0$ and $\beta = 1$) both suggest a distribution of relaxation times. But the polar–polar binary mixtures volume percentage of all concentration of Ethyl acetate with alcohols could fit Debye type dispersion. Hence, here ($\alpha = 0$ and $\beta = 1$) and experimental values of $\epsilon^*(\omega)$ were fitted to the Debye equation as,

Table 4: Values of kirkood correlation factors (g^{eff} , g_r), Bruggeman factor (f_B), Excess dielectric constant (ϵ^E) and excess inverse relaxation time ($1/\tau$)^E with volume fraction of Butyl acetate (ϕ_2) + 2-Alkoxyethanols

ϕ_2	g^{eff}	g_r	f_B	ϵ^E	$(1/\tau)^E$ ps
System-I: Butyl acetate + 2-methoxyethanol					
0	1.7964	1.0000	1.0000	0.0000	0.0000
0.25	1.6658	1.0087	0.8100	0.1114	-0.0282
0.50	1.2555	0.8612	0.4709	-1.2932	-0.0297
0.75	1.0150	0.8556	0.2312	0.9193	-0.0396
1.0	0.7774	1.0000	0.0000	0.0000	0.0000
System-II Butyl acetate + 2-ethoxyethanol					
0	2.1000	1.0000	1.0000	0.0000	0.0000
0.25	1.4993	0.7992	0.6157	-2.3000	-0.0241
0.50	1.3770	0.8617	0.4675	-1.2474	-0.0392
0.75	1.2013	0.9658	0.2968	-0.2563	-0.0253
1.0	0.7774	1.0000	0.0000	0.0000	0.0000
System-III: Butyl acetate + 2-butoxyethanol					
0	1.5633	1.0000	1.0000	0.0000	0.0000
0.25	1.2342	0.8800	0.6306	-0.7932	-0.0200
0.50	1.1834	0.9667	0.5160	-0.1894	-0.0445
0.75	0.8763	0.8546	0.1540	-0.6028	-0.0795
1.0	0.8026	1.0000	0.0000	0.0000	0.0000

Table 5: Values of excess Helmholtz free energy (ΔF^E) and its components with volume fraction of Butyl acetate (ϕ_2) + 2-Alkoxyethanols

ϕ_2	ΔF_{0r}^E J/mol	ΔF_{rr}^E J/mol	ΔF_{12}^E J/mol	ΔF^E J/mol
System-I: Butyl acetate + 2-methoxyethanol				
0	0.0000	0.0000	0.0000	0.0000
0.25	-55.2791	62.1273	-65.9063	-59.0581

0.50	7.4372	111.3023	-4.0565	114.6830
0.75	11.3958	70.8917	1.2740	83.5615
1.0	0.0000	0.0000	0.0000	0.0000
System-II Butyl acetate + 2-ethoxyethanol				
0	0.0000	0.0000	0.0000	0.0000
0.25	52.2770	151.1544	-30.3396	173.0917
0.50	-23.7954	123.0749	-11.1330	88.1466
0.75	-82.2499	75.3064	7.0072	0.0636
1.0	0.0000	0.0000	0.0000	0.0000
System-III: Butyl acetate + 2-butoxyethanol				
0	0.0000	0.0000	0.0000	0.0000
0.25	37.1167	51.4407	-8.8618	79.6956
0.50	-25.9676	41.9289	-4.6733	11.2880
0.75	39.2582	24.7879	-6.5392	57.5069
1.0	0.0000	0.0000	0.0000	0.0000

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

The values of (ε_0), (τ) and (ε_{∞}) are the fitting parameters. The parameters like effective Kirkwood correlation factor (g^{eff}), corrective Kirkwood correlation factor (g_f), Bruggeman factor (f_B), excess dielectric constant (ε^E) and excess inverse relaxation time ($1/\tau$)^E values of BA with 2-Alkoxyethanol binary mixtures were reported in Table 4. The excess Helmholtz free energy values were also calculated and reported in Table 5 with the volume fractions of Butyl acetate.

