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High Frequency Dielectric Response of Glycerol – NN Dimethyl Formamide Binary Mixture at 288,298,308 & 318 K using Time-Domain Reflectometry

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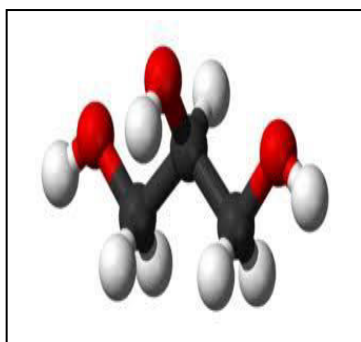
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ABSTRACT: The dielectric relaxation measurement on binary mixture of glycerol with Dimethyl formamide have been carried out for 11 different concentration at 288,298,308 & 318 K using the picoseconds' time domain reflectometry (TDR) over the frequency range 10 MHz to 20 GHz. The mixture exhibit a principle 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 10 GHz, from complex permittivity Dielectric parameters were obtained by fitting in non linear least square fit method to the Havriliak-Nigami expression. The excess permittivity (ϵ^E) has negative value through a system indicates glycerol and Dimethyl formamide interact such that total effective dipoles reduces and form multimers. Excess relaxation time $(1/\tau)^E$ has negative value through a system indicates glycerol and Dimethyl formamide interaction produces a field such that the effective dipoles rotate slowly. Kirkwood correlation factor (g^{eff}) has decreasing trend from pure liquid to mixture indicates dipoles are alien antiparallel which does not cooperate the field. Activation energy and Bruggeman factor are also calculated seen systematic variation to study the solute solvent interaction. Deviation from the linearity of various model suggest molecular association through hydrogen bonding between the -OH Group of alcohol and C=O group of amide.

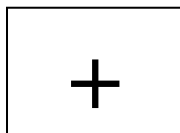
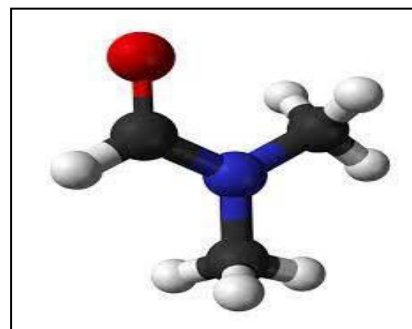
KEYWORDS: Time domain reflectometry; Glycerol; N methyl acetamide; excess parameters; Kirkwood correlation factor; Bruggeman factor; activation energy.

I. INTRODUCTION

Glycerol



NN Dimethyl formamide



Material	ρ	MP	BP	n_D (RI)	μ_D	UV λ_{max}
Glycerol	1.261	17.9 ^o c	290 ^o c	1.4746	---	192nm
Dimethyl Formamide	0.948	-61 ^o c	153 ^o c	1.4305	3.86D	270nm

P-Density, MP-Melting point, BP- Boiling point, n_D - Refractive index, Dipole moment, UV- λ_{max} – Maximum Wavelength.



Dimethyl formamide is industrially important chemical it represent an important class of organic solvents of amides due to high polarity, strong solvating power and a large liquid state range. Substitution at the amide nitrogen atom allow to control the extent of intermolecular hydrogen bonding, which is the dominating factor for the physical properties exhibited by the liquid further more amides may be used as model system for peptide [1] Alcohol play an important role in many chemical reactions on account of their ability to undergo self association with manifold internal structures and are widely used in industry and science as reagent and humectant, solvent and fuels [2] and attract great attention as useful solvent in the green technology [3,4] reported the dielectric parameters for methyl acetate- Alcohol and ethyl acetate – alcohol mixture at different temperature and concentrations dielectric parameter for dimethyl sulphoxide- alcohol and dimethyl formamide- alcohol mixture were reported by khirade et al using time domain reflectometry [5,6] Chaudhary and mehrotra [7] reported the dielectric parameters pyridine alcohol mixture using TDR [8] P. Sivagurunathan et al. Reported the dielectric parameter for acrylate – alcohol mixture [psivagurunathan] using time domain reflectometry. Prabhakar undre et al. Reported microwave dielectric characterization of binary mixture of formamide- NNdimethyl amino ethanol

Dielectric relaxation study of liquid mixture gives information about molecular interaction. Dielectric relaxation spectroscopy has proven a powerful tool for an investigation of H-Bond rearrangement dynamics and been widely applied for investigating pure solvent, solute solvent mixture, super cooled and glass forming liquid, water organic compound mixture & electrolyte solutions. Glycerol is associated polar liquid with an –OH group and Dimethyl formamide is non associated polar liquid with C=O group. It is interesting to see the nature of interaction between alcohol and Dimethyl formamide at different temperature range.

