

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

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ABSTRACT - Microwave dielectric spectra for binary mixtures of Monoethanolamine with 2-Alkoxyethanols have been determined over the frequency range of 10 MHz to 20 GHz at 303.15K using Time Domain Reflectometry technique (TDR). The complex dielectric spectra of Monoethanolamine, 2-Methoxyethanol, 2-Ethoxyethanol and 2-Butoxyethanol and their binary mixtures were measured at different concentrations. The dielectric permittivity (ϵ'), dielectric loss (ϵ''), dielectric constant (ϵ_0) and relaxation time (τ) were determined from the complex dielectric spectra of pure liquids and binary liquid mixtures by fitting the Debye model using the least-square fitting method. The molecular interaction parameter like Bruggeman factor (f_B), effective Kirkwood correlation factor (g_{eff}), corrective Kirkwood correlation factor (g_r) were calculated and interpreted accordingly. Similarly the excess dielectric constant (ϵ^E), excess inverse relaxation time ($1/\tau$) and thermodynamic properties like excess Helmholtz free energy (ΔF^E) and Free energy of activation for relaxation time ($\Delta F\tau$) were also calculated and interpreted on the basis of nature of molecular interaction.

Keywords: Time domain Reflectometry, Monoethanolamine, 2-Alkoxyethanols, Dielectric relaxation time, Bruggeman factor, Kirkwood correlation factor and Excess thermodynamic Parameters.

1. INTRODUCTION

Time domain reflectometry technique is a powerful tool to identify the inter and intra-molecular interactions of the liquid and liquid mixtures. Dielectric studies on mixtures of polar liquids either in the pure state or with the other polar liquids has been a subject of interest because they provide useful information regarding molecular complex formation in solution [1]. Dielectric approach is a powerful tool for the determination of molecular structure. Recently dielectric relaxation behavior of mixtures of polar molecules under varying conditions, of compositions, temperature and environmental factors has evoked considerable interest [2-5].

Alcohols play an important role in many chemical reactions due to the ability to undergo self-association with manifold internal structures and are widely used in industry and science as reagents, solvents and attract great attention as useful solvents in the green technology [6-8]. Amines selected were of industrial importance particularly MEA is used as feed stock in the production of detergents, emulsifiers, polishers, pharmaceuticals, corrosion inhibitors, chemical intermediates. The aim of our present investigation is to study the molecular interaction between the molecules of the participating liquids using Time domain Reflectometry technique at 303.15K over the frequency range of 10 MHz to 20 GHz. The systems studied here are monoethanolamine (MEA) with 2-Methoxyethanol, 2-Ethoxyethanol, 2-Butoxyethanol.

2. MATERIAL AND METHODS

2.1 MATERIALS

AR Grade samples of Monoethanolamine, 2-methoxyethanol, 2-ethoxyethanol and 2-butoxyethanol were purchased from SD Fine chemical Pvt. Ltd., Mumbai. In the present study the chemicals were used without any further purification.

2.2. METHODS

The complex dielectric spectra were measured using Time Domain Reflectometry (Agilent infinity DCA-J 86100A with sample oscilloscope HP 54754A). A repetitive fast rising time step voltage pulse of 39 picoseconds (ps) was fed through a 50Ω impedance semi-rigid slim probe having 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 refractive indices of the pure and binary liquid mixtures under investigation were measured using an Abbe's refractometer at 303.15K. The dielectric constant at infinite dilution (ϵ_∞) has been calculated by using the following relation ($\epsilon_\infty = n_D^2$).

3. RESULTS AND DISCUSSION

Table-1: Dielectric constant (ϵ_0) and Relaxation time (τ) of pure liquids

Liquids	(ϵ_0)		(τ) ps	
	Experimental	Literature	Experimental	Literature
Monoethanolamine	31.36	31.46 ⁹	116.12	119.64 ⁹
2-Methoxyethanol	16.76	16.54 ¹⁰	27.79	30.16 ¹¹
2-Ethoxyethanol	15.91	16.45 ¹²	40.24	40.43 ¹²
2-Butoxyethanol	08.86	08.00 ¹³	52.61	52.69 ¹³

3.1 Dielectric permittivity (ϵ')

The complex permittivity spectra of two pure liquids as well as the three binary mixtures of Monoethanolamine (MEA) with 2-methoxyethanol(2-ME), 2-ethoxyethanol(2-EE) and 2-butoxyethanol (2-BE) are shown in Figs.1(a),2(a) and 3(a). In the case of MEA with 2-alkoxyethanols systems, a graph is drawn between dielectric permittivity (ϵ') on the Y-axis and Log F on the X-axis. From the graph it is inferred that the dielectric permittivity (ϵ') is comparatively high for MEA and is low for 2-alkoxyethanols. As the concentration of MEA increases, the dielectric permittivity (ϵ') values gets increases. In other words as the concentration of 2-alkoxyethanols increases the dielectric permittivity (ϵ') values gets decreases. Hence (ϵ') values are directly proportional to the 2-alkoxyethanols concentrations and inversely proportional to the MEA concentration.

