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Dielectric Study of Ethylene Glycol, Diethanolamine at Giga Hertz Frequency, using TDR

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ABSTRACT: The dielectric relaxation measurement on binary mixture of ethylene glycol with Diethanol amine have been carried out for 11 different concentration at 288, 298, 308 & 318 K using the picosecond's time domain reflectometry (TDR) over the frequency range 10 MHz to 20 GHz. The mixture exhibits a principal dispersion of Debye relaxation model at microwave frequencies. Bilinear calibration method is used to obtain complex permittivity $\epsilon^*(\omega)$ from complex reflection coefficient $\rho^*(\omega)$ over the frequency range of 10 MHz to 20 GHz from complex permittivity. Dielectric parameters were obtained by fitting in nonlinear least square fit method to the Havriliak-Negami expression. The excess permittivity (ϵ^E) has positive value through a system indicates ethylene glycol and Diethanol amine interact such that total effective dipoles get increased and form monomers or dimers. Excess relaxation time ($1/\tau$)^E has negative value through a system indicates ethylene glycol and Diethanol amine interaction produces a field such that the effective dipoles rotate slowly. Deviation from the linearity of various model suggest molecular association through hydrogen bonding between the -OH Group of alcohol and C=O group of Amine.

KEYWORDS: Time domain reflectometry; Ethylene glycol; Diethanol amine; excess parameters.

I. INTRODUCTION

Material	Chemical formula	Density	Refractive Index	ϵ_0	τ
Ethylene Glycol	$C_2H_6O_2$	1.1103 gm/liter.	1.431	42.00	55
Diethanol amine	$C_4H_{11}NO_2$	1.097 gm/liter.	1.477	24.69	285.94

Diethanol amine is a white solid that often exists as a colorless, viscous liquid due to its tendency to absorb water. DEA is widely used in various industries, including personal care products, detergents, and industrial processes [1]. DEA is used as a concrete admixture to improve concrete properties it also used as an emulsifier, dispersing agent, and solvent in various formulations

Ethylene glycol is a clear, colorless, odorless, and viscous liquid with a sweet taste. It is commonly used in antifreeze, deicing solutions, and as a raw material for polyester fibers. While it has many industrial and practical uses, ethylene glycol is toxic and can cause serious health problems if ingested.

Ethylene glycol is studied because it is a good solvent for biological molecule and has a static permittivity half of the pure water.

The importance of measuring the dielectric constant of a liquid lies in the fact that it provides valuable information about intermolecular interaction and dynamics of molecules at molecular levels. In DEAM and ETG molecules the charge distribution is exposed and formation of hydrogen bond. When there is an exposed distribution of charges, there may be very strong intermolecular interaction, however, in shielded distribution relative contribution to neighbor molecules is absent and hence there may be weak intermolecular interaction between the molecules of the liquids. Because of the industrial and biological importance, we have chosen these liquids for present study. Here the picoseconds Time domain reflectometry [1- 4] in reflection mode has been used to obtain dielectric parameters at temperatures of 288, 298, 308 and 318 K. From the dielectric parameters, excess permittivity, excess inverse relaxation time, based on above parameters, intermolecular interaction, and dynamics of molecules at molecular level are discussed.

1. ϵ' and ϵ'' have been widely used in deriving information about intermolecular and intramolecular interaction in liquids.
2. Relaxation time (τ) gives the idea about molecular properties such as size shape, rigidity etc.
3. Excess Permittivity (ϵ^E) and Excess Inverse Relaxation time ($1/\tau \epsilon^E$) gives significant information about the formation of structures like monomers and multimers.

The permittivity of a material (ϵ_s) is a property which describes the charge storing ability of that substance. The application of a static electric field to a solution containing polar molecules will have the effect of aligning the molecules in the direction of the external field. If the field is switched off the molecules do not immediately adopt random orientations. The relaxation time (τ) is a measure of the time taken to reorient its randomizing state. The relaxation time (τ) depends on the temperature and decreases as the temperature is increased, i.e. the larger translation motions of the molecules enable them to randomize their position more quickly when the electric field is switched off [5].

Alcohols (ethylene glycol) have several -OH group attached to the carbon chain. These compounds are able to form hydrogen bond very extensively, which in turn correlate with a long relaxation time.

