DIELECTRIC STUDY OF DIMETHYL FORMAMIDE WITH ETHOXY ETHANOL USING TIME DOMAIN REFLECTOMETRY TECHNIQUE

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ABSTRACT

Dielectric relaxation studies of Dimethyl Formamide (DMF) with Ethoxy Ethanol (EE) mixture for different concentrations over the frequency range 10 MHz to 20 GHz in the temperature range 278K to 308K have been investigated using time domain reflectometry (TDR) technique. Static permittivity (ε_s), dielectric constant at high frequency (ε_∞) and relaxation time (τ) were found through dielectric measurements. The excess dielectric parameters, Bruggeman factor, Kirk wood correlation factor and thermodynamic parameters like change in enthalpy (ΔH) and change in entropy (ΔS) have been determined and discussed to yield information on the molecular interactions and microdynamics of the mixture of the system.

KEY WORDS

Dielectric Relaxation, Dimethyl Formamide, Ethoxy Ethanol, Bruggeman Factor, Cole Davidson model, Kirkwood Correlation factor.

INTRODUCTION

Studies on frequency dependent dielectric relaxation of binary mixture DMF and aqueous solutions have been reported [1-2] to understand the microdynamics and hydrogen bond structure in these systems. The hydrogen bonding causes a significant effect upon the structure, thermodynamic properties like change in enthalpy (ΔH) and change in entropy (ΔS). Referring work of Gestblom and J. Sjoblom [3-4] small - chain alcohols like methanol have faster relaxation time and low activation energy where as long chain molecules have slower relaxation τ and high activation energy.

Several researchers have studied the temperature dependent dielectric relaxation parameters, activation energy and Kirkwood correlation factor of various binary mixtures [5-7]. In this paper an attempt has been made to report a systematic investigation of dielectric properties and dielectric mechanism, thermodynamic properties, Bruggeman factor and Kirkwood correlation factor and the results are discussed over the seven different mole fractions at four different temperatures from 278K to 308K.

MATERIALS AND METHODS

(i) Chemicals and Sample Preparation:
Analytical reagent grade samples of Dimethyl Formamide (DMF) and Ethoxy Ethanol (EE)) were procured from S.D. fine-Chem. Pvt. Ltd., Mumbai, India. In the present study they are used without further purification. The solutions were prepared at seven different mole fractions of DMF and EE at room temperature. The mole fraction of components DMF (1) and EE (2) is calculated using the following **Equation 1** [7-8].

$$X_1 = \frac{\dfrac{V_A \rho_A}{M_A}}{\dfrac{V_A \rho_A}{M_A} + \dfrac{V_B \rho_B}{M_B}}$$

$$X_2 = \frac{\dfrac{V_B \rho_B}{M_B}}{\dfrac{V_A \rho_A}{M_A} + \dfrac{V_B \rho_B}{M_B}}$$

And ---------- (1)

Where M_A, M_B are the molecular weights V_A, V_B are the volumes and ρ_A, ρ_B are the density of liquid A and B respectively. The limiting high frequency ε_∞ of pure ideal solvents and $\varepsilon_{\infty m}$ of the binary mixtures were taken as the square of refractive index n_D at the wavelength of sodium D-line.

(ii) Apparatus:

The Hewlett Packard HP54750A sampling oscilloscope with HP54754A TDR plug-in module has been used. After observing TDR response for the sample under study, the time window was kept to 5 ns. Also by observing TDR response for the sample under study, the SMA sample cell with 1.35 mm effective pin length has been used. 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 wave-form. First, the reflected pulse from the empty cell is acquired and stored in the memory and then, the reflected pulse from the cell with sample is acquired and stored in the memory. The empty cell wave-form is used as the reference wave-form. Both response wave-forms are the reflected wave-forms from the sample cell with open termination of transmission line.

The data acquisition is carried out for 7 concentrations in the temperature range 278K to 308K with an accuracy of ±1 ^{0}C. At each time the response wave-forms without sample and with sample were recorded. The time-dependent response wave-form without sample is referred as *R*1 (*t*) and with sample is referred as *Rx* (*t*).

In this process, the time-dependent data were processed to obtain complex reflection coefficient spectra $\rho^*(\omega)$ using Fourier transformation [9-10] in the frequency range of 10 MHz to 10 GHz.

(iii) Data Analysis:

As explained earlier the reflection coefficient is related to dielectric response of a sample under study for the frequency range 10 MHz to 10 GHz in terms of complex permittivity spectra. The complex permittivity ε^* can be written as $\varepsilon' - i\varepsilon''$, where ε' is real part, is called dielectric dispersion and it is proportional to stored energy. Where ε'' is imaginary part and is called dielectric loss. The value of ε_∞ is not so sensitive to ε^* and it is taken as a fixed value 3.0. A sample of complex permittivity dispersion spectra with ε' and ε'' is shown in **Graph 1**. This corresponds to 0.5438 mole fraction of EE at 278K.

Graph 1: Complex permittivity dispersion spectra with ε' and ε" corresponds to 0.5438 mole fraction of EE at 278K
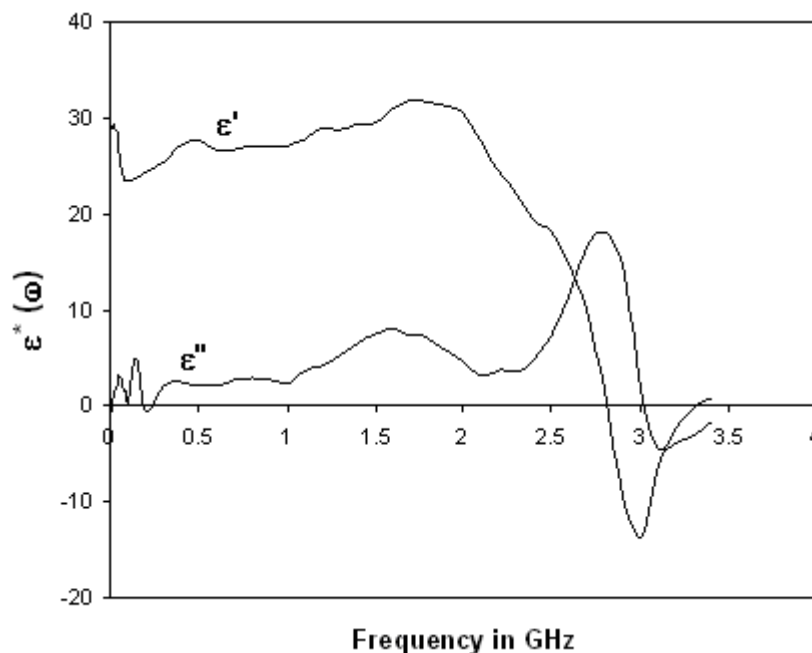
The frequency dependent complex permittivity $\varepsilon^* = \varepsilon' - i\varepsilon''$ data was obtained by using dielectric parameters of raw data. The static dielectric constant (ε_s) and relaxation time (τ) for the mixture obtained by using Havriliak-Negami equation 2 [11].

$$\varepsilon^*(\varpi) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{\left[1 + (i\varpi t)^{1-\alpha}\right]^\beta} \quad \text{------ (2)}$$

Where ε_s is the static dielectric constant, ε_∞ is the high frequency dielectric constant, ω is the angular frequency and τ is the relaxation time, α and β are the experimental parameters for the distribution of relaxation time. While fitting the data, equation 2 includes Cole-Cole (β=1) [12], Davidson–Cole (α=0) [13] and Debye ((α=0, β=1) [14] relaxation models.

RESULTS

The