3.2 Dielectric loss (ϵ'')

Similarly a graph is drawn between dielectric loss (ϵ'') on Y-axis and Log F on X-axis and is shown in Figs.1(b),2(b) and 3(b). The position of the peak of the curves shifts towards higher side (right) of Log F. As the Log F increases the dielectric loss (ϵ'') also increases. It is found that when comparing all the three alcohols with Monoethanolamine. The dielectric loss is in the order of 2-ME > 2-EE > 2-BE. It also refers that as the chain length of alcohol increases the dielectric loss (ϵ'') decreases (ie) the chain the chain length of alcohol is inversely proportional to dielectric loss.

The relaxation behavior of MEA with 2-Alkoxyethanols system agrees with Debye model. The experimental values of $\epsilon^*(\omega)$ were fitted with the Debye equation [14 -16] To determine the values of dielectric parameters The static dielectric constant (ϵ_0), static permittivity at high frequency(ϵ_∞) and relaxation time (τ) were obtained by using the non-linear least-squarefit [17] method. The general form of the relaxation model is given by Havriliak-Nigami equation [18].

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

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.

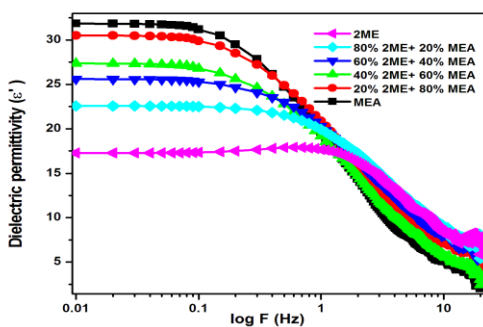


Fig 1 : (a) Dielectric permittivity spectra vs. Log F (Hz) of Monoethanolamine with 2-Methoxyethanol

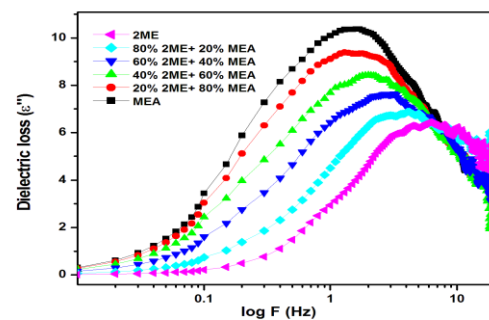


Fig 1 : (b) Dielectric loss spectra vs. Log F (Hz) of Monoethanolamine with 2-Methoxyethanol

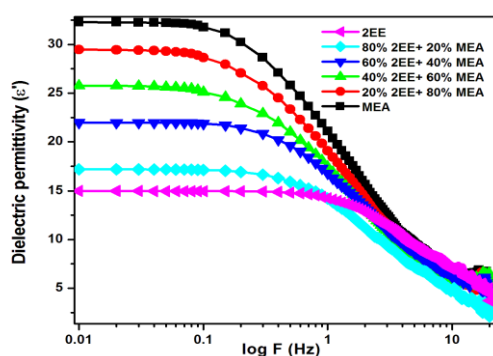


Fig 2 : (a) Dielectric permittivity spectra vs. Log F (Hz) of Monoethanolamine with 2-Ethoxyethanol

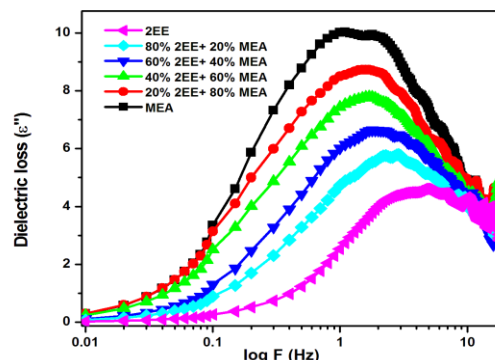


Fig 2 : (b) Dielectric loss spectra vs. Log F (Hz) of Monoethanolamine with 2-Ethoxyethanol

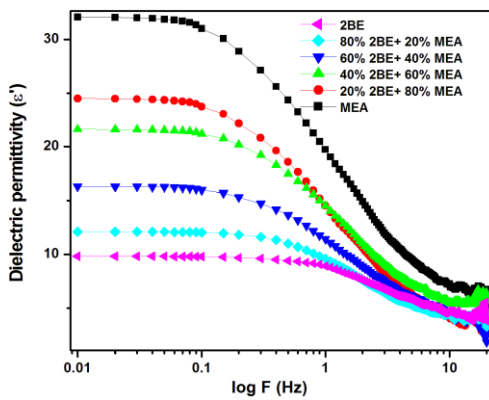


Fig 3 : (a) Dielectric permittivity spectra vs. Log F (Hz) of Monoethanolamine with 2-Butoxyethanol