4. DISCUSSION

The polar – polar binary liquid systems taken for the study of molecular interactions here are

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

4.1 Static dielectric constant (ε_0)

The static dielectric constant values of Butyl acetate (BA) is 4.56, 2-methoxyethanol (2-ME) is 16.06, 2-ethoxyethanol (2-EE) is 15.46 and 2-butoxyethanol (2-BE) is 9.21. In the case of BA with 2-ME, 2-EE and 2-BE systems, as the volume percent of BA increases the static dielectric constant (ε_0) values starts decreases from the 2-Alkoxyethanols values and approaching towards the Butyl acetate value.

4.2 Dielectric constant at an optical frequency (ε_{∞})

As the volume percent of the Butyl acetate molecule increases, the dielectric constant at an optical frequency (ε_{∞}) values gets increases at the initial concentration and then decreases at higher concentration of Butyl acetate (BA) with 2-ME, 2-EE systems. Whereas it decreases gradually in the 2-BE systems.

4.3 Relaxation time (τ)

The relaxation time depends on the nature of participating functional groups and volume of molecule. Functional groups are those able to form the hydrogen bonding which have a strong influence on relaxation times. In the pure state the experimental relaxation time values of Butyl acetate is 6.52 ps, 2-methoxyethanol (2-ME) is 29.20 ps, 2-ethoxyethanol(2-EE) is 36.46 ps and 2-butoxyethanol(2-BE) is 51.93 ps at 308.15 K. The 2-methoxyethanol relaxation time is low when compared to 2-ethoxyethanol and 2-butoxyethanol. The relaxation time value is high for 2-butoxyethanol due to the higher chain length of alkyl group.

Alcohols play a vital role in the structural dynamics and relaxation mechanism of the individual components. This is due to the formation of intramolecular hydrogen bonding between one alcohol molecule and another alcohol molecule (R–O–H···OH–R) and leads to the formation of self associated groups. There is an increment in the number of self associated groups which causes the alcohol molecule to absorb more electromagnetic energy. Due to this, molecule rotate slowly leading to higher relaxation times. Further, it is observed that the relaxation times of pure 2-BE is greater than that of pure 2-ME, 2-EE due to larger effective radius of the rotating unit [27].

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

The dielectric parameters like the static dielectric constant (ϵ_0), dielectric constant at an optical frequency (ϵ_∞) and relaxation time (τ) values calculated are found to be non linear behaviour and can be attributed to the appearance of aggregates in solutions.

4.4 Free energy of activation for relaxation time (ΔF_τ)

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

The study of thermodynamic properties like free energy of activation for dielectric relaxation (ΔF_τ) for polar liquids may be useful in accordance with the states of dipoles under the influence of applied field. The measurement of free energy of activation for dielectric relaxation (ΔF_τ) is calculated for all the systems studied. It is clear from the data that the dielectric relaxation time (ΔF_τ) involves rotational motion only and not due to translational motion, which is pertaining to the free energy of activation for viscous flow (ΔF_η). The values are given in the Table 3.

4.5 Effective Kirkwood correlation factor (g^{eff})

The structural information about the molecules of the liquids by dielectric relaxation can be obtained by Kirkwood correlation factor 'g' [28]. The Kirkwood correlation factor provides useful information regarding the orientation of dipoles in polar liquids. The 'g' factor for the pure liquid may be obtained from the expression,

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

Modified forms of this equation have been used to study the orientation of electric dipoles in binary mixture of Butyl acetate with 2–Alkoxyethanols. Equation (4) is modified and called as (g^{eff}) the effective Kirkwood correlation factor [29],

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

The effective Kirkwood correlation factor (g^{eff}) is calculated by using equation (5) and is given in Table 4. If the g^{eff} values are greater than unity, which indicates the parallel orientation of dipoles and if less than unity, it indicates the anti-parallel orientation of dipoles. In the pure state the g^{eff} values of 2–methoxyethanol is (1.7964), 2–ethoxyethanol is (2.1000) and 2–butoxyethanol is (1.5633) which are greater than unity. It means parallel orientation of electric dipoles take place. The g^{eff} values calculated for pure Butyl acetate is less than unity, indicating anti-parallel orientation of dipoles or no dipole correlation of electric dipoles. As the volume percentage of Butyl acetate increases, the g^{eff} values gets decreases from the 2–Alkoxyethanol values and approaching towards the Butyl acetate values for all the systems studied.

