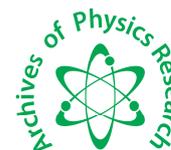




Scholars Research Library

Archives of Physics Research, 2012, 3 (6):420-431
(<http://scholarsresearchlibrary.com/archive.html>)



Scholars Research
Library

ISSN : 0976-0970

CODEN (USA): APRRC7

Dielectric relaxation studies of ketones with 2-methoxyethanol and 2-butoxyethanol using time domain reflectometry technique

S.Kumar¹, P.Periyasamy¹, P.Jeevanandham¹, Praveen G. Hudge² and A.C.Kumbharkhane²

¹Department of Physics, Annamalai University, Annamalai nagar-608002, Tamilnadu, India.

²School of Physical Sciences, S.R.T.M. University, Nanded-431606, Maharashtra (MS), India.

ABSTRACT

The complex permittivity spectra of Ketones like, Dimethylketone (DMK), Ethylmethylketone (EMK) and Diethylketone (DEK) with 2-Methoxyethanol (2-ME) and 2-Butoxyethanol (2-BE) were taken using Time Domain Reflectometry Technique in the frequency range of 10 MHz to 30 GHz at 25°C. The static dielectric constant (ϵ_0) and relaxation time (τ) for all the selected concentrations were obtained by using least square fit method. Using these parameters, the values of Bruggeman factor (f_B), excess static permittivity (ϵ^E) and excess inverse relaxation time ($1/\tau^E$) were also calculated. The Bruggeman plot shows a deviation from linearity. This deviation was attributed to some sort of molecular interaction, which may take place between the unlike molecules. The effective Kirkwood correlation factor (g^{eff}) and corrective Kirkwood correlation factor (g_f) of the mixtures have been determined and discussed to yield information on the structure and dynamics of the mixtures. It confirms that there is a structural formation due to intermolecular interaction between Ketones with 2-ME and 2-BE. The long range and short range interaction between the dipoles can be studied from the thermodynamic parameter, excess Helmholtz free energy (ΔF^E).

Keywords: Dielectric relaxation, Time Domain Reflectometry, Bruggeman factor, Kirkwood Correlation factor, Thermodynamic parameters.

INTRODUCTION

The phenomenon of dielectric relaxation of binary mixtures of polar liquids in non-polar solvents at microwave frequencies has been attempted by many workers [1-4]. Dielectric studies of binary liquid mixtures of polar-polar are also important for understanding the intermolecular interactions and the consequent structural rearrangement of molecules in solution [5-10]. Dielectric studies provide meaningful information regarding intermolecular and intramolecular association between the solute and solvent molecules. Advanced microwave technique like Time Domain Reflectometry (TDR) has been used as a powerful tool for the measurement of complex permittivity of liquids and their mixtures over a wide range of frequencies. (i.e) from 10 MHz to 30 GHz [11-13]. A great deal of interest has been evidenced in the study of dielectric relaxation behavior in ketone systems with a view to understanding the role of hydrogen bonding and C=O group in the system. The importance of measuring the static permittivity of liquid lies in the fact that it provides valuable information about the ordering of the molecular interaction in a binary mixture.

Static dielectric constant of materials is an intrinsic property, which can play an important role in the solution properties. Measurement of relative permittivity has been shown to be a useful technique in characterizing molecular structure, solute-solute, and solvent-solute interactions in solutions [14-16]. Madhurima et al, studied nitriles and ketones with alcohol in pure as well as their dilute solutions in benzene at different microwave frequencies and found that the molecular association takes place between two components of the molecules [17-21]. Alcohols are among the most important organic compounds, because they are of central importance to organic chemistry and

biochemistry. Due to the presence of the –OH group in the molecule, the solution chemistry of these compounds can be strongly influenced by the intermolecular hydrogen bond formation, which can play an important role in the physical properties of these molecules. Therefore, they have been subject of extensive practical and theoretical investigations to study intermolecular hydrogen bonding [22–26]. The aliphatic alcohols are excellent H–bond donors/acceptors. On the other hand, ketones are an important class of industrial chemicals with many scientific and industrial applications [22].

2–methoxyethanol and 2–butoxyethanol it is an organic compound that was used mainly as a solvent. 2–methoxyethanol was used as a solvent for many different purposes such as varnishes, dyes, and resins.

The main use of 2–butoxyethanol is a solvent and it is used in paints and surface coatings, followed by cleaning products and inks. These compounds with a carbonyl group (C=O) are strongly hydrogen–bond acceptors. Ketones are also polar, since ketones possess lack of hydroxyl groups and they are incapable to create intermolecular hydrogen bonds, but due to the presence of oxygen, they can form hydrogen bonds with alcohol or water molecules which lead to the complete solubility of low ketones in the former solvents. The lower molar mass aliphatic ketones are stable, colorless liquids and generally have a pleasant, slightly aromatic odour. In the present paper, the detailed dielectric relaxation studies of ketones such as dimethylketone, ethylmethylketone and diethylketone with 2–methoxyethanol (2–ME) and 2–butoxyethanol (2–BE) solutions at different volume percentage of concentrations have been carried out using Time Domain Reflectometry technique in the frequency range of 10 MHz to 30 GHz. Resulting dielectric parameter such as static dielectric constant, relaxation time, effective Kirkwood correlation factor (g^{eff}), corrective Kirkwood correlation factor (g_r) excess dielectric properties, thermodynamic properties and Bruggeman factor for each concentration of ketones with 2–ME and 2–BE solutions have been evaluated.

MATERIALS AND METHODS

2.1. Materials

AR grade chemicals such as dimethylketone, ethylmethylketone and diethylketone, 2–methoxyethanol (2–ME) and 2–butoxyethanol (2–BE) were obtained commercially and used without further purification. The solutions were prepared at different volume percentages from 0% to 100% in step of 25%, at 25°C. The experimental and literature values of static dielectric constant and relaxation time for both experimental and literature are given in Table (1).