II. PERMITTIVITY AND RELAXATION TIME

The frequency dependent complex permittivity $\epsilon^* = \epsilon' - j\epsilon''$ data was obtained by using calibration process by using dielectric parameters of raw data. The static dielectric constant (ϵ_s) and relaxation time (τ) for the mixture obtained by fitting experimental data with the Debye equation at four different temperatures have been given in table (1) and are shown in figures (1) and (2) respectively. [4,8,9,10]

Table: 1. Temperature dependent dielectric parameters for binary mixture of Ethylene glycol +Diethanol amine

Conc. of DEAM	ϵ_s				τ			
	288	298	308	318	288	298	308	318
0	42.41	42.18	41.58	41.34	106.33	94.69	83.47	71.61
0.0753	41.39	40.21	39.56	38.81	130.51	107.84	88.69	75.99
0.1549	38.01	37.37	36.09	35.04	183.33	165.22	128.53	102.32
0.2390	36.5	35.56	34.47	33.52	280.46	223.28	177.35	144.8
0.3282	36.02	35.46	34.4	33.55	294.44	234.23	178.32	149.55
0.4229	33.88	33.34	32.06	31.95	391.02	320.47	251.35	178.77
0.5237	31.38	32.09	31.14	30.62	515.39	476.75	326.42	251.56
0.6310	27.78	28.1	29.26	29.07	623.07	595	412.93	310.18
0.7457	26.48	26.86	27.51	27.53	697.1	655.2	507.04	383.16
0.8684	22.21	23.21	24.59	25.27	784.21	725.07	634.78	466.99
1	18.58	19.62	22.28	23.04	905.65	827.59	780.14	616.23

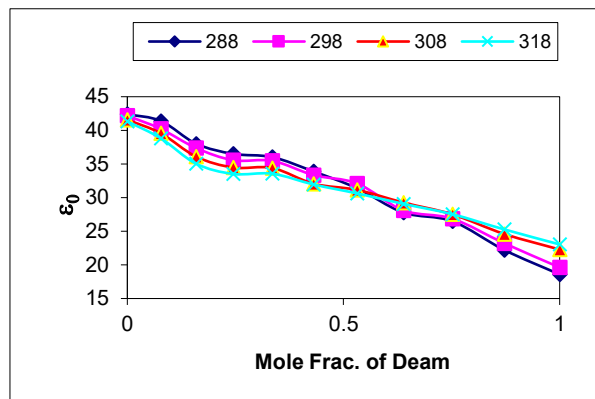


Fig 1: Variation of static dielectric constant (ϵ_s) as a function of mole fraction of Diethanol amine in ethylene glycol at temperatures 288, 298, 308 and 318K.

Table.1 reports the values of dielectric parameters obtained by fitting experimental data to Debye equation [11]. It can be seen that by increasing the concentration of DEAM in ETG the static permittivity of values decreases towards DEAM rich region. This decrease in dielectric constant is due to the transition of elongated molecular aggregate in to spherical aggregate giving rise to anti parallel orientation of the dipoles. Similar conclusion were drawn by shirke et al. [3, 4] for alkyl acetate alcohol system. It is found that in the DEAM rich region the dielectric constant decreases whereas, when the concentration of ETG dominates in the mixture, the static permittivity increases. It is also found that the ϵ_0 and τ values of mixture lie between the individual component values which indicates the solute solvent interaction between the $-OH$ group of ETG and $(C=O)-NH$ group of amine.

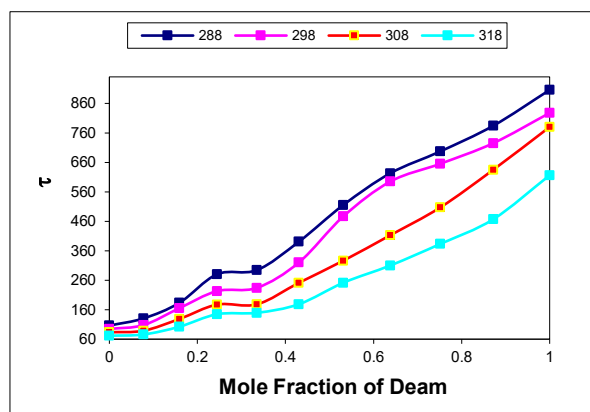


Figure 2: Variation of relaxation time (τ) as a function of mole fraction of Diethanol amine at temperatures 288, 298, 308 and 318K

The relaxation time shows continuous increase with increase in concentration of DEAM in ETG and offers hindrance to the rotation of the molecule. The increase in relaxation time with increase in concentration of DEAM is to be expected in view of the fact that hydroxyl group reorientation depends to some extent on the no of molecules of DEAM to be added in mixture, due to viscosity of mixture get increases. The relaxation time increases with addition of DEAM, which indicate that the degree of cooperativity for reorientation of the molecules increases with increasing length and bulk of the cluster increases. The relaxation time increases with increasing size of molecule, ie relaxation time is directly related to the size of molecules. From this calculated data dielectric constant (static permittivity) & relaxation time we can obtain excess parameter & thermodynamic parameter which gives information about the interaction of solute solvent among the system.