4.6 Corrective Kirkwood correlation factor (g_f)

The structural information on the interacting species is obtained by another correlation factor named as corrective Kirkwood correlation factor (g_f). It is a dielectric parameter which supplies essential information regarding interaction of the participating molecules in the mixture. For an ideal mixture, (g_f) must be unity and the deviation of (g_f) from unity indicates the magnitude of interaction between the liquids i.e., If there is a greater deviation from unity means a larger the strength of interactions between molecules of the liquids [30]. The corrective Kirkwood correlation factor (g_f) was calculated by using equation (6) and was given in Table (4)

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

If (g_f) values will remain close to unity then there is no interaction between the molecules. In the present study, the values of (g_f) are close to unity for BA+2–ME and BA+2–BE system. But (g_f) values are found to be deviate slightly more from unity for BA + 2–EE system. This indicates that effective dipoles in the mixture are greater than the average of those in the pure

compounds. The values of (ϵ_f) are found to depend more on concentration than the temperature, as reported by Balamurugan et al., [31].

4.7 Bruggeman factor (f_B)

The information about the polar-polar interaction is given by the Bruggeman factor (f_B). The effective volume of the solute gets modified by solute – solute interactions and is best illustrated by the non – linearity of the Bruggeman formula [32].

$$f_B = \left(\frac{(\epsilon_{0m} - \epsilon_{02})}{(\epsilon_{01} - \epsilon_{02})} \right) \left(\frac{\epsilon_{01}}{\epsilon_{0m}} \right)^{1/3} = (1 - \phi_2) \dots \dots \dots (7)$$

According to equation (7), a non linear relationship is expected between f_B and Volume fraction of Butyl acetate which are calculated and is given in Table 4.

The non linear relation of (f_B) of Butyl acetate with 2-ME, 2-EE and 2-BE suggest that there is an intermolecular interaction between the mixed components. A graph is drawn between Bruggeman factor (f_B) and volume fraction (ϕ_2) of Butyl acetate which is shown in Fig. 1.