The aim of present investigation is to reported a systematic variation in dielectric parameter of binary mixture at 11 different concentration at 15, 25, 35 & 45^oC temperature by using time domain reflectometry in the frequency range 10 MHz to 20 GHz. The experimental data are fitted to different relaxation model [11, 12, and 13] by the non-linear least square fit method. It is observed that the Debye model is adequate to describe major dispersion for present system. Static dielectric constant and dielectric relaxation time could be obtained by fitting the spectra to the Debye model. The static dielectric constant and relaxation time have been used to determine the excess permittivity, excess inverse relaxation time and other dielectric parameters.

II. EXPERIMENTAL SETUP

Chemical and sample preparation

GLY and DMF are obtain commercially with 99.9% purity and analytical reagent (AR) grade and are used without further purification. The solutions were prepared at different volume percentage in the step of 10% at room temperature. The concentration were prepared for 5 ml solution at room temperature assuming ideal mixing behavior, within 0.02% Error limit

Apparatus

The complex permittivity was studied using time domain reflectometry. The hewlet pacard HP54750A sampling oscilloscope with HP54754A TDR plug in model was used. After observing TDR response for the sample under study the time window was kept on 5 ns & a fast rising step voltage pulse of about 39 ps rise time generated by a pulse generator was propagated through a coaxial line having characteristic impedance of 50 Ω . The system under study was placed at the end of coaxial line in the SMA (standard military Application) coaxial cell with 3.5 mm outer diameter and 1.3 mm effective pin length. To reduce noise, time dependent response curve was averaged for 64 times and then stored in the memory of the oscilloscope. With 1024 points per waveform

all measurement done under open load condition. The change in the pulse after reflection from sample placed in the cell was maintained by the sampling oscilloscope. The reflected pulse without sample $R_1(t)$ and with sample $R_x(t)$ were stored in the memory and transfer to pc through 1.44flopy disc drive.

A temperature controller system with a water bath and thermostat has been used to maintain the constant temperature with in the accuracy limit of $\pm 1^{\circ}\text{c}$. the sample cell was surrounded by a heat insulating container through which the water of constant temperature using a temperature controller system was circulated.

III. DATA ANALYSIS

The waveform $R_1(t)$ & $R_x(t)$ obtained from TDR are analyzed further to obtain reflection coefficient spectra. In this process the time dependent waveform is converted to frequency dependent waveform using Fourier transformation in the frequency range of 10 MHz to 10 GHz [9,10] as



$$\rho^*(\omega) = \left(\frac{c}{j\omega d} \right) \left[\frac{p(\omega)}{q(\omega)} \right] \dots\dots (1)$$

Where p(ω) and q(ω) are fourier transform of [R1(t)-Rx(t)] by summation and [R1(t) +Rx(t)] by samulon respectively, c is the velocity of light, ω is the angular frequency, d is the effective pin length & j = √-1
 The complex permittivity spectra ε*(ω) were obtain from reflection coefficient ρ*(ω) by applying bilinear calibration method [11] the experimental values of ε*are fitted with the Debye equation [12,23,31]

$$\epsilon^*(\omega) = \epsilon_\infty + \frac{\epsilon_s - \epsilon_\infty}{1 + j\omega\tau} \dots\dots\dots (2)$$

With ε₀, ε_∞, and τ as fitting parameter a non linear least square fit method [23] was used to determine the values of dielectric parameters.

IV. RESULT AND DISCUSSION

Table No 1 Static permittivity and Relaxation time GLY+ DMF

Conc of DMF	ε ₀				τ			
	288	298	308	318	288	298	308	318
0	28.67	33.53	35.52	34.54	486.2	388.9	358.3	271.3
0.0954	28.76	34.71	37.28	37.86	497.7	429.5	340.7	251.3
0.1918	34.69	37.99	39.39	38.79	442	371.5	293	197.9
0.2892	39.16	41.35	41.61	40.5	376.3	275.3	217.4	167
0.3876	42.92	43.21	43.29	40.97	288.3	207.5	164.6	118.3
0.4870	43.81	43.22	42.72	41.74	173.4	137.7	118	89.59
0.5874	43.24	43.9	42.57	41.78	112.1	96.53	82.82	66.17
0.6890	44.8	42.71	42.09	40.79	78.12	65.16	56.36	47.42
0.7915	43.57	42.24	42.71	40.36	49.82	44.33	39.92	39.32
0.8952	41.27	41.29	40.48	38.66	31.51	27.83	25.87	23
1	41.13	40.71	39.49	37.74	18.62	17.36	16.84	14.9

Table 1 reports the values of dielectric parameters obtained by fitting experimental data to Debye equation. It can be seen that by increasing the concentration of DMF in GLY the static permittivity of values increases towards DMF rich region. Increase of dielectric constant is due to the transition of spherical molecular aggregate in to elongated aggregate giving rise to 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 DMF rich region the dielectric constant increases where as, when the concentration of GLY dominates in the mixture, the static permittivity decreases. It is also found that the ε₀ and τ values of mixture lie between the individual component values which indicates the solute solvent interaction between the –OH group of GLY and (C=O) –NH₂ group of amide.

