



Study of Solute-Solvent Interaction through Dielectrics Behavior of N-Methyl Acetamide in Ethanol at High Frequency

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Abstract

Dielectric Behavior of N-methyl Acetamide [C₃H₇NO] – Ethanol [C₂H₅OH] binary mixture at different temperatures 15, 25, 35 and 45°C have been determined over frequency range of 10 MHz to 20 GHz. Using the Time Domain Reflectometry Technique in reflection mode for 11 different concentrations of given binary system has been used to measure reflection coefficient. Further Fourier transform and least square fit method have been used to obtain dielectric parameters such as dielectric constant (ϵ_0) and relaxation time (τ). The dielectric constant decreased with an increase in temperature where as it increased with increase in concentration of NMA in Ethanol. Relaxation time decreased with an increase in temperature and increases with the concentration of NMA in Ethanol. By using dielectric parameters excess permittivity (ϵ^E) has negative values for all concentrations and temperature indicates that total effective dipoles are decreases in the mixture. excess inverse relaxation time ($1/\tau^E$) has positive values in ethanol reach region which indicates that formation of cooperative field to rotate dipole faster, while negative in NMA reach region which indicates the formation of linear structure (non cooperative field) results the slower rotation of dipoles. Kirkwood factor (g^{eff}) g_f , B_j coefficient gives systematic behavior of solute solvent for different concentrations and temperature at high frequency.

Key words: Time domain reflectometry, Dielectric parameters, Excess parameters, Kirkwood correlation factor, and Bruggeman factor.

1. Introduction:

Dielectric relaxation studies on binary mixtures are important for understanding the hydrogen bonding and inter molecular interaction in the mixture. A dielectric study yields the Kirkwood correlation factor, which is strongly correlated with the solute solvent interaction these parameters give systematic change in structure of solute and solvent at different temperature for different concentrations.

Dielectric parameters for Ethanol-tetrahydrofuron, ethanol-dimethyl formamide, ethanol-dimethylsulfoxide, ethanol-2ethoxy ethanol, ethanol-aniline, ethanol-nitrobenzene, ethanol-nitro toluene, were studied by our earlier group (*choudhari et al 1999, 2001, Khirade et al 1999a, 1999b, patil et al 1999*).

All the above systems showed systematic change in the dielectric parameters with Concentration and temperature.

The aim of present work is to report a dielectric study on ethanol – N Methyl Acetamide mixtures conducted using Time Domain Reflectometry [TDR] at the frequency range 10MHz to 20GHz

The dielectric parameters viz. the static dielectric constant ϵ_0 relaxation time τ was determined. The Kirkwood correlation factor, excess dielectric parameters obtained for 15°C, 25°C, 35°C & 45°C in order to obtain structural information about the binary mixtures

2. Experimental setup

Ethanol [AR grade] N Methyl acetamide [AR grade sd. Fine chem. Limited Mumbai] was used without further purification. The solution were prepared by mixing N Methyl Acetamide and ethanol with different concentrations at room temperature assuming ideal mixing behavior Composition in step of 10% by volume with in a 0.02% error limit.

The complex permittivity spectra were studied using TDR (*Cole et al 1989*). A 200mv pulse from a tunnel diode pulse generator block with a rise time of 25ps to 45ps and repetitive frequency of 1 kHz was transmitted along a 3.5mm transmission line with characteristic impedance of 50 Ohms. The sample cell was placed at the end of the transmission line, after the sample head.

The length of transmission line which connects pulse generator and Sampling head was about twice of the transmission line which connects sampling head and cell so that the incident pulse was well separated from the reflected pulse. The required cell was designed in such a way that its impedance matched with the transmission line

A Tektronics 7854 sampling oscilloscope was used to sample the reflected pulse. The time window used for the experiment was kept at 500ps/division or 5ns. The reflected pulse was digitized with 1024 points in the selected time window. The oscilloscope is transfer to computer through 1.44MB floppy.