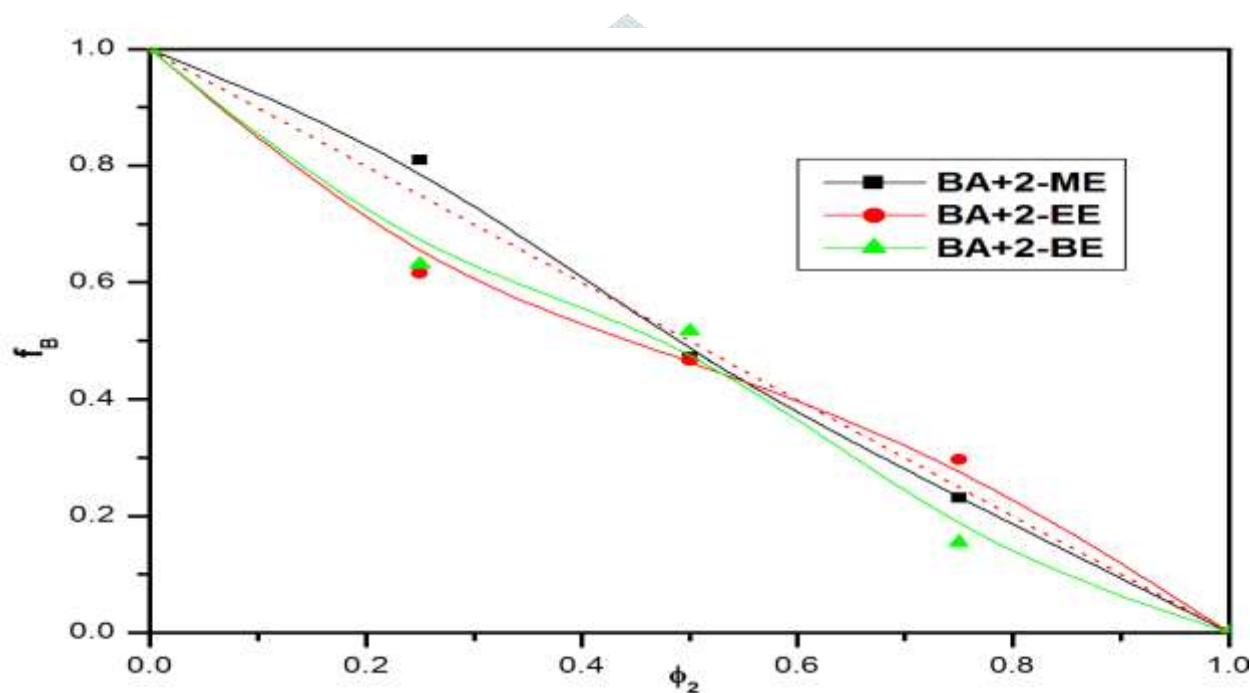


Fig. 1: Bruggeman factor (f_B) vs. volume fraction of Butyl acetate (ϕ_2)

In our studied systems, it is observed that there are deviations from the ideal linearity of Bruggeman line (dotted line). It means that there exists some sort of interactions prevailing among the participating liquids. The non linearity of the (f_B) behavior indicates that the hetero interaction takes place in between the molecules of the participating liquids. Which may be due to hydrogen bonding of the –OH group of alcohol with C=O group of Ester [31 – 33].

4.8 Excess dielectric constant (ϵ^E)

The excess permittivity is defined as [34],

$$\epsilon^E = (\epsilon_0 - \epsilon_\infty)_m - \{(\epsilon_0 - \epsilon_\infty)_1 \phi_1 + (\epsilon_0 - \epsilon_\infty)_2 \phi_2\} \dots \dots \dots (8)$$

Where ϕ_1 and ϕ_2 represents the volume fraction of liquid 1(2-Alkoxyethanols) and liquid 2 (Butyl acetate) respectively.

In an ideal mixture of polar liquids if the molecules are interacting, a non linear variation in dielectric constant and relaxation time occurs. This confirms that the intermolecular association is taking place in the system. Similarly a non linear variation in excess dielectric constant (ϵ^E) occurs confirms that there exists some sort of inter molecular interactions between the molecules of the liquids and are given in the table (4).

In the present study excess dielectric constant (ϵ^E) value are negative for all the systems selected (i.e) Butyl acetate with 2-EE and 2-BE systems and only one negative value for Butyl acetate with 2-ME system. As told above the positive values of (ϵ^E) indicates that the effective dipole moment is increased for lower and higher concentration. The negative value of (ϵ^E) indicates that molecules of the mixtures may form closed multimers structures via hydrogen bonding in such a way that the effective dipoles gets reduced. The excess property related to

static dielectric constant and relaxation time provides significant information regarding interaction between the polar-polar liquid mixtures [35, 36].

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

The excess inverse relaxation time is defined as,

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

where $(1/\tau)^E$ is excess inverse relaxation time which represents the average broadening of dielectric spectra. The inverse relaxation time analogy is taken from spectral line broadening in the resonant spectroscopy [37].

The excess inverse relaxation time $(1/\tau)^E$ is calculated for Butyl acetate with 2-Alkoxyethanols systems and shown in Table 4. From the data it reveals that all the $(1/\tau)^E$ values are negative. It means that the interaction between liquid 1 and liquid 2 produces a field such that the effective dipoles rotate slowly due to the formation of H – bonded structures [30, 31].

4.10 Excess Helmholtz free energy (ΔF^E)

The study of Excess Helmholtz free energy can also give information on the interaction between the components in the mixture through the breaking mechanism of the H-bonds. The excess free energy due to mixing is given as [36];

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

where, (ΔF_{0r}^E) represents the excess dipolar energy due to long range electrostatic interaction between similar molecules [38]. (ΔF_{rr}^E) represents the excess dipolar energy due to short range interaction between similar molecules and (ΔF_{12}^E) represents the excess free energy due to short range interaction between dissimilar molecules. The above terms are given in detail in equation (11):

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

$$+ \left[X_1 X_2 \mu_1 \mu_2 (g_{12} - 1)(R_{f1} + R_{f2} - R_{f1}^0 - R_{f2}^0) \right]$$

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

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

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

The long range and short range interaction between dipoles can be studied from the thermodynamic parameter, (i.e) excess Helmholtz free energy (ΔF^E) . The different components of ΔF^E such as ΔF_{0r}^E , ΔF_{rr}^E and ΔF_{12}^E are given in Table 5.