Table–1: Physical constant of pure compounds at 25° C

Compounds	Static dielectric constant (ϵ_0)		Relaxation time (τ) ps	
	Experiment	Literature	Experiment	Literature
2–ME	17.81	17.80 ^[27]	29.99	30.05 ^[27]
2–BE	9.99	9.98 ^[28]	47.86	47.78 ^[28]
DMK	21.24	26.38 ^[29]	3.58	4.62 ^[29]
EMK	18.41	25.67 ^[29]	5.45	5.31 ^[29]
DEK	17.21	24.82 ^[29]	7.31	6.08 ^[29]

2.2. Measurements

The dielectric spectra were obtained by the Time Domain Reflectometry (TDR) technique [30–31]. The Tektronix model no. DSA 8200 Digital Serial Analyzer sampling main frame along with the sampling module 80E08 has been used for the Time Domain Reflectometer (TDR). A repetitive fast rising voltage pulse with 18 ps incident pulse rise time and 20 ps reflected pulse rise time was fed through coaxial line system of impedance 50Ω. Sampling oscilloscope monitor changes in step pulse after reflection from the end of line. Reflected pulse without sample $R_1(t)$ and with sample $R_x(t)$ were recorded in time window of 2 ns and digitized in 2000 points. The Fourier transformation of the pulses and data analysis were done earlier to determine complex permittivity spectra $\epsilon^*(\omega)$ using nonlinear least square fit method [31].

RESULT AND DISCUSSION

The frequency dependent values of permittivity ϵ' and dielectric loss ϵ'' of Dimethylketone (DMK) with 2–butoxyethanol (2–BE) mixtures at 25° C are shown in Fig (1) and Fig (2). It is observed from the plot that the values of ϵ' decreases with increase in concentration of 2–BE systems and maxima of dielectric loss ϵ'' max shifts from the lower to higher frequency. It indicates the relaxation time values are decreases with increasing concentration of ketones [32],

Fig. 1: Plot of Frequency dependent log F (Hz) vs. dielectric permittivity (ε') for DMK +2-BE.

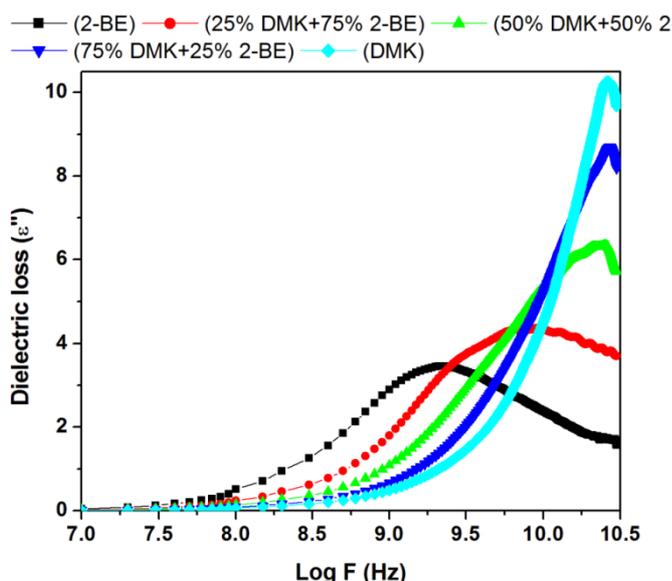
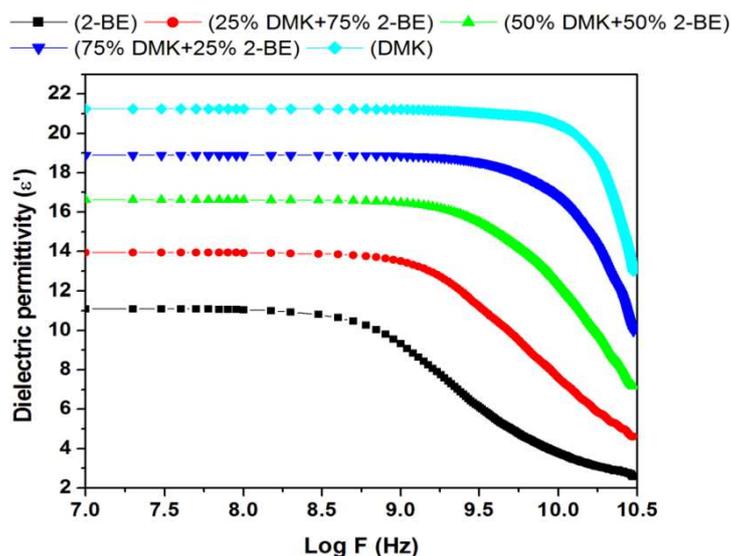


Fig. 2: Plot of Frequency dependent log F (Hz) vs. dielectric loss (ε'') for DMK + 2-BE.



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 [33]. The general form of the relaxation model is given by Havriliak-Negami equation [34]

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

where $\epsilon^*(\omega)$ is the complex reflection coefficient, ϵ_0 is the static dielectric constant, ϵ_∞ is the static permittivity at high frequency, τ is the relaxation time, 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 ketones with alcohols could fit Debye type dispersion. Therefore, here ($\alpha = 0$ and $\beta = 1$) and experimental values of $\epsilon^*(\omega)$ were fitted to the Debye equation as,

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{(\varepsilon_0 - \varepsilon_\infty)}{[1 + (j\omega\tau)]^\beta} \dots\dots\dots(1.1)$$

The values of (ε_0) , (τ) and (ε_∞) are fitting parameters. The static dielectric constant (ε_0), Relaxation time (τ), Bruggeman factor (f_B), Effective Kirkwood correlation factor (g^{eff}), Corrective Kirkwood correlation factor (g_f), Excess permittivity (ε^E), Excess inverse relaxation time $(1/\tau)^E$, Free energy of activation for relaxation time (ΔF_τ) for a mixture of ketones with alcohols and are listed in Table 2 to Table 7. The volume percentage of ketone increases the static dielectric constant (ε_0) increases in all the systems except DEK + 2-ME. The increases in (ε_0) values are may be due to the transition of spherical molecular aggregates into elongated aggregates giving rise to parallel orientation of the dipoles. In the case of DEK + 2-ME systems anti-parallel orientation of dipoles takes place. Similar conclusion was drawn by Shirke et al [35] for ethylacetate – alcohol systems. The volume percentage of ketone increases the relaxation time (τ) decreases for all the studied systems.