The relaxation time shows continuous decrease with increase in concentration of DMF in GLY and offers hindrance to the rotation of the molecule. The increase in relaxation time with increase in concentration of DMF is to be expected in view of the fact that hydroxyl group reorientation depends to some extent on the no of molecules of DMF to be added in mixture, due to viscosity of mixture get increases. The relaxation time increases with addition of DMF, 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.

The excess parameters [13, 14.] 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 I the mixture due to intermolecular interaction.[15]

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.

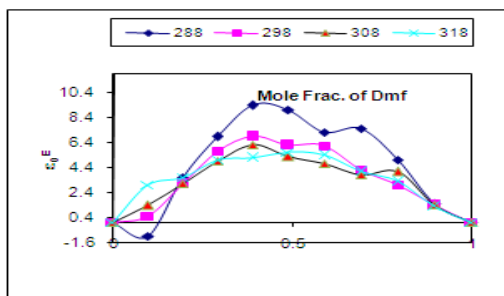


Fig 1 Excess static permittivity against Mole fraction of DMF in GLY

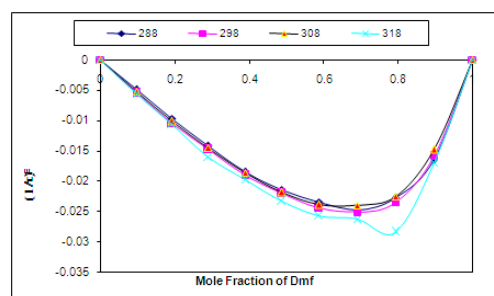


Fig 2 Excess inverse relaxation time against Mole fraction of DMF in GLY

Fig 1 shows the plot of excess permittivity against mole fraction of DMF for all four temperatures. In the present study excess permittivity values are found to be negative for all temperatures and concentrations, which indicate that the total effective dipoles are decreases in the mixture. This is due to antiparallel or opposite 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 [32]

The information regarding the dynamics of solute solvent interaction gives 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 DMF at 15, 25, 35 and 45^oc and at 11 concentration as shown in fig.2 From fig 2 it can be seen that, for all the four temperature excess inverse relaxation 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 DMF to GLY has created a hindering field such that the effective dipoles rotate slowly.

The information about the solute solvent interaction is also given by the Bruggman factor. The effective volume of the solute gets modified by solute –solvent interaction and is best illustrated by non linearity of the bruggman formula [16]



$$F_{BM} = \frac{\epsilon_0 M - \epsilon_0 A}{\epsilon_0 B - \epsilon_0 A} \left(\frac{\epsilon_0 B}{\epsilon_0 M} \right)^{1/3} = 1 - x \quad \dots\dots\dots (3)$$

From fig it can be seen that F_{BM} is not a linear function of volume fraction of DMF. The non linearity of the curve indicates hetero interaction which may be due to hydrogen bonding of the -OH group of GLY with C=O of DMF. The similar interpretation was given by P. Sivagurunathan, Prabhakar et al [17, 18, 26]

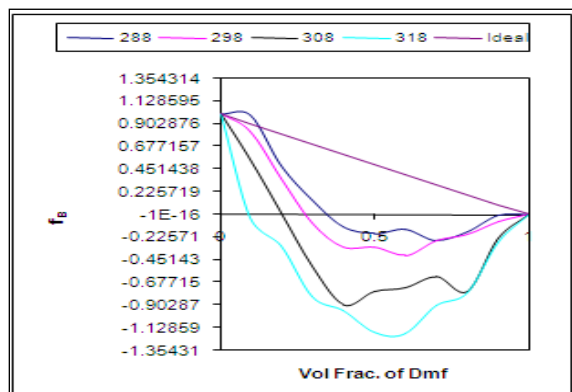


Fig 3 Brugman plot for DMF with GLY

The structural information about the liquid from the dielectric relaxation parameter may be obtained using the Kirkwood correlation parameter g . [19] this factor is also a parameter for obtaining information regarding the orientation of electric dipoles in polar liquids. The g for pure liquid can be obtained by the expression.

$$(4\pi N \mu^2 \rho / 9KT M) g = (\epsilon_0 - \epsilon_\infty) (2\epsilon_0 + \epsilon_\infty) / \epsilon_0 (\epsilon_\infty + 2)^2 \quad \dots\dots\dots (4)$$

Where μ is the dipole moment, ρ is the density at temperature T , M is the molecular weight, K is the Boltzmann constant and N is Avogadro's number. For a binary mixture of two liquids A and B equation 4 is modified [24,25] using the following assumption.