First, the reflected pulse $R_1(t)$ & $R_x(t)$ without and with a sample in the cell respectively, were recorded. Time referencing was done by matching small reflection due to a particular discontinuity at the beginning of the cell in $R_1(t)$ & $R_x(t)$ subtraction and addition of these pulses were done in the memory of the oscilloscope after proper time shifting. The subtracted pulse and added pulse were transferred to the computer for further analysis

The temperature controller system with a water bath and a thermostat was used to maintain the constant temperature with an accuracy limit of $\pm 1^{\circ}\text{C}$. The sample was surrounded by an insulating container, through which water obtained at a constant temperature using temperature controller system was circulated. The temperature at the cell was checked using an electronic thermometer

3 Data analysis:

The time dependent data were processed to obtain complex reflection coefficient spectra $\rho^*(\omega)$ over the frequency range from 10MHz to 20GHz using Fourier transformation [shannon1949, samulon1951]

$$\rho^*(\omega) = (c/j\omega d) [p(\omega)/q(\omega)] \quad \dots(1)$$

Where ω is the angular frequency, $p(\omega)$ and $q(\omega)$ are the Fourier transform of $R_1(t)-R_x(t)$ and $R_1(t)+R_x(t)$, respectively, c is the velocity of light, d is the effective pin length and

$$j = -1^{1/2}$$

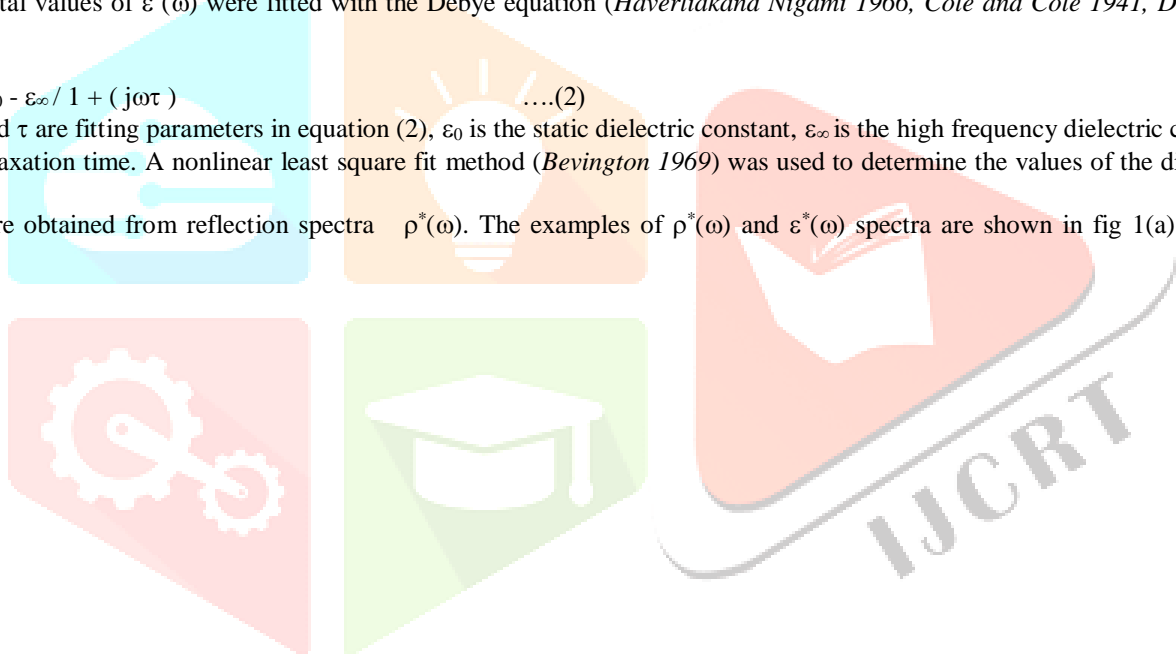
The complex permittivity spectra $\varepsilon^*(\omega)$ were obtained from reflection coefficient spectra $\rho^*(\omega)$ by applying bilinear calibration method (Cole *et al* 1989) in the calibration process, pure liquids were used as a calibrating liquids