3.1. Bruggeman factor

The information about the solute – solvent interaction is given by the Bruggeman factor. The effective volume of the solute gets modified by solute – solvent interactions and is best illustrated by the non – linearity of the Bruggeman formula [36],

$$f_B = \left(\frac{(\varepsilon_{0m} - \varepsilon_{02})}{(\varepsilon_{01} - \varepsilon_{02})} \right) \left(\frac{\varepsilon_{01}}{\varepsilon_{0m}} \right)^{1/3} = (1 - \phi_2) \dots\dots\dots(2)$$

According to equ (2), a non linear relationship is expected between f_B and Vol. fraction of ketones. The estimated values of f_B are shown in Fig (3) and Fig (4). It can be seen from these figures that f_B is not a linear function of volume fraction of ketones.

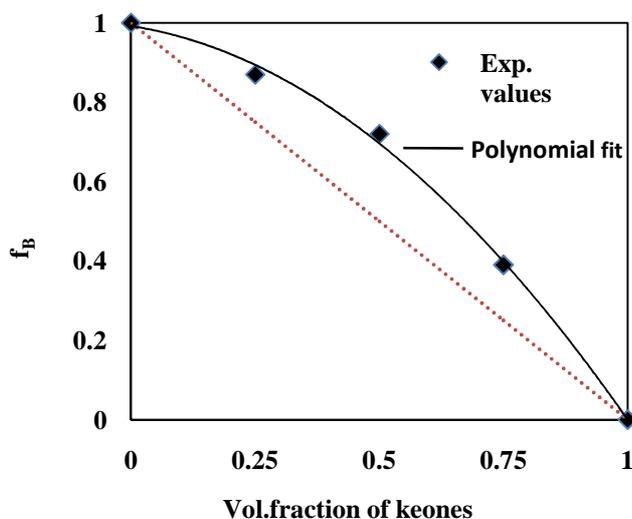


Fig. 3. Plot of Bruggeman factor Vs volume fraction of ketones in 2-ME.

The Bruggeman factor f_B shows a negative deviation for the DMK + 2-ME, DEK + 2-ME, DMK + 2-BE and DEK + 2-BE systems, which indicate that intermolecular interaction is taking place in the mixture. The maximum negative deviation from the linearity is observed for DEK + 2-ME and DEK + 2-BE systems. The positive deviation occurs in EMK + 2-ME and EMK + 2-BE systems. The non-linearity of the curves indicate heterointeraction which may be due to hydrogen bonding of the –OH group of alcohol with C=O group of ketone. Similar interpretations were given by Thenappan and Prabakar Devaraj [37] and Patil et al., [38].

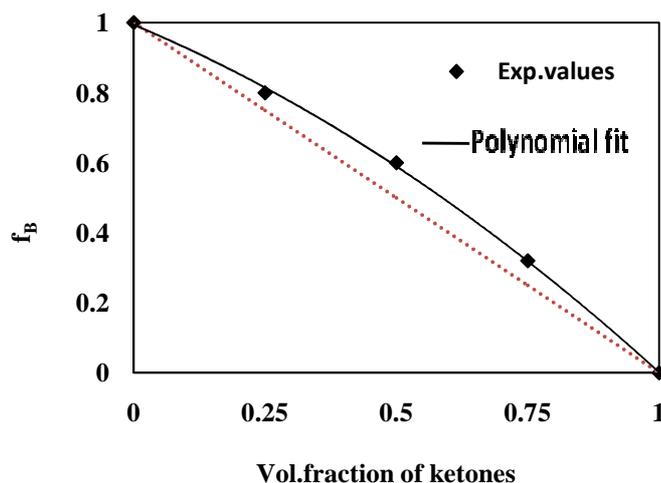


Fig. 4: Plot of Bruggeman factor vs. volume fraction of ketones in 2-BE.

3.2. Kirkwood correlation factor

The structural information about the liquids from the dielectric relaxation parameter may be obtained using the Kirkwood correlation parameter 'g' [39]. This parameter is useful for obtaining information regarding orientation of electric dipoles in polar liquids. The 'g' for the pure liquid may be obtained from the expression,

$$\frac{4\pi N_A \mu^2 \rho}{9kTM} g = \frac{(\epsilon_0 - \epsilon_\infty)(2\epsilon_0 + \epsilon_\infty)}{\epsilon_0(\epsilon_\infty + 2)^2} \dots\dots\dots(3)$$

where N_A is Avogadro's number, μ is the dipole moment in the gas phase, ρ is the density, K is the Boltzmann constant, T is the temperature in Kelvin, M is the molecular weight, ϵ_0 is the static dielectric constant and ϵ_∞ is the dielectric constant at optical frequency which is the square of the refractive index.