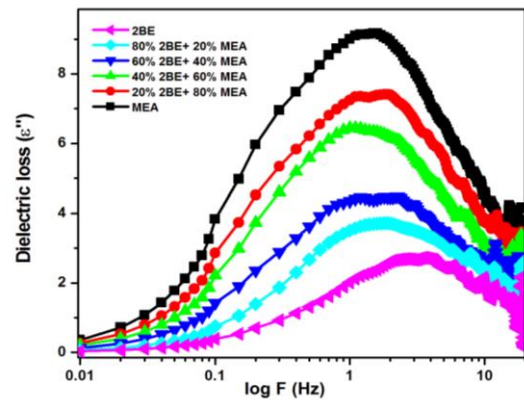


Fig 3 : (b) Dielectric loss spectra vs. Log F (Hz) of Monoethanolamine with 2-Butoxyethanol

But for the polar-polar binary mixtures volume percentage of all concentration of monoethanolamines with alcohols could fit Debye dispersion. Therefore The experimental values of $\epsilon^*(\omega)$ were fitted to the Debye equation as,

$$\epsilon^*(\omega) = \epsilon_\infty + \frac{(\epsilon_0 - \epsilon_\infty)}{[1 + (j\omega\tau)]^\beta} \quad (2)$$

3.3 Static dielectric constant (ϵ_0)

The static dielectric constant values of MEA is (31.36), 2-ME is (16.76), 2-EE is (15.91) and 2-BE is (8.86) and are listed in Table (1), respectively. In the case of MEA with 2-ME,2-EE and 2-BE systems, as the volume percent of MEA increases the static dielectric constant (ϵ_0) values are also gets increases.

3.4 Dielectric constant at an optical frequency (ϵ_∞)

The dielectric constant at an optical frequency (ϵ_∞) values gets increases as the volume percentage of monoethanolamine increases from the 2-alkoxyethanol values and approaching towards the monoethanolamine values.

Table: 2. 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 the volume fraction of Monoethanolamine (ϕ_2)

ϕ_2	ϵ_0	ϵ_∞	τ Ps	ΔF_τ KJ/mol
System I: Monoethanolamine+2-Methoxyethanol				
0	16.76	1.968	27.79	123.24
0.2	21.95	2.005	51.48	124.80
0.4	24.53	2.036	73.86	125.71
0.6	25.77	2.066	92.68	126.28
0.8	29.01	2.092	102.57	126.53
1.0	31.36	2.113	116.12	126.85
System II: Monoethanolamine+2-Ethoxyethanol				
0	15.91	1.986	40.24	124.18
0.2	16.72	2.020	67.69	125.49
0.4	21.24	2.053	85.07	126.06
0.6	24.35	2.067	104.01	126.57
0.8	27.81	2.088	105.89	126.61
1.0	31.36	2.113	116.12	126.85
System III: Monoethanolamine+2-Butoxyethanol				
0	8.86	2.019	52.61	124.68
0.2	11.58	2.037	67.15	125.47
0.4	15.18	2.054	89.42	126.19
0.6	20.25	2.080	98.34	126.43
0.8	22.27	2.089	103.42	126.56
1.0	31.36	2.113	116.12	126.85

Table: 3. Values of kirkood correlation factors (g^{eff} , g_f), Bruggeman factor (f_B), Excess dielectric constant (ϵ^E) and excess inverse relaxation time ($1/\tau$)^E with the volume fraction of Monoethanolamine (ϕ_2)

ϕ_2	g^{eff}	g_f	f_B	ϵ^E	$(1/\tau)_{PS}^E$
System I: Monoethanolamine+2-Methoxyethanol					
0	1.415	1.000	1.000	0.000	0.000
0.2	1.762	1.127	0.589	2.262	-0.011
0.4	1.846	1.096	0.412	1.919	-0.012
0.6	1.864	1.014	0.331	0.239	-0.008
0.8	1.976	1.022	0.134	0.562	-0.004
1.0	2.036	1.000	0.000	0.000	0.000
System II: Monoethanolamine +2-Ethoxyethanol					
0	2.096	1.000	1.000	0.000	0.000
0.2	1.816	0.875	0.932	-2.284	-0.007
0.4	1.982	0.962	0.594	-0.862	-0.006
0.6	1.993	0.972	0.393	-0.832	-0.005
0.8	2.019	0.989	0.190	-0.459	-0.002
1.0	2.035	1.000	0.000	0.000	0.000
System II: Monoethanolamine +2-Butoxyethanol					
0	1.572	1.000	1.000	0.000	0.000
0.2	1.453	0.827	0.851	-2.339	-0.002
0.4	1.555	0.832	0.636	-3.097	-0.004
0.6	1.646	0.897	0.396	-2.394	-0.003
0.8	1.744	0.824	0.314	-4.724	-0.001
1.0	2.035	1.000	0.000	0.000	0.000