In the present study, ΔF_{0r}^E values are majoritively positive and at a single volume percentage of Butyl acetate it has negative value. From this it is inferred that positive values of ΔF_{0r}^E indicates the existence of attractive forces and negative values of ΔF_{0r}^E indicates the repulsive forces between the dipoles.

The second term (ΔF_{rr}^E) gives the excess free energy due to short range interaction between the like molecules. (i.e) (ΔF_{rr}^E) indicates rupture of H – bonds between the acid (ester) molecules formed by short range interaction. The positive values of (ΔF_{rr}^E) indicates the strong short range interaction through H-bonding. The (ΔF_{rr}^E) values gradually increases first and attains maximum at equimolar concentrations and then gradually decreases in Butyl Acetate + 2-methoxyethanol system. Whereas in the remaining two system, the maximum (ΔF_{rr}^E) values occurs at 25% volume fraction of Butyl acetate.

(ΔF_{12}^E) represents excess free energy due to short range of interaction between dissimilar molecules. In our studied systems, two systems (i.e) BA+2-ME and BA+2-EE have both positive and negative values. Which indicate the hetro interaction between the compounds. BA+2-BE system has negative values of (ΔF_{12}^E) .

The excess Helmholtz free energy values are completely positive for BA+ 2-EE and BA+2-BE systems. Whereas it is found to be positive and negative for BA+2-ME system. Which indicates the formation of β -clusters to α -clusters (i.e) anti-parallel to parallel alignment of dipoles takes place [30, 39]. From the results of the studied systems, intermolecular interaction depends on the molecular size, volume and the functional group.

5. FTIR STUDIES

The FT-IR spectroscopic studies have been carried out on the binary solutions of Butyl acetate with 2-Alkoxyethanols namely 2-methoxyethanol, 2-ethoxyethanol and 2-butoxy ethanol and is shown in Fig. 2. The FT-IR spectra of pure BA, 2-Alkoxyethanols and their equimolar binary mixtures wave number, corresponding to various vibrational modes have been listed in Table 6. In our study, the O-H stretching vibrations appear at 3411 cm^{-1} for 2-methoxyethanol, 3421 cm^{-1} for 2-ethoxyethanol and 3421 cm^{-1} for 2-butoxyethanol. FT-IR spectrum considered at room temperature and equimolar concentration, the resultant absorption bands of Butyl acetate + 2-ME at 3429 cm^{-1} , Butyl acetate + 2-EE at 3432 cm^{-1} and Butyl acetate + 2-BE at 3442 cm^{-1} , this frequency shift which indicates formation of weak inter-molecular interactions the participating molecules.

Generally, the carbon-oxygen double bond is formed by $P\pi-P\pi$ bonding between carbon and oxygen atoms. Carbonyl ($C=O$) group stretching vibration is expected to occur in the region $1680-1715\text{ cm}^{-1}$ [40]. In our case, the $C=O$ vibrations appeared at 1762 cm^{-1} in pure butyl acetate, similarly at 1740 cm^{-1} in BA+2-ME system, 1742 cm^{-1} in BA+2-EE and 1743 cm^{-1} in BA+2-BE systems respectively. We also observed that the O-H and $C=O$ shifted to the higher frequency with increase in mole fraction of Butyl acetate in 2-Alkoxyethanols. From this study it has been found that there are possibilities for hydrogen bond formation between hydrogen in hydroxyl group of 2-Alkoxyethanols and oxygen in carbonyl group of Butyl acetate. In addition, the Red shift and blue shifts have been observed in the asymmetric stretching modes of methyl (CH_2) and methylene (CH_3) group of butyl acetate in the binary solutions.