Modified forms of this equation have been used to study the orientation of electric dipoles in binary mixture of ketones with 2-ME and 2-BE. Equation (3) is modified by assuming that for the mixture, g^{eff} has become effective Kirkwood correlation factor in the mixture. The Kirkwood equation for the mixture may be expressed as [40],

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

Where, g^{eff} is the effective Kirkwood correlation factor for a binary mixture, with ϕ_1 and ϕ_2 as volume fractions of liquids 1 and 2 respectively. The effective Kirkwood correlation factor (g^{eff}) calculated using equ (4) is given in Table (3) and (6). The (g^{eff}) values get decreases as the concentration of ketones increases in the systems of DMK + 2-ME, DEK + 2-ME, DMK + 2-BE and DEK + 2-BE, where as in the cases of EMK + 2-ME and EMK + 2-BE systems, the calculated (g^{eff}) values first gets decreases upto 50 % volume percentage of ketones and then gets increases. It means that in the cases of DMK + 2-ME, DEK + 2-ME, DMK + 2-BE and DEK + 2-BE, at the initial concentration of ketones (g^{eff}) values are far greater than 1 and hence the molecular dipoles have parallel orientation among themselves. As the concentration of ketones increases (g^{eff}) values gets decreases steadily and approaching towards the antiparallel orientation of dipoles. In the case of EMK + 2-ME and EMK + 2-BE systems, (g^{eff}) values are far greater than 1 which indicates that antiparallel orientation dominates. Hence this tendency leads to the conclusion that heterogeneous interaction between -OH group of alcohol and C=O group of ketone, leads to the formation of multimers with antiparallel orientation of the electric dipoles [37]. The corrective Kirkwood correlation factor (g_f) is a dielectric parameter which supplies essential information regarding interaction of the compounds of the mixture. For an ideal non-interacting mixture g_f must be unity and the magnitude of the deviation of (g_f) from unity indicates the magnitude of interaction between the compounds i.e., a greater deviation from unity means a larger strength of interactions [41],

$$\frac{4\pi N_A}{9kT} \left(\frac{\mu_1^2 \rho_1 g_1}{M_1} \phi_1 + \frac{\mu_2^2 \rho_2 g_2}{M_2} \phi_2 \right) g_f = \frac{(\epsilon_{0m} - \epsilon_{\infty m})(2\epsilon_{0m} + \epsilon_{\infty m})}{\epsilon_{0m}(\epsilon_{\infty m} + 2)^2} \dots\dots\dots(5)$$

where N_A is Avogadro's number, μ is the dipole moment in the gas phase, ρ is the density, K is the Boltzmann constant, T is the temperature in Kelvin, M is the molecular weight, ϵ_{0m} is the static dielectric constant of mixture and ϵ_∞ is the dielectric constant at optical frequency which is the square of the refractive index of the mixture.

The corrective Kirkwood correlation factor (g_f) was calculated by using equ (5) for 25°C. In the present system ketones with alcohols, the values of (g_f) are close to unity for all the studied systems. But, the (g_f) values are found to be slightly greater than unity for DMK + 2-ME, DEK + 2-ME, DMK + 2-BE and DEK + 2-BE systems, indicating that effective dipoles in the mixture are greater than the average of those in the pure compounds. Further, the (g_f) values are found to be slightly less than unity for EMK + 2-ME and EMK + 2-BE systems for all the concentrations, indicating that the effective dipoles in the mixture are smaller than the average of those in the pure compounds. The values of (g_f) are found to depend more on concentration than temperature, as reported by Balamurugan and Pawar [42–43].

3.3. Excess dielectric constant

The excess permittivity is defined as [44],

$$\epsilon^E = (\epsilon_0 - \epsilon_\infty)_m - \{(\epsilon_0 - \epsilon_\infty)_1 \phi_1 + (\epsilon_0 - \epsilon_\infty)_2 \phi_2\} \dots \dots \dots (6)$$

where ϕ_1 and ϕ_2 – volume fraction and suffixes m, 1 and 2 represents mixture, liquid 1 (2ME) & (2BE) and liquid 2 (DMK, EMK and DEK) respectively. The excess permittivity may provide qualitative information about multimers formation in the mixture as follows:

1. $\epsilon^E = 0$ indicates that there is no interaction between the components in the mixture.
2. $\epsilon^E < 0$ reveals that components in the mixture may form closed multimers leading to the less effective dipoles due to the interaction between the components in such a way that the effective dipole moment gets reduced.
3. $\epsilon^E > 0$ denotes that components in the mixture interact in such a way that the effective dipole moment is increased. There is a probability for the formation of linear multimers.

In an ideal mixture of polar liquids if the molecules are interacting, a non linear variation in dielectric constant and relaxation time occurs. This confirms that the intermolecular association is taking place in the system.

The excess property related to static dielectric constant and relaxation time provides significant information regarding interaction between the polar – polar liquid mixtures. In the case of ketones with alcohols such as DMK + 2-ME, DMK + 2-BE and DEK + 2-BE systems, positive value of excess dielectric constant (ϵ^E) is obtained. The positive values of excess dielectric constant (ϵ^E) indicates that molecules of the mixtures may form monomers or dimers structures in such a way that the number of effective dipoles increases. The negative values of excess permittivity are obtained for the following ketone + alcohol systems such as EMK + 2-ME, DEK + 2-ME and EMK + 2-BE systems. The negative value of (ϵ^E) indicates that molecules of the mixtures may form multimer structures via hydrogen bonding in such a way that the effective dipoles get reduced [45–46]. The excess dielectric constant (ϵ^E) of mixtures was calculated using equation (6) and its variation with volume fraction of ketones in 2-ME & 2-BE at 298 K shown in Fig (5) and Fig (6). It is also seen from the plots of (ϵ^E) V_S volume fraction of ketones, the (ϵ^E) values are found to be maximum at 0.5 volume fraction of ketones with 2-ME and 2-BE systems. The hetero interaction is between the –OH group of alcohol and C=O group of ketone and it is an agreement with the conclusions reported by Pawar and Mehrotra et al [47] for dimethylene chloride–ethanol mixtures.

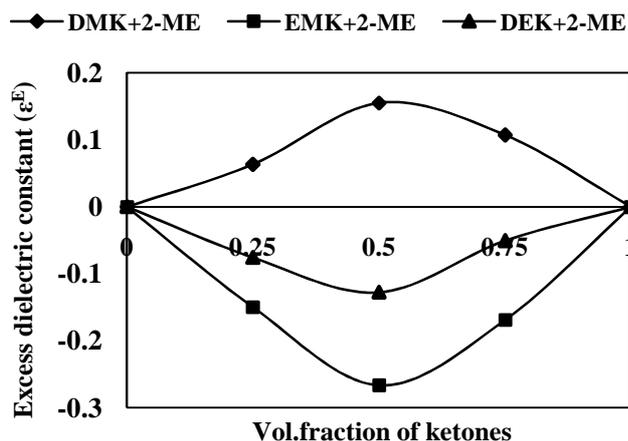


Fig. 5. Plot of excess dielectric constant vs. volume fraction of ketones in 2-ME.