Table: 4. Values excess Helmholtz free energy (ΔF^E) and its components with the volume fraction of Monoethanolamine (ϕ_2)

ϕ_2	ΔF_{or}^E J/mol	ΔF_{rr}^E J/mol	ΔF_{12}^E J/mol	ΔF^E J/mol
System I: Monoethanolamine +2-Methoxyethanol				
0	0.000	0.000	0.000	0.000
0.2	-95.06	-113.98	8.40	-200.64
0.4	-81.98	-79.02	-15.53	-176.53
0.6	-33.71	-25.90	-27.32	-86.93
0.8	-28.11	-1.32	-41.64	-71.07
1.0	0.000	0.000	0.000	0.000
System II: Monoethanolamine +2-Ethoxyethanol				
0	0.000	0.000	0.000	0.000
0.2	75.80	28.10	52.68	131.29
0.4	29.12	-63.52	22.98	45.74
0.6	25.47	28.65	-11.85	42.27
0.8	13.31	37.52	-28.73	22.11
1.0	0.000	0.000	0.000	0.000
System II: Monoethanolamine +2-Butoxyethanol				
0	0.000	0.000	0.000	0.000
0.2	99.52	0.29	51.12	150.94
0.4	98.37	50.12	36.97	185.47
0.6	53.40	83.12	-14.17	122.36
0.8	110.88	141.19	-18.42	233.66
1.0	0.000	0.000	0.000	0.000

3.4 Relaxation time (τ)

The relaxation time (τ) values of pure liquids are monoethanolamine (116.12 ps), 2-Methoxyethanol (27.79ps), 2-Ethoxyethanol (40.24 ps) and 2-Butoxyethanol (52.61 ps) which are given in Table (1). The relaxation times of 2-alkoxyethanols gets increases as the chain length of the alcohol increases. It means relaxation time of 2-Butoxyethanol ($C_6H_{14}O_2$) > 2-Ethoxyethanol ($C_4H_{10}O_2$) > 2-Methoxyethanol ($C_3H_8O_2$). In the case of polar-polar binary liquid system of monoethanolamine+ 2-methoxyethanol, monoethanolamine+2-ethoxyethanol, and monoethanolamine+2-butoxyethanol systems, as the volume percentage of monoethanolamine increases the relaxation time values gets increases step by step from the 2-alkoxyethanol values and approaching towards the monoethanolamine values (116.12 ps). Which are shown in the table(2) respectively. This result shows that

the relaxation time values may be due to the change in the molecular volume or change in the effective length of the dipole involved in the orientation process [19].

3.5 Bruggeman Factor (f_B)

The information about the solute solute interaction is given by the Bruggeman factor. The effective volume of the solute gets modified and is best illustrated by the non-linearity of the Bruggeman Factor[20]

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

According to equation (3) a linear relationship is expected between Bruggeman factor (f_B) and Volume fraction of monoethanolamine. The linear variation means there is no molecular interaction. But in actual experiment a non linear variation is observed. The calculated (f_B) values are listed in table (3) for all the three systems. Which are shown in fig (4). The ideal Bruggeman equation is indicated by the dotted lines.

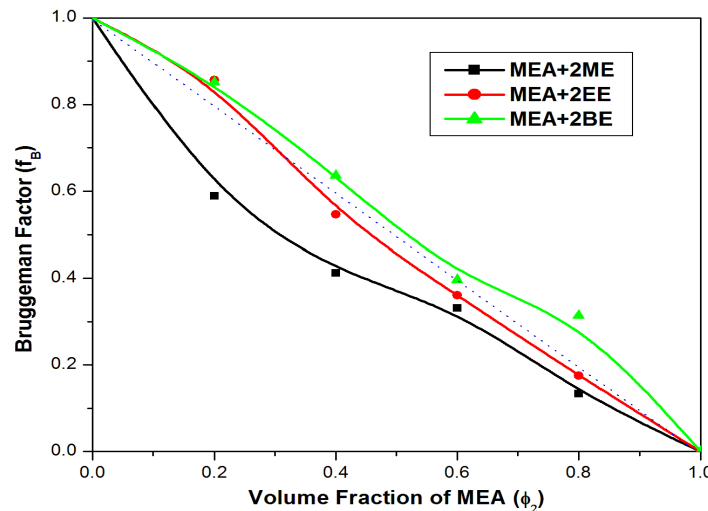


Fig. 4. Bruggeman factor Vs volume fraction of monoethanolamine

The Bruggeman factor (f_B) shows a positive deviation for the MEA+2-BE system whereas it shows a negative deviation for MEA+2-ME and MEA +2-EE systems. The non – linearity of the curves indicate hetero interaction which may be due to hydrogen bonding of the –OH group of alcohol with N-H group of MEA. Similar interpretations were given by Thenappan and Prabakar Devaraj [21] and Patil et al [22]. The positive deviation means more interaction taking place which is observed in the monoethanolamine +2-Butoxyethanol system. The high negative deviation is observed for monoethanolamine+2-methoxyethanol system which means the interaction is comparatively less in this system.