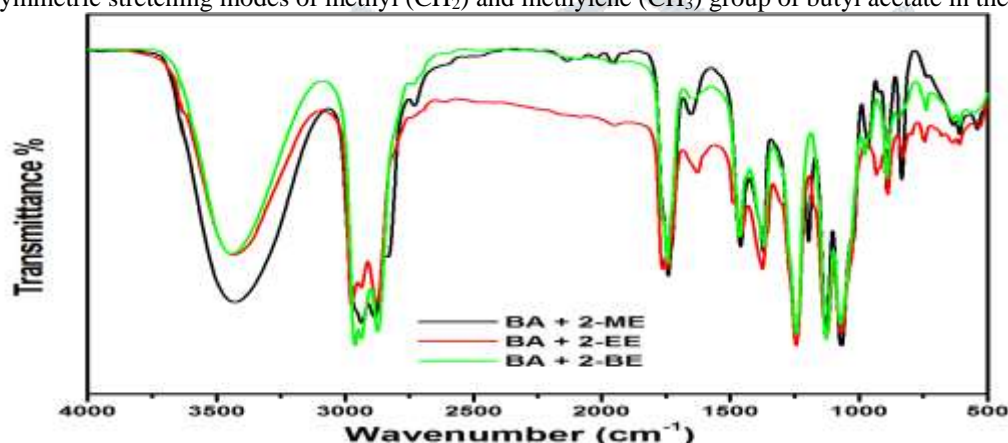


Fig.2: FTIR spectra of equimolar ratio of Butyl acetate (BA) with 2-methoxyethanol (2-ME), 2-ethoxyethanol(2-EE) and 2-butoxyethanol(2-BE) and corresponding peaks shift in the binary mixtures.

Table 6: FT-IR Spectral band assignments for pure Butyl acetate, 2-alkoxyethanols and their equimolar binary solutions

Liquids	Vibration modes	Frequency cm^{-1}	
		$\nu\text{ cm}^{-1}$	$\Delta\nu\text{ cm}^{-1}$
2-Methoxyethanol	O-H	3411	-
2-Ethoxyethanol	O-H	3421	-
2-Butoxyethanol	O-H	3421	-
Butyl acetate	CH_3 asymmetric stretch	3006	-
	CH_2 asymmetric stretch	2968	-
	$C=O$ stretch	1762	-
	C-C-O stretch	1241	-
	O- CH_2 -C asymmetric stretch	1069	-
	Butyl acetate + 2-Methoxyethanol	O-H	3429
CH_3 asymmetric stretch		2984	22
CH_2 asymmetric stretch		2935	33
$C=O$ stretch		1740	22
C-C-O stretch		1242	01
O- CH_2 -C asymmetric stretch		1067	02
Butyl acetate + 2-Ethoxyethanol	O-H	3432	11
	CH_3 asymmetric stretch	2974	32
	CH_2 asymmetric stretch	2936	32
	$C=O$ stretch	1742	20
	C-C-O stretch	1242	01
	O- CH_2 -C asymmetric stretch	1067	02
Butyl acetate + 2-Butoxyethanol	O-H	3442	21
	CH_3 asymmetric stretch	2960	46

	CH ₂ asymmetric stretch	2936	32
	C=O stretch	1743	02
	C-C-O stretch	1242	01
	O-CH ₂ -C asymmetric stretch	1068	01

6. CONCLUSION

The study is concerned with the molecular interaction of Butyl acetate with 2-Alkoxyethanols. The conclusion from the above three systems of molecular interaction are as follows:

1. Pertaining to the relaxation time, the relaxation time of Pure 2-Alkoxyethanols gets increases with increase of chain length of alcohol molecules (i.e) Butyl acetate with 2-butoxyethanol have more relaxation time than that of 2-methoxyethanol and 2-ethoxyethanol. This conclusion was supported by Sivagurunathan *et al.*, [41] in the case of butyl methacrylate with alcohol systems. In our study, Butyl acetate with 2-butoxyethanol system has more relaxation time values when compared to Butyl acetate with 2-ethoxyethanol and 2-methoxyethanol systems. The relaxation time values are in the order of BA + 2-BE > BA + 2-EE > BA + 2-ME. This implies that the interaction order is also the same.
2. The dielectric constants, the relaxation times, the Kirkwood correlation factors, Bruggeman factor, excess dielectric constant, excess inverse relaxation times, excess Helmholtz free energies of activation were calculated and interpreted on the basis of the nature of the molecular interaction.
3. FT-IR spectra analysis confirms that H-bond interaction is taking place in between the participating liquid molecules. It is confirmed that the interaction takes place between the liquid mixtures are weak type of interactions like dispersion forces, dipole induced dipole interaction or H- bonding interaction.

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