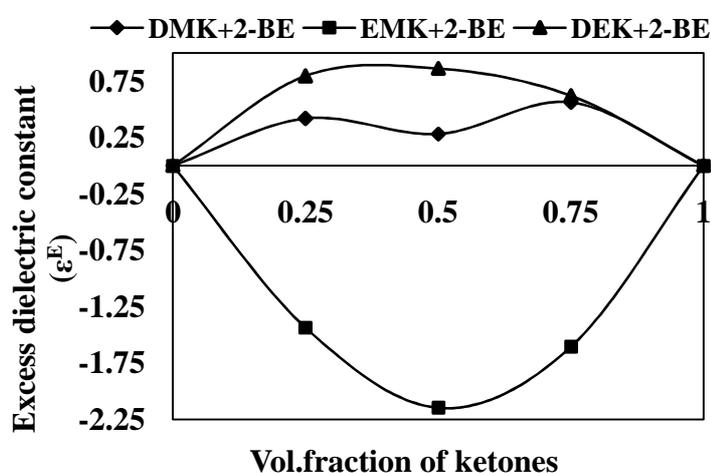


Fig. 6. Plot of excess dielectric constant Vs volume fraction of ketones in 2-BE.

3.4. Excess inverse relaxation time

The excess inverse relaxation time is defined as,

$$\left(\frac{1}{\tau}\right)^E = \left(\frac{1}{\tau}\right)_m - \left\{ \left(\frac{1}{\tau}\right)_1 \phi_1 + \left(\frac{1}{\tau}\right)_2 \phi_2 \right\} \dots \dots \dots (7)$$

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 [48]. The information regarding the dynamic of liquids 1 and 2 interaction from this excess property is as follows:

- (i) $(1/\tau)^E = 0$: there is no change in the dynamics of liquids 1 and 2 interaction.
- (ii) $(1/\tau)^E < 0$: the liquids 1 and 2 interaction produces a field such that the effective dipoles rotate slowly.
- (iii) $(1/\tau)^E > 0$: the liquids 1 and 2 interaction produces a field such that the effective dipoles rotate fastly i.e. the fields will co-operate in the rotation of dipoles.

The variation of $(1/\tau)^E$ with volume fraction of ketones are calculated by using the equation (7) at 298K is shown in Fig (7) and Fig (8).

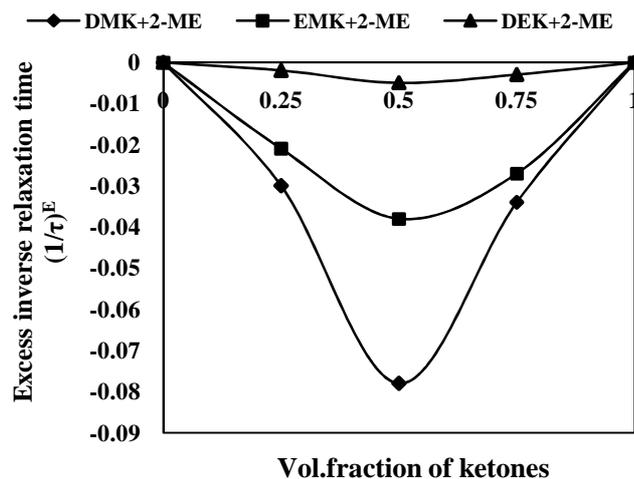


Fig. 7: Plot of excess relaxation time vs. volume fraction of ketones in 2-ME.

As seen from the plots, $(1/\tau)^E$ is negative for all the ketones with 2-ME and 2-BE. This indicates that the addition of ketones with 2-ME and 2-BE has created a hindering field such that the effective dipole rotates slowly.

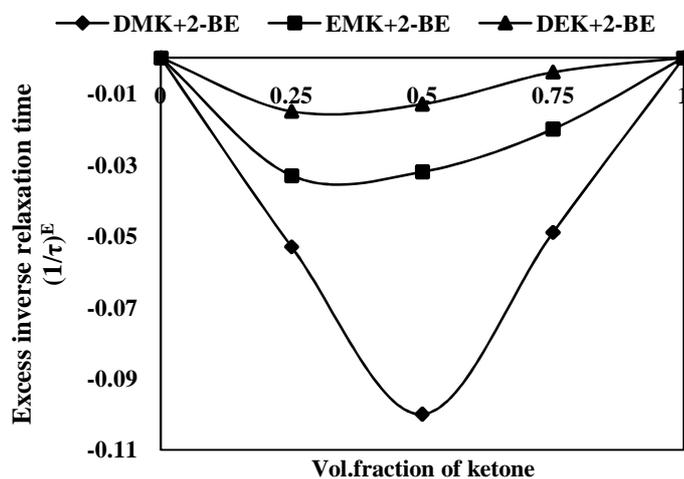


Fig. 8: Plot of excess relaxation time vs. volume fraction of ketones in 2-BE.

Table-2: Variation of ϵ_0 , τ , f_B and ΔF_r values with volume fraction of ketones in 2-ME.