The experimental values of $\varepsilon^*(\omega)$ were fitted with the Debye equation (Haverliakand Nigami 1966, Cole and Cole 1941, Davidson and Cole 1950)

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

Where ε_0 , ε_{∞} and τ are fitting parameters in equation (2), ε_0 is the static dielectric constant, ε_{∞} is the high frequency dielectric constant and τ is the relaxation time. A nonlinear least square fit method (Bevington 1969) was used to determine the values of the dielectric parameters.

ie $\varepsilon^*(\omega)$ were obtained from reflection spectra $\rho^*(\omega)$. The examples of $\rho^*(\omega)$ and $\varepsilon^*(\omega)$ spectra are shown in fig 1(a) & 1(b) respectively.



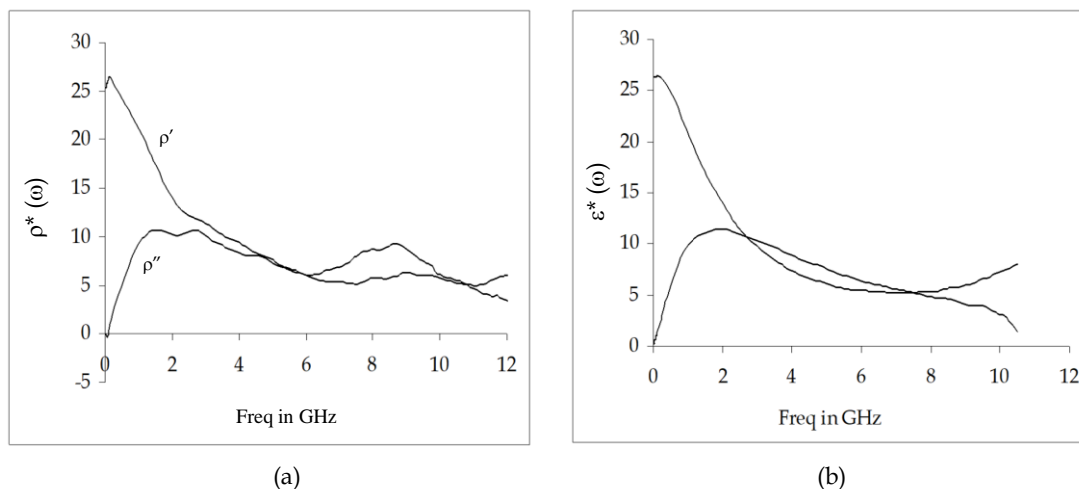


Fig. 1 Spectra for the mixture of 20 % NMA + 80 % Ethanol at 25°C

4. Results and Discussion:

The density, ϵ_0 and τ values for the pure liquids used are given in table 1, along with the values taken from the literature. The static dielectric constant (ϵ_0) and relaxation time (τ) obtained by fitting experimental data to the Debye equation are listed in the table 2.

Table.1. Comparison of data for the liquids with values from the literature at 25°C

Liquids	ϵ_0		τ		$\rho/g\text{ cm}^{-3}$
	This work	literature	this work	literature	
A - Ethanol	24.3	24.7	126.54	146.9	0.7850
B – N Methyl Acetamide	120.12	126.5	586.12	590.22	0.95