Hence the interaction is in the order of monoethanolamine (MEA)+2-Butoxyethanol (2-BE) > monoethanolamine (MEA)+2-ethoxyethanol (2-EE) > monoethanolamine (MEA)+2-methoxyethanol (2-ME).

3.6. Effective Kirkwood correlation factor (g^{eff})

The structural information about the liquids from the dielectric relaxation parameter may be obtained by using the effective Kirkwood correlation factor, g^{eff} [23]. This factor 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,

$$\frac{4\pi N_A \mu^2 \rho}{9KT M} g = \frac{(\epsilon_0 - \epsilon_\infty)(2\epsilon_0 + \epsilon_\infty)}{\epsilon(\epsilon_\infty + 2)^2} \tag{4}$$

N_A is the Avogadro number, μ is the dipole moment in the gas phase, ρ is the density, K is the Boltzmann’s constant, T is the temperature in Kelvin, M is the molecular weight, (ϵ_0) 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 monoethanolamine with 2-Alkoxyethanols. Equation (4) is modified by assuming that for the mixture g^{eff} has become effective Kirkwood correlation factor in the mixture. The Kirkwood correlation equation for the mixture may be expressed as [24].

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

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}) is calculated by using equation (5).

The effective kirkwood correlation factor(g^{eff}) values are given in Table(3). In general, if the(g^{eff}) values are greater than unity which indicates the parallel orientation of dipoles and if it is less than unity which indicates the antiparallel orientation of dipoles. In our study, the (g^{eff}) Values are increases with the increasing molefraction of MEA. The(g^{eff}) values are greater than one in all the systems studied, it means antiparallel orientation of dipoles are takes place. Hence this tendency leads to the interaction between –OH group of alcohol and N-H group of MEA.

3.7 Corrective kirkwood correlation factor (g_f)

The corrective kirwood correlation factor(g_f) is an another dielectric parameter which supplies essential information regarding interaction of the liquids of the mixture. For an ideal non-interacting mixture(g_f) must be unity and the the deviation of (g_f) from unity indicates the magnitude of interaction between the liquids(i.e) the greater the deviation from unity means the larger the strength of interactions [25].

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

The corrective Kirkwood correlation factor (g_f) was calculated by using equation (6). In the System of MEA with 2-Alkoxyethanols, the values of (g_f) are close to unity for all the system taken for the study. The (g_f) values are found to be slightly greater than unity for MEA+2-ME system indicating that effective dipoles in the mixture are greater than the average of those in the pure liquids. Further, the (g_f) values are found to be slightly less than unity for MEA+2-EE and MEA+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 liquids. The values of (g_f) are found to depend more on concentrations than the temperature, as reported by Balamurugan and Pawar [26-27].

3.8 Excess dielectric constant (ϵ^E)

The excess dielectric constant is defined as [28].

$$\epsilon^E = (\epsilon_0 - \epsilon_\infty)_m - \{(\epsilon_0 - \epsilon_\infty)_1 \phi_1 + (\epsilon_0 - \epsilon_\infty)_2 \phi_2\} \quad (7)$$

Where ϕ_1 and ϕ_2 are volume fraction and suffixes m, 1 and 2 represents mixture liquid 1 (MEA) liquid2 (2-ME), (2-EE) and (2-BE) 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 moments 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 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. Table(3) In our studies of monoethanolamine with 2-Alkoxyethanols, MEA+2-ME System shows positive value. The positive values of excess dielectric constant (ϵ^E) indicate that molecules of the mixtures may form monomers or dimers structures in such a way that the number of effective dipoles increases [29-30]. There is a probability of formation of linear multimers. The negative values of excess permittivity are obtained for the MEA+2-EE & MEA+2-BE systems. The negative value of (ϵ^E) indicates that molecules of the mixtures may form closed multimer structures leading to less effective dipoles [31].