ϕ_2	ϵ_0 (a)	τ (ps) (a)	f_B	ΔF_r (kJ/mol)
Dimethylketone+2-methoxyethanol				
0	17.81(1)	29.99(5)	1	13.056
0.25	18.70(1)	15.62(10)	0.72	11.428
0.50	19.64(1)	12.78(5)	0.45	10.928
0.75	20.46(3)	5.45(1)	0.21	8.802
1	21.24(2)	3.58(1)	0	7.753
Ethylmethylketone+2-methoxyethanol				
0	17.81(1)	29.99(5)	1	13.056
0.25	17.90(1)	18.88(1)	0.87	11.901
0.50	18.01(4)	13.03(2)	0.72	10.976
0.75	18.25(1)	7.82(6)	0.39	9.702
1	18.54(1)	5.10(1)	0	8.636
Diethylketone+2-methoxyethanol				
0	17.81(1)	29.99(5)	1	13.056
0.25	17.55(2)	17.60(9)	0.56	11.726
0.50	17.35(1)	12.53(5)	0.23	10.878
0.75	17.29(1)	9.28(3)	0.13	10.129
1	17.21(1)	7.31(4)	0	9.534

Numbers in bracket denote uncertainties in the last significant digits obtained by the least square fit method. e.g. 17.81(1) means 17.81 ± 0.01 .

Table-3: Variation of ϵ_0 , τ , f_B and ΔF_τ values with volume fraction of ketones in 2-BE.

ϕ_2	ϵ_0 (a)	τ (ps) (a)	f_B	ΔF_τ (kJ/mol)
Dimethylketone+2-butoxyethanol				
0	9.99(1)	47.86(24)	1	14.222
0.25	13.25(2)	31.30(22)	0.64	13.163
0.50	15.93(1)	20.22(7)	0.40	12.072
0.75	19.01(2)	6.04(1)	0.16	9.058
1	21.24(2)	3.58(1)	0	7.753
Ethylmethylketone+2-butoxyethanol				
0	9.99(1)	47.86(24)	1	14.222
0.25	11.32(2)	24.22(13)	0.80	12.523
0.50	12.85(1)	11.79(4)	0.60	10.727
0.75	15.26(8)	7.54(1)	0.32	9.611
1	18.41(3)	5.45(9)	0	8.802
Diethylketone+2-butoxyethanol				
0	9.99(1)	47.86(24)	1	14.222
0.25	12.62(1)	28.64(11)	0.58	12.941
0.50	14.50(1)	15.29(5)	0.33	11.375
0.75	16.05(8)	9.71(2)	0.13	10.243
1	17.21(1)	7.31(4)	0	9.534

^(a)Numbers in bracket denote uncertainties in the last significant digits obtained by the least square fit method. e.g. 47.86(24) means 47.86 ± 0.24 .

Table-4: Variation of g^{eff} , g_r , ϵ^E and $(1/\tau)^E$ values with volume fraction of ketones in 2-ME.

ϕ_2	g^{eff}	g_r	ϵ^E	$(1/\tau)^E$ ps^{-1}
Dimethylketone+2-methoxyethanol				
0	1.277	1	0	0
0.25	1.270	1.009	0.063	-0.030
0.50	1.264	1.017	0.155	-0.078
0.75	1.246	1.012	0.107	-0.034
1	1.219	1	0	0
Ethylmethylketone+2-methoxyethanol				
0	1.277	1	0	0
0.25	1.266	0.962	-0.150	-0.021
0.50	1.265	0.934	-0.267	-0.038
0.75	1.333	0.959	-0.169	-0.027
1	1.425	1	0	0
Diethylketone+2-methoxyethanol				
0	1.277	1	0	0
0.25	1.260	1.008	-0.076	-0.002
0.50	1.225	1.003	-0.128	-0.005
0.75	1.196	1.002	-0.051	-0.003
1	1.163	1	0	0

Table-5: Variation of g^{eff} , g_r , ϵ^E and $(1/\tau)^E$ values with volume fraction of ketones in 2-BE.

ϕ_2	g^{eff}	g_r	ϵ^E	$(1/\tau)^E$ ps^{-1}
Dimethylketone+2-butoxyethanol				
0	1.928	1	0	0
0.25	1.629	1.042	0.418	-0.053
0.50	1.424	1.024	0.281	-0.100
0.75	1.333	1.035	0.561	-0.049
1	1.219	1	0	0
Ethylmethylketone+2-butoxyethanol				
0	1.928	1	0	0
0.25	1.523	0.886	-1.435	-0.033
0.50	1.385	0.853	-2.147	-0.032
0.75	1.406	0.897	-1.606	-0.020
1	1.531	1	0	0
Diethylketone+2-butoxyethanol				
0	1.928	1	0	0
0.25	1.752	1.083	0.794	-0.015
0.50	1.525	1.079	0.861	-0.013
0.75	1.333	1.050	0.621	-0.004
1	1.163	1	0	0

The excess inverse relaxation time values are more negative at 0.5 concentrations of ketones. The negative value of excess inverse relaxation time indicates slower rotation of the dipoles of the system. The free energy of activation for relaxation time (ΔF_r) for all the systems is reported in Table 2 and Table 5. It is clear from the table that as the ketone concentration increases, (ΔF_r) values gets decrease. The (ΔF_r) values are greater at initial concentration of ketones with 2-ME and 2-BE systems [49],

3.5. Excess thermodynamic properties

The study of thermodynamic 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 [50];

$$(\Delta F^E) = (\Delta F_{0r}^E) + (\Delta F_{rr}^E) + (\Delta F_{12}^E) \dots \dots \dots (8)$$

where, (ΔF_{0r}^E) represents the excess dipolar energy due to long range electrostatic interaction. (ΔF_{rr}^E) represents the excess dipolar energy due to short range interaction between identical 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 (9):

$$\Delta F^E = - \left[\frac{N_A}{2} \right] \left\{ \left[\sum_{r=1,2} X_r^2 \mu_r^2 (R_{fr} - R_{fr}^0) \right] + \left[\sum_{r=1,2} X_r^2 \mu_r^2 (g_{rr} - 1) (R_{fr} - R_{fr}^0) \right] \right\} \dots \dots \dots (9)$$

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

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

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.

Table-6: Variation of thermodynamic parameters (ΔF_{0r}^E , ΔF_{rr}^E , ΔF_{12}^E and ΔF^E) values with volume fraction of ketones in 2-ME.