Assume that for the mixture, g^{eff} is the effective correlation factor in the mixture. The Kirkwood equation for the mixture may be expressed as

$$\frac{4\pi N}{9KT} \left(\frac{\mu_A^2 \rho_A}{M_A} \phi_B + \frac{\mu_B^2 \rho_B}{M_B} \phi_A \right) g^{eff} = \frac{(\epsilon_{0m} - \epsilon_{\infty m})(\epsilon_{0m} + \epsilon_{\infty m})}{\epsilon_{0m} (\epsilon_{\infty m} + 2)^2} \quad \dots\dots\dots (5)$$

Where X_A and X_B are the mole fraction of liquids A (GLY) and B (DMF) resp. The calculated values of g^{eff} using equation (5) for all the systems at different concentrations are given in table (2). It can be seen from table (2) that g^{eff} values are smaller at equal concentration region of two liquids and are near to unity at both ends i.e. near to pure liquid rich region g^{eff} values less than unity indicates the antiparallel arrangement of dipoles and near to unity indicates no correlation.



Table No 2 g^{eff} values for GLY+DMF

Volume fraction of DMF	288	298	308	318
0	1.00	1.18	1.25	1.21
0.1	0.96	1.16	1.25	1.27
0.2	1.11	1.22	1.27	1.25
0.3	1.21	1.28	1.29	1.25
0.4	1.28	1.29	1.29	1.22
0.5	1.26	1.24	1.22	1.20
0.6	1.20	1.21	1.18	1.15
0.7	1.20	1.14	1.12	1.09
0.8	1.13	1.09	1.10	1.04
0.9	1.03	1.03	1.01	0.97
1	1.00	0.99	0.96	0.92

Table No 3 g_r values for GLY+DMF

Volume fraction of DMF	288	298	308	318
0	1	1	1	1
0.1	0.96	1.01	1.04	1.09
0.2	1.11	1.09	1.09	1.10
0.3	1.21	1.16	1.14	1.14
0.4	1.28	1.19	1.17	1.15
0.5	1.26	1.17	1.14	1.16
0.6	1.20	1.16	1.12	1.15
0.7	1.20	1.11	1.10	1.11
0.8	1.13	1.08	1.11	1.09
0.9	1.03	1.03	1.04	1.03
1	1	1	1	1

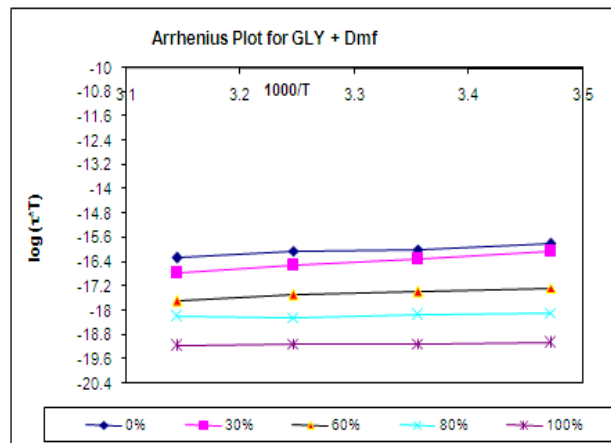


Fig 7 Arrrahenius plot of GLY+DMF Binary mixture

The arrhenius plot of $\ln(1/t)$ vs $(1000/T)$ are plotted in fig (5) for various concentrations. The $\ln(1/T)$ values increases with increase in concentration of DMF all plots having similar slope, which indicates that at all concentrations the activation energy remain almost same.

Conclusion:-

The dielectric parameter (ϵ, τ) excess parameter, the Kirkwood correlation factor and bruggman factor have been reported for GLY – DMF mixture for different concentrations and temperatures. These data provide information regarding solute solvent interaction in liquid. The investigated values of dielectric parameter show systematic change in dielectric values with increase in temperature and concentration. The positive excess dielectric parameter values indicate the faster rotation of effective dipoles of the system. The dielectric constant increases and relaxation time decreases with increase in concentration of DMF where as decrease with increase in temperature. These studies suggest a interaction between GLY and DMF.

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