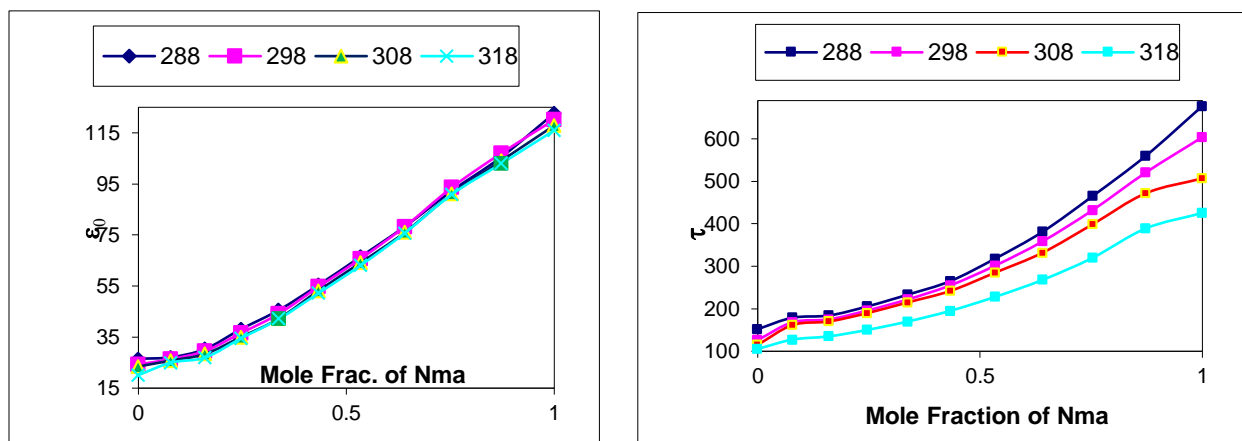
a) Permittivity and relaxation time

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 2.

Table. 2. Dielectric parameters for the N Methyl Acetamide – Ethanol binary system

Conc of NMA	ϵ_0				τ			
	288	298	308	318	288	298	308	318
0	26.20	24.3	23.51	20.11	146.3	126.54	115.2	105.5
0.0783	27.12	26.41	25.82	25.01	179	168.23	161.8	127.5
0.1604	30.33	29.55	28.41	27	184.2	175.12	170.2	135.2
0.2467	38.11	36.57	35.02	34.52	205.7	196.02	189.9	150.4
0.3375	45.56	44.12	42.22	42.08	233.4	222.15	215.2	170.1
0.4332	55.41	54.72	53.22	52.2	265.3	255.25	242.1	195.2
0.5341	66.46	65.64	64.11	63.07	318.3	301.64	285.2	228.1
0.6407	78.32	78.29	76.03	75.76	381.3	358.79	332.1	268.1
0.7535	92.25	93.57	91.05	90.89	465.6	432.49	399.2	320.2
0.8731	105.58	107.07	104.11	103	560.2	520.89	472.1	389.3
1	122.65	120.12	117.89	115.98	675.3	586.04	515.9	458.4

Fig.1. Variation of static dielectric constant (ϵ_s) and Relaxation Time as a function of mole fraction of N Methyl acetamide in Ethanol at temperatures 288, 298, 308 and 318K.



b) Excess Permittivity and Excess Inverse Relaxation Time

The variation of Excess permittivity (ϵ^E) and Excess inverse relaxation time with change in mole fraction of NMA at different temperatures is shown in fig. 2a and 2b. The experimental values of both the excess parameters were fitted to the Redlich - Kister equation [M. I. Aralagappi et al, 1991] 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 3.

The excess parameters 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 parameters (hosamani et al 1995) related ϵ_0 and τ
 ie. Excess permittivity and excess relaxation time provide information about formation of Multimers or monomers in the mixture.

The excess permittivity is defined as

$$\epsilon^E = (\epsilon_0 - \epsilon_\infty)_m - [(\epsilon_0 - \epsilon_\infty)_A X_A + (\epsilon_0 - \epsilon_\infty)_B X_B] \quad \dots 3$$

Where X is the mole fraction and suffix m, A & B represent the mixture, solvent and solute, respectively.

- 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 dimers.