ϕ_2	ΔF_{0r}^E (J/mol)	ΔF_{rr}^E (J/mol)	ΔF_{12}^E (J/mol)	ΔF^E (J/mol)
Dimethylketone+2-methoxyethanol				
0	0	0	0	0
0.25	-13.96	-4.31	2.91	-15.36
0.50	-0.78	-1.25	-1.73	-3.77
0.75	12.37	2.34	-4.29	10.42
1	0	0	0	0
Ethylmethylketone+2-methoxyethanol				
0	0	0	0	0
0.25	-0.61	0.07	0.97	0.43
0.50	3.14	1.67	0.64	5.46
0.75	5.36	2.46	-0.65	7.17
1	0	0	0	0
Diethylketone+2-methoxyethanol				
0	0	0	0	0
0.25	5.60	1.67	-0.05	7.22
0.50	3.55	1.18	1.01	5.74
0.75	-0.72	0.05	0.87	0.19
1	0	0	0	0

The long range and short range interaction between dipoles can be studied from the thermodynamic parameter, 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 4 and Table 7. The long range electro static interaction ΔF_{0r}^E calculated for first two concentrations (i.e) 0.25 and 0.5 of volume fraction of ketones such as DMK with 2-ME are found to be negative and after that it was positive. As the concentration of ketone increases ΔF_{0r}^E values are found to be negative at 0.25 volume fraction of ketones such as EMK + 2-ME, DMK + 2-BE and DEK + 2-BE systems. If the contributions to ΔF_{0r}^E values are negative then it indicates the presence of dipole-induced dipole interaction or depressive interaction. The values of

the excess dipolar energy due to long-range interaction ΔF_{0r}^E are all positive in the entire concentration range of EMK + 2-BE system studied. This shows the existence of dipole-dipole interaction between ketone molecules.

The volume fraction of ketone increases the excess dipolar energy ΔF_{0r}^E due to long range electro static interaction is found to be maximum at 0.75 concentration for all the ketones except DEK + 2-ME system. The second term ΔF_{rr}^E gives the excess free energy due to short-range interaction between the like molecules. As the concentration of ketone increases ΔF_{rr}^E values are negative for DMK + 2-BE and DEK + 2-BE systems. It indicates the non-specific interaction of the above said systems. The values of ΔF_{rr}^E are positive for EMK + 2-ME and DEK + 2-ME systems indicating that the strong short range interaction through hydrogen bonding.

Table-7: Variation of thermodynamic parameters (ΔF_{0r}^E , ΔF_{rr}^E , ΔF_{12}^E and ΔF^E) values with volume fraction of ketones in 2-BE.

ϕ_2	ΔF_{0r}^E (J/mol)	ΔF_{rr}^E (J/mol)	ΔF_{12}^E (J/mol)	ΔF^E (J/mol)
Dimethylketone+2-butoxyethanol				
0	0	0	0	0
0.25	-36.71	-57.04	26.85	-66.90
0.50	25.40	-27.73	-3.31	-5.65
0.75	42.80	-1.27	-15.16	26.35
1	0	0	0	0
Ethylmethylketone+2-butoxyethanol				
0.	0	0	0	0
0.25	19.18	-0.19	30.71	49.70
0.50	85.53	38.25	9.09	132.88
0.75	88.08	44.48	-6.29	126.27
1	0	0	0	0
Diethylketone+2-butoxyethanol				
0	0	0	0	0
0.25	-39.37	-51.08	14.36	-76.10
0.50	0.41	-29.80	-10.33	-39.73
0.75	22.53	-5.44	-12.37	4.70
1	0	0	0	0

The magnitude of ΔF_{12}^E gives information on the strength of interactions between unlike molecules. The values of ΔF_{12}^E calculated in the systems of ketones + alcohols are both the positive and negative, which indicate that the hetero interaction between the compounds which are varying with concentration and temperature. Finally the high positive values of ΔF^E were observed for the EMK + 2-ME, DEK + 2-ME and EMK + 2-BE systems, which indicate that, the formation of β -clusters with anti-parallel alignment of dipoles [51]. In DMK + 2-ME, DMK + 2-BE and DEK + 2-BE systems there is both negative and positive values of ΔF^E . It indicates that the formation of α -clusters to β -clusters with parallel to antiparallel alignment of dipoles takes place. The ΔF^E values are contribution of mainly due to the long range electrostatic interaction ΔF_{0r}^E and not due to the short range electrostatic interaction ΔF_{rr}^E .

CONCLUSION

From the above study, dielectric relaxation parameters, excess inverse relaxation time and Kirkwood correlation factor have been reported for various ketones with 2-ME and 2-BE at 25°C. These data provide information regarding solute-solute interaction in liquids. The excess inverse relaxation time values are negative for all concentrations, of the above systems. It indicates that the slower rotation of the dipoles, due to the solute-solute interaction and form the hydrogen bonded structures produce a field in such a way that the effective dipole rotation is hindered. The electron contribution of the methyl group in C=O group of ketone is significantly greater than that of other group. Also the Dimethylketone with alcohol systems have higher $(1/\tau)^E$ negative values than that of other ketone systems, revealing that the tendency of complex formation is stronger in ketone + alcohol systems. Therefore, expect the strongest intermolecular hydrogen bonds would be formed between the C=O group of Dimethylketone with alcohols system and weakest between the other ketone such as EMK and DEK with alcohol systems viz., 2-ME and 2-BE. This observation is reflected in the dielectric constant, Kirkwood correlation factor, excess dielectric constant and excess inverse relaxation time values.