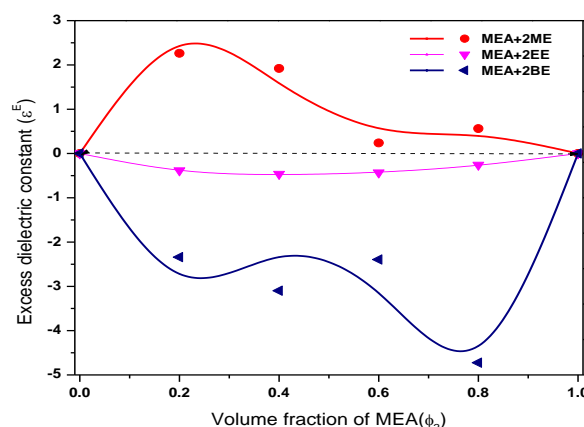


Fig. 5 Excess dielectric constant Vs volume fraction of monoethanolamine (ϕ_2)

3.9 Excess inverse relaxation time $\left(\frac{1}{\tau}\right)^E$

The excess inverse relaxation time is defined as

$$\left(\frac{1}{\tau}\right)^E = \left(\frac{1}{\tau}\right)_m - \left\{ \left(\frac{1}{\tau}\right)_1 \phi_1 + \left(\frac{1}{\tau}\right)_2 \phi_2 \right\} \tag{8}$$

Where $\left(\frac{1}{\tau}\right)^E$ 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 [32]. The information regarding the dynamics of liquids 1 and 2 from this excess property is as follows:

- i. $\left(\frac{1}{\tau}\right)^E = 0$: there is no change in the dynamics of liquids 1 and 2 interaction.
- ii. $\left(\frac{1}{\tau}\right)^E < 0$: the liquids 1 and 2 interactions produces a field such that the effective dipoles rotates slowly.
- iii. $\left(\frac{1}{\tau}\right)^E > 0$: 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 $\left(\frac{1}{\tau}\right)^E$ with volume fraction of MEA are calculated by using the equation (8). As seen from the values of $\left(\frac{1}{\tau}\right)^E$ it is observed that $\left(\frac{1}{\tau}\right)^E$ is negative for all the systems studied in table(3). This indicates that the addition of monoethanolamine with 2-Alkoxyethanols has created a hindering field such that the effective dipole rotates slowly due to the formation of hydrogen bonded structures

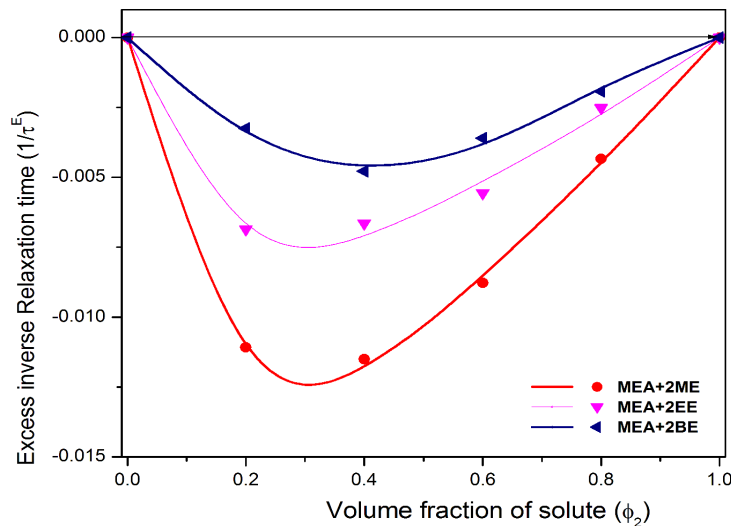


Fig. 6. Excess inverse relaxation time $(1/\tau)^E$ Vs volume fraction of monoethanolamine (ϕ_2)

3.10 Free energy of Activation for relaxation time (ΔF_τ)

$$\Delta F_\tau = RT \cdot 2.303 \log_{10} \left[\frac{\tau_0 K T}{h} \right] \tag{9}$$

The free energy of activation for relaxation time (ΔF_τ) for all the three systems are reported in Table (2). It is clear from the (ΔF_τ) values of monoethanolamine(MEA) with 2-Alkoxyethanols systems that the relaxation time involves rotational motion only and not due to translational motion [34] which is pertaining to the free energy of activation for viscous flow (ΔF_η).

3.11 Excess Helmholtz free energy (ΔF^E)

The Excess Helmholtz free energy give information on the interaction between the molecules of participating liquids in the mixture through the breaking mechanism of the H-bonds. The excess free energy due to mixing is given as [35].

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

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 similar molecules and (ΔF_{12}^E) represents the excess free energy due to short range interaction between dissimilar molecules. The above equation is given in detail as

$$\Delta F^E = -\frac{N_A}{2} \left\{ \begin{aligned} & \left[\sum_{r=1,2} X_r^2 \mu_r^2 (R_{fr} - R_{fr}^0) \right] \\ & + \left[\sum_{r=1,2} X_r^2 \mu_r^2 (g_{rr} - 1) \times (R_{fr} - R_{fr}^0) \right] \\ & + \left[X_1 X_2 \mu_1 \mu_2 (g_{12} - 1) \times (R_{f1} + R_{f2} - R_{f1}^0 - R_{f2}^0) \right] \end{aligned} \right\} \quad (11)$$

$$R_{fr}^0 = \left(\frac{8\pi N_A}{9V_r} \right) \frac{(\epsilon_r - 1)(\epsilon_{\infty} + 2)}{(2\epsilon_m + \epsilon_{\infty r})} \quad (12)$$

$$R_{fr} = \left(\frac{8\pi N_A}{9V_r} \right) \frac{(\epsilon_m - 1)(\epsilon_{\infty r} + 2)}{(2\epsilon_m + \epsilon_{\infty r})} \quad (13)$$

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 frequency, of the pure liquids respectively.