III. EXCESS PERMITTIVITY AND EXCESS INVERSE RELAXATION TIME

The variation of Excess permittivity (ϵ^E) and Excess inverse relaxation time $(1/\tau)^E$ with change in mole fraction of DEAM at different temperatures is shown in fig.3 and 4. The experimental values of both the excess parameters were fitted to the Redlich - Kister equation [15] to obtain B_j coefficients at different temperatures. Using these B_j values excess parameters at various concentrations were calculated and used to draw the smooth curves. The estimated values of B_j are given in table (2)

The excess parameters [20, 23.] related to ϵ_0 & τ provides valuable information regarding solute solvent interaction these properties are also useful for the detection of cooperative domain in the mixture and may give evidence for the formation of multimers in the mixture due to intermolecular interaction.

The excess permittivity is defined as

$$\epsilon^E = (\epsilon_0 - \epsilon_\infty)_m - [(\epsilon_0 - \epsilon_\infty)_A X_A + (\epsilon_0 - \epsilon_\infty)_B X_B]$$

Where X is the weight fraction and suffices M, A, B represent mixture, liquid A and liquid B respectively the excess permittivity provides qualitative information about structure formation in the mixture as follows

1. $\epsilon^E = 0$ indicates the solute and solvent do not interact at all
2. $\epsilon^E < 0$ indicates the solute and solvent interact in such a way that the total effective dipoles are reduced. The solute and solvent may be form multimers leading to the less effective dipoles
3. $\epsilon^E > 0$ indicates the solute and solvent interact in such a way that the total effective dipole moment increases. There is a formation of monomers and dimmers.

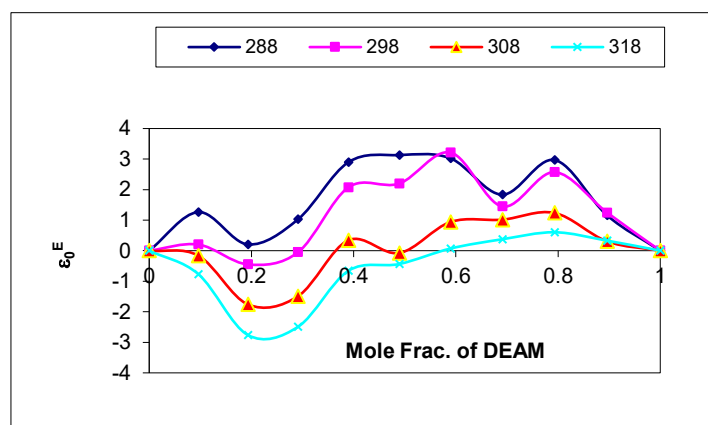


Fig 3. Variation of excess permittivity (ϵ^E) as a function of mole fraction of Diethanolamine at 288, 298, 308 and 318K.

Fig.3 shows the plot of excess permittivity against mole fraction of DEAM for all four temperatures. In the present study excess permittivity values are found to be near to zero in ETG reach region and positive near mixture of equal concentration, for all temperatures and concentrations, which indicates that the total effective dipoles are increases in the mixture. This is due to parallel or cooperative alignment of the dipoles of the two interacting solvent molecules. The curves are more deviated from zero at equal concentration region indicates strong intermolecular interaction in this region.

The excess inverse relaxation time is defined as

$$(1/\tau)^E = (1/\tau)_m - [(1/\tau)_A X_A + (1/\tau)_B X_B]$$

Where $(1/\tau)^E$ is the excess inverse relaxation time, which represent the average broadening of dielectric spectra. The inverse relaxation time analogy is taken from spectral line broadening (which is the inverse of relaxation time) from resonant spectroscopy [30]

The information regarding the dynamics of solute solvent interaction given from this excess property is as follows

1. $(1/\tau)^E = 0$ there is no change in the dynamics of solute solvent interaction
2. $(1/\tau)^E < 0$ the solute solvent interaction produces a field such that the effective dipoles rotate slowly.
3. $(1/\tau)^E > 0$ the solute solvent interaction produces a field such that the effective dipoles rotate faster. ie the field facilitates rotation of dipoles.