REFERENCES

- [1] A L G Sadd; A G Shafik; F Hanna; *Ind J Phys*, **1998**, 72B (5), 495.
- [2] R H Fattepur; M T Hosami; D K Despande; S C Mehrotra; *J Chem Phys*, **1994**, 101, 9956.
- [3] K K Gupta; A K Bansal; P J Singh; K S Sharma; *Ind J Pure and Appl Phys*. **2004**, 42, 849.
- [4] A N Prajapati; V A Rana; A D Vyas; *Ind J Pure and Appl Phys*, **2006**, 44, 620.
- [5] A Ghanadzadeh; M S Beevers; *J Mol Liq*, **2002**, 100, 47–57.
- [6] A Ghanadzadeh; M S Beevers; *J Mol Liq*, **2003**, 102, 365–377.
- [7] A Ghanadzadeh; M Mamaghani; L Anbir; *J Sol Chem*, (**2003**), 32/7, 625–636.
- [8] P Sivagurunathan; K Dharmalingam; K Ramachandran; B Prabhakar Undre; P W Khirade; S C Mehrotra; *J Mol Liq*, (**2007**), 133, 139–145.
- [9] T Thenappan; A Prabakar Devaraj; *J Mol Liq*, (**2006**), 123, 72–79.
- [10] G Parthipan; T Thenappan; *J Mol Liq*, (**2007**), 133, 1–6.
- [11] S Mashimo; S Kuwabata; S Yagihara; K Higasi; *J Chem Phys*, (**1989**), 90, 3292.
- [12] R H Cole; J G Berbarian; S Mashimo; A Burns; E Tombari; *J Appl Phys*, (**1989**), 66, 793.
- [13] A C Kumbharkhane; S M Puranik; S C Mehrotra; *J Mol Liq*, (**1992**), 51, 307.
- [14] J W Smith; Butterworth's Publications Ltd, **1955**.
- [15] G M Janini; A H Katrib; *J Chem Educ*, (**1983**), 60, 1087–1088.
- [16] C P Smyth; Vol. II, John Wiley & Sons Ltd, **1980**.
- [17] T Sato; R Buchner; *J Chem Phys*, (**2003**), 118, 4606–4613.
- [18] R J Sengwa; *J Mol Liq*, (**2003**), 108, 47–60.
- [19] K Sarojini; T Thenappan; *J Mol Liq*, (**2010**), 151, 39–41.
- [20] R J Sengwa; Sonu Sankhla; *J Mol Liq*, (**2007**), 130, 119–131.
- [21] V Madhurima; V R K Murthy; J Sobhanadri; *Ind J Pure and Appl Phys*, (**1998**), 36, 144–148.
- [22] K Rajagopal; T A Parasada Rao; V Madhurima; J Sobhanadri; *J Mol Liq*, (**1998**), 76, 13.
- [23] U Becker; M Stockhausen; *J Mol Liq*, (**1999**), 81, 89–100.
- [24] V A Durov; *J Mol Liq*, (**1998**), 78, 51–82.
- [25] A Ghanadzadeh; H Ghanadzadeh; R Sariri; L Ebrahimi; *J Chem Thermodyn*, (**2005**), 37, 357–362.
- [26] A Ghanadzadeh Gilani; H Ghanadzadeh; K Bahrpaima; A Ranjkesh; *Thermodyn*, (**2010**), 42, 967–972.
- [27] Y S Joshi; A C Kumbharkhane; *J Mol Liq*, (**2011**), 161, 120–124.
- [28] Y S Joshi; A C Kumbharkhane; *Fluid phase equilibria*, (**2012**), 317, 96–101.
- [29] V Madhurima; M S Moni; J Sobhanadri; V R K Murthy; *J Mol Liq*, (**2005**), 122, 38–42.
- [30] J B Hasted; Chapman and Hall, London, (**1973**).
- [31] R H Cole; J G Berbarian; S Mashimo; G Chryssikos; A Burns; E Tombari; *J Appl Phys*, (**1989**), 66, 793–802.
- [32] L S Gabrielyan; S A Markarian; *J Mol Liq*, (**2011**), 162, 135–140.
- [33] A C Kumbharkhane; S M Puranik; S C Mehrotra; *J Chem Soc, Faraday Trans*. (**1991**), 87, 1569–1573.
- [34] S Havriliak; S Negami; *J Poly Sci, Part C Polym Symp*, (**1966**), 14, 99.
- [35] R M Shirke; A Chaudhari; N M More; P B Patil; *J Mol Liq*, (**2001**), 94, 27–36.
- [36] D A G Bruggeman; *Ann Physik*, (**1935**), 24, 636–644.
- [37] T Thenappan; A Prabakar Devaraj; *J Mol Liq*, (**2006**), 123, 72.
- [38] A V Patil; B D Achole; G N Shinde; V P Pawar; *Archives of App Sci Res*, **2012**, 4 (4), 1665–1669.
- [39] J G Kirkwood; *J Chem Phys*, (**1939**), 7, 911.
- [40] S M Puranik; A C Kumbharkhane; S C Mehrotra; *J Mol Liq*, (**1991**), 50, 143.
- [41] A Chaudhari; D Antia; G Raju; H Chaudhari; K Prakash; N Navinkumar; M Suresh; *Proc. Natl Sci counc, ROC A*, (**2001**), 25, 205–210.
- [42] D Balamurugan; S Kumar; S Krishnan; *J Mol Liq*, (**2005**), 122, 11–14.
- [43] V P Pawar; A R Patil; S C Mehrotra; *J Mol Liq*, (**2005**), 121, 88–93.
- [44] A C Kumbharkhane; S M Puranik and S C Mehrotra; *J Sol Chem*, (**1993**), 22, 219.
- [45] A Chaudhari; S Ahire; S C Mehrotra; *J Mol Liq*, (**2001**), 94, 17.
- [46] G Parthipan; Thenappan, *J Sol Chem*, (**2007**), 36, 1231.
- [47] V P Pawar; S C Mehrotra; *J Mol Liq*, (**2003**), 108, 95.
- [48] S C Mehrotra; J E Boggs; *J Chem Phys*, (**1977**), 66, 5306.
- [49] S Glasstone; K J Laidler; H Eyring; Mc Graw Hill; Newyork, 1941.
- [50] K K Gupta; A K Bansal; P J Singh; K S Sharma; *Ind J Phys*, (**2005**), 79, 147–152.
- [51] G Parthipan; G Arivazhagan; T Thenappan; *Philhos Mag Lett*, (**2008**), 88, 125–136.