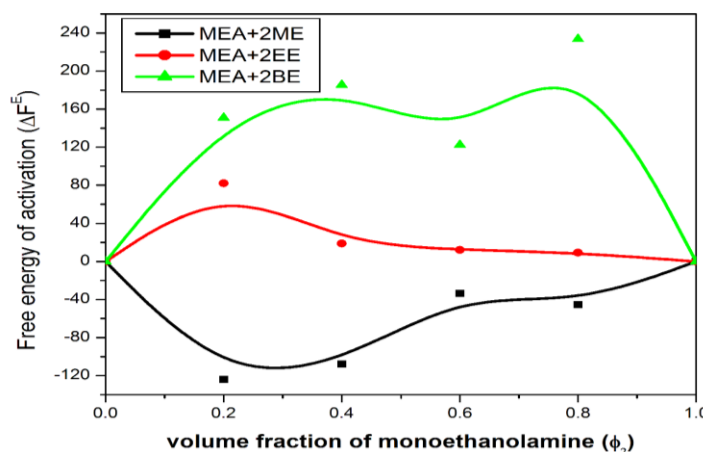


Fig. 7. Free energy of Activation (ΔF^E) VS volume fraction of Monoethanolamine (ϕ_2)

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 calculated for monoethanolamine+2-alkoxyethanols and are given in Table (4). In the case of MEA+2-ME System the values of (ΔF_{0r}^E) are negative for all concentration of MEA. It means that the repulsive forces are dominant. Whereas in the case of MEA+2-EE and MEA+2-BE systems the (ΔF_{0r}^E) values are positive. It means that the attractive forces are dominant.

The second term ΔF_{rr}^E , gives the excess free energy due to short range interaction between the similar molecules. As the concentration of monoethanolamine increases ΔF_{rr}^E , values for all the concentration of MEA+2-ME system is negative and MEA+2-EE systems at only one concentration is negative. The ΔF_{rr}^E values for MEA+2-EE and MEA+2-BE systems are all positive and indicates strong short ranges interaction through H-bonding.

The magnitude of ΔF_{12}^E , gives information on the strength of interactions between dissimilar molecules. The values of ΔF_{12}^E , calculated in the systems of MEA+2-Alkoxyethanols are both the positive and negative, which indicates that the hetero interaction between the compounds which are varying with concentration and temperature. A graph is drawn between the total Helmholtz free energy (ΔF^E) Vs volume fraction of monoethanolamine and is shown in fig (7). The high negative values of ΔF^E were observed for the MEA+2-ME system, which indicates that, the formation of α - clusters with parallel alignment of dipoles. In MEA+ 2-EE, and MEA+ 2-BE system, positive ΔF^E values are observed which indicates that the formation of β -cluster with anti-parallel alignment of dipoles[36-37].

3.12. Molecular interaction of NH₂ and OH group

Molecular interactions are important in diverse fields of protein folding, drug design, material science, sensors, nanotechnology, separations, and origin of life. Molecular interactions are also known as non-covalent interactions or intermolecular interactions. Molecular interactions are not bonds. Especially, hydrogen bonds are by far the most important specific interactions in biological recognition processes. In our case, the molecular interactions between NH₂ and OH group are shown in Figs. (7), (8) and (9).

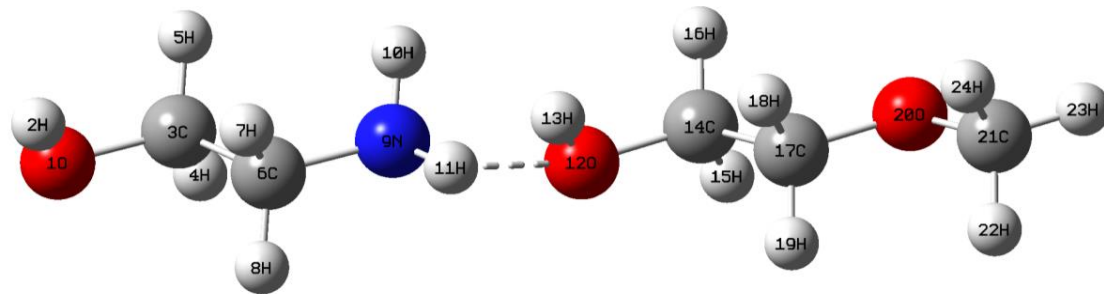


Fig:7. Hydrogen bond interaction between Monoethanolamine (C_2H_7NO) + 2-Methoxyethanol ($C_3H_8O_2$)