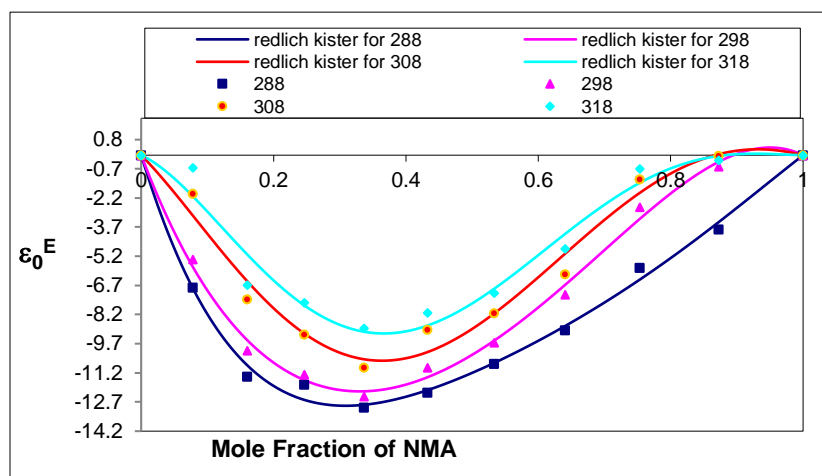
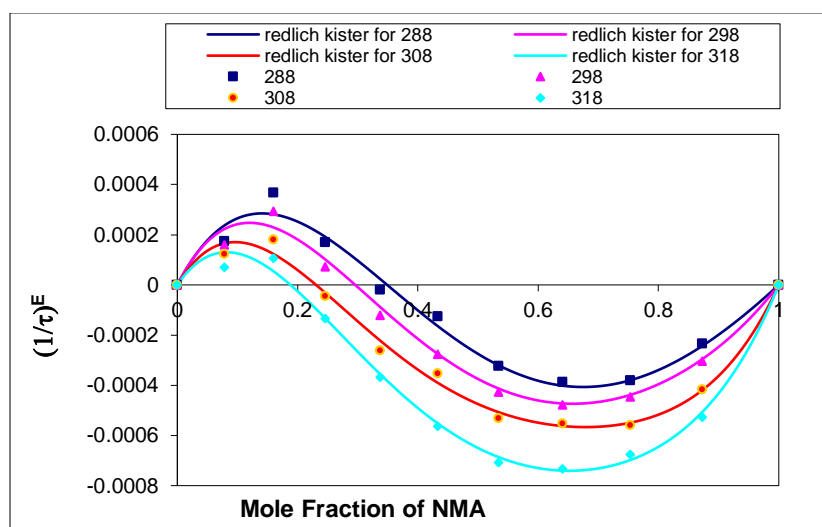
Similarly the excess inverse relaxation time is defined as

$$(1/\tau)^E = (1/\tau)_m - [(1/\tau)_A X_A + (1/\tau)_B X_B] \quad \dots 4$$

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 (Mehrotra and Boggs, 1977)

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 slower.
- 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.

Fig.2a. Variation of excess permittivity (ϵ^E) as a function of mole fraction (x_2) of NMA at 288, 298, 308 and 318K.Fig.2b. Variation of excess inverse relaxation time ($1/\tau$)^E, as a function of mole fraction (x_2) of NMA at 288, 298, 308 and 318K.

In the present work (ϵ^E) is positive in the solvent rich region. This indicates the formation of monomeric structure, which increases the total number of dipoles. Where as in the solute rich region, ϵ^E is negative, indicating formation of dimeric structures, which leads to a decrease of the total number of dipoles in the system

The excess relaxation time of these systems is positive in the solvent rich region. This indicates fast rotation of dipole. This may be due to the formation of monomeric structures in this region. In the DMA rich region these values are negative. This indicates the formation of structure probably dimeric, which rotate slowly.

The experimental values of both excess parameters were fitted to the redlich- kister equation

$$Y^E = (X_A X_B) \sum_K B_K (X_A - X_B)^K \quad \dots 5$$

Where Y is either ϵ^E or $(1/\tau)^E$ By using the B_K values Y^E values were calculated & used as to draw curves shown in fig 2a and 2b.

Table 3. The estimated values of B_j coefficients in Redlich-Kister equation for Ethanol- N Methyl acetamide mixture at different temperatures.