The variation of $(1/\tau)^E$ with mole fraction of DEAM at 15, 25, 35 and 45^oc at 11 concentration as shown in following fig.

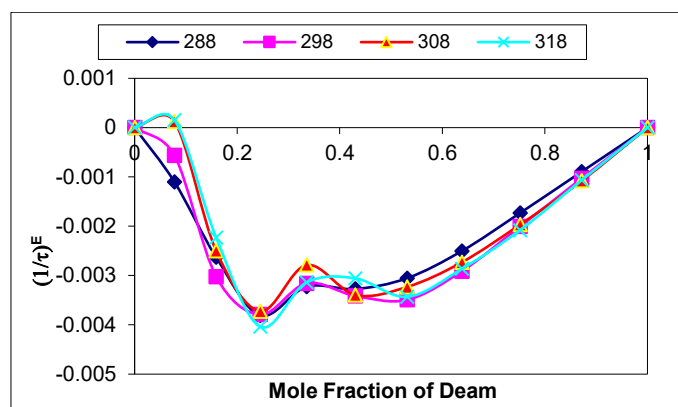


Fig 4 Variation of excess inverse relaxation time $(1/\tau)^E$, as a function of mole fraction of Diethanolamine at 288, 298, 308 and 318K.

From fig.4 it can be seen that, for all the four temperature excess inverse relaxation time values are negative which indicates the formation of linear structure which rotates slowly under the influence of an external varying field. It indicates that addition of DEAM to ETG has created a hindering field such that the effective dipoles rotate slowly.

The variation of Excess permittivity and Excess inverse relaxation time with change in mole fraction of DEAM at different temperatures is shown in fig (3) and (4). The experimental values of both the excess parameters were fitted to the Redlich - Klistler equation [15] to obtain B_j coefficients at different temperatures. Using these B_j values excess parameters at various concentrations were calculated and used to draw the smooth curves.

IV. STATIC PERMITTIVITY AND RELAXATION TIME

From fig 1 it can be seen that the values of static dielectric constant (ϵ_s) decreases with concentration of DEAM in the mixtures. However from fig 2 it can be seen that on addition of DEAM in ETG, value of relaxation time increases gradually. This suggests strong intermolecular interaction among the system which is due to replacement of OH group of ETG by NH₂ of amine and form long Chain molecule so it require more time for reorientation. Due to exposed charge distribution in DEAM strong intermolecular interaction is occurred [19].

Diethanol amine is a polar molecule which have mono-substituted l amine group. The intermolecular forces between molecules containing this substituent and OH group of alcohol are probably larger because of larger dipole moments associated with them and this is probably the primary reason for large relaxation times [5].

V. EXCESS PARAMETERS

The excess parameters related to $(\epsilon_s)^E$ and $(1/\tau)^E$ provides valuable information regarding interaction between the (solute-solvent) liquid mixtures and may give evidence for the formation of monomers or dimers in the mixture due to intermolecular interaction [20].

From figure3. it can be seen that $(\epsilon_s)^E$ is changing from zero to positive with increase of temperature and it has maximum value at equal concentration. This indicates that the molecules of mixture may form monomer or dimer structures in such a way that the effective dipoles get increased. This is due to the parallel (cooperative) alignment of the dipoles in the mixture.

The behavior of $(1/\tau)^E$ is seen in the figure 4 the values of $(1/\tau)^E$ are negative for all concentrations at all temperatures. This suggests that addition of DEAM in the ETG molecule produces hindering field which makes effective dipole rotation slower. i.e. Intermolecular interaction produces field such that the total effective dipoles are rotate slower.

VI. CONCLUSION

The dielectric parameter (ϵ, τ) excess parameter $(\epsilon^E, (1/\tau)^E)$, have been reported for ETG – DEAM mixture for different concentrations and temperatures. These data provide information regarding solute solvent interaction. The investigated values of dielectric parameter show systematic change in dielectric values with increase in temperature and concentration. The negative excess dielectric parameter values indicate the slower rotation of effective dipoles of the system. The dielectric constant decreases and relaxation time increases with increase in concentration of DEAM whereas decrease with increase in temperature. These studies suggest an interaction between ETG and DEAM.

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