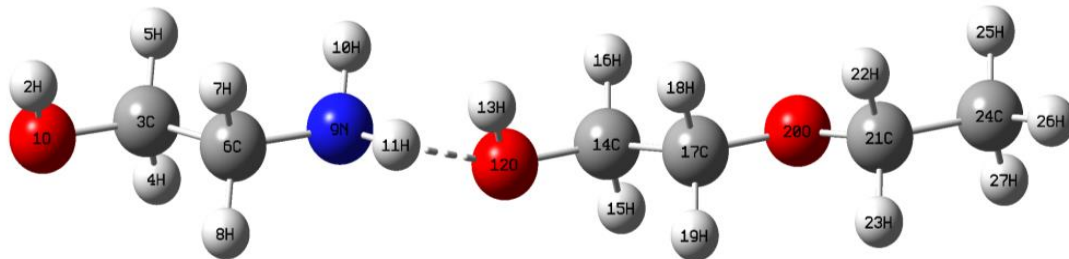


Fig:8. Hydrogen bond interaction between Monoethanolamine (C_2H_7NO) + 2-Ethoxyethanol ($C_4H_{10}O_2$)

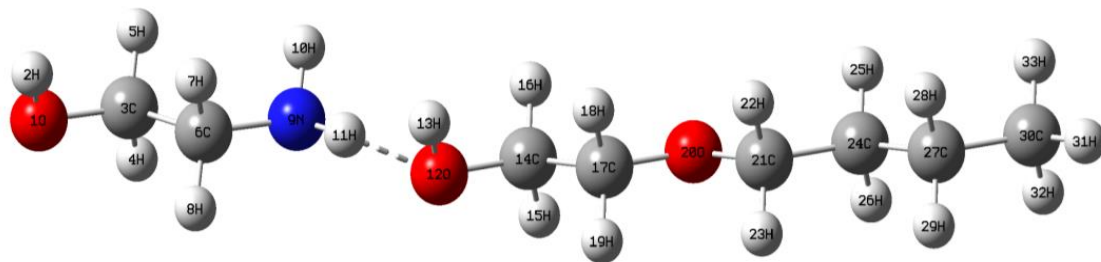


Fig:9. Hydrogen bond interaction between Monoethanolamine (C_2H_7NO) + 2-Butoxyethanol ($C_6H_{14}O_2$)

4. CONCLUSION

Time domain reflectometry technique is a powerful tool to identify the inter and intra-molecular interactions between the Monoethanolamine with 2-Methoxyethanol, 2-Ethoxyethanol, 2-Butoxyethanol. The Dielectric permittivity (ϵ'), Dielectric loss (ϵ''), Relaxation time (τ) were determined from the complex permittivity spectra of pure liquids and binary mixtures.

Bruggeman factor (f_B) shows a higher interaction for monoethanolamine +2-Butoxyethanol system by showing positive deviation (i.e) above the Bruggeman dotted line. Where as it shows a lesser interaction in case of monoethanolamine + 2-Methoxyethanol system (i.e) below the Bruggeman dotted line. From this parameter it is understood that the nature of molecular interaction is higher for large chain length alcohol liquid (MEA+2-BE) when compared to lower chain length alcohol liquid (MEA + 2-ME).

Effective Kirkwood correlation factor (g^{eff}) values are greater than one which indicate anti-parallel orientation of dipoles takes place between the system studied. The (g_f) values for MEA+2-ME system shows that effective dipoles in the mixture are greater than the average of those in the pure liquids. where as in the case of MEA+2-EE and MEA+2-BE systems the effective dipoles in the mixture are smaller than the average of those in the pure liquids.

From the excess dielectric constant (ϵ^E) values of MEA+2-ME System, the molecules of the mixtures may form monomers or dimers structures which leads to the increase of the number of effective dipoles. Where as in the case of MEA+ 2-EE and MEA+2-BE systems, the molecules of the mixtures may form closed multimer structures leading to less effective dipoles.

$(1/\tau)^E$ values obtained are all negative. Which means they created a hindering field such that the effective dipole rotates slowly, due to the formation of hydrogen bonded structures. The free energy of activation for relaxation time (ΔF_τ) for MEA+ 2-Alkoxyethanols systems indicates that the relaxation time involves rotational motion only and not due to translational motion.

From the excess Helmholtz free energy (ΔF^E) it is observed that in MEA+2-ME system, there is a formation of α - clusters with parallel alignment. But in the case of MEA+ 2-EE and MEA+ 2-BE system, there is a formation of β -cluster with anti parallel alignment of dipoles.

Hence it is concluded from the Bruggeman interaction parameters that the interaction is in the order of MEA+ 2-BE>MEA+2-EE>MEA+2-ME, Which indicates the existence of hydrogen bonding interaction or dipole - dipole interaction or weak interaction between solute-solute mixtures.

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