Parameter	B_j coefficient	Temperature			
		288 K	298 K	308 K	318 K
$(\epsilon_s)^E$	B_0	-44.802	-41.081	-35.759	-30.512
	B_1	29.456	40.881	44.356	42.218
	B_2	-24.556	4.3499	22.758	22.905
	B_3	13.386	12.403	-22.904	-33.892
$(1/\tau)^E$	B_0	-0.0011	-0.0015	-0.0019	-0.0026
	B_1	-0.0029	-0.0025	-0.0021	-0.0024
	B_2	0.0023	0.0023	0.0013	0.0014
	B_3	-0.0005	-0.0014	-0.0025	-0.0023

c) The Kirkwood correlation factor

The structural information about the liquids by dielectric relaxation parameters can be obtained by Kirkwood correlation parameter (H frohlich 1949). The Kirkwood correlation factor g is also a parameter for getting information regarding the orientation of electric dipoles in polar liquids may be obtained by the expression

$$(4\pi N \mu^2 \rho / 9KT M) g = (\epsilon_0 - \epsilon_\infty) (2\epsilon_0 + \epsilon_\infty) / \epsilon_0 (\epsilon_\infty + 2)^2 \quad \dots 6$$

Where μ is the dipole moment is in gas phase, ρ is the density at temperature T , M is the molecular weight, K is the Boltzman constant & N is the Avogadro's number.

The modified form of this equation [ac kumbarkhane 1993, S.M. Puranic1994] has been used to study the orientation of electric dipole in binary mixtures of the two polar liquids say A&B, the above equation is modified assuming that for the mixture g^{eff} has become effective correlation factor in the mixture.

The Kirkwood equation for the mixture can be expressed as

$$(4\pi N / 9KT) [(\mu^2 A \rho_A \Phi_A / M_A) (\mu^2 B \rho_B \Phi_B / M_B)] g^{\text{eff}} = (\epsilon_{0m} - \epsilon_{\infty m}) (\epsilon_{0m} + \epsilon_{\infty m}) / \epsilon_{0m} (\epsilon_{\infty m} + 2)^2 \quad \dots 7$$

Where g^{eff} is the effective Kirkwood correlation factor for a binary mixture with Φ_A & Φ_B as weight fraction of liquids A & B respectively. The calculated values of g^{eff} are tabulated in following table

Table No 4 Kirkwood correlation factor g^{eff} values for ETH+NMA

Volume fraction of NMA	288	298	308	318
0	1.00	0.91	0.88	0.75
0.1	0.76	0.74	0.72	0.70
0.2	0.68	0.66	0.63	0.60
0.3	0.71	0.68	0.65	0.64
0.4	0.72	0.70	0.67	0.66
0.5	0.76	0.75	0.73	0.72
0.6	0.81	0.80	0.78	0.77
0.7	0.85	0.85	0.83	0.82
0.8	0.90	0.92	0.89	0.89
0.9	0.94	0.95	0.93	0.92
1	1.00	0.98	0.96	0.95

Table No 5. Kirkwood correlation factor g_f values for ETH+NMA

Volume fraction of NMA	288	298	308	318
0	1	1	1	1
0.1	0.76	0.79	0.80	0.86
0.2	0.68	0.70	0.69	0.71
0.3	0.71	0.71	0.69	0.73
0.4	0.72	0.72	0.71	0.74
0.5	0.76	0.78	0.77	0.79
0.6	0.81	0.82	0.82	0.83
0.7	0.85	0.87	0.87	0.89
0.8	0.90	0.94	0.93	0.95
0.9	0.94	0.98	0.97	0.98
1	1	1	1	1

The g_f^{eff} values decrease with increase in percentage of ETH in NMA. These values are approximately close to unity for pure NMA and in NMA rich region it indicates no correlation, but deviation from unity in the ETH rich region is more, which indicates the antiparallel alignment of dipoles and suggest the monomeric type structure, this reveals the inter molecular attraction.

i.e. in this system alignment of dipoles changes from anti parallel to parallel arrangement with increasing concentration of NMA.

d) Conclusion:

The binary mixture of Ethanol and N methyl Acetamide has been studied at various temperature and concentrations using time domain reflectometry. The static permittivity and relaxation time have been obtained with various concentrations at different temperature for the mixture. The parameters such as Kirkwood correlation factor, excess permittivity and excess inverse relaxation time gives information about interaction of molecules in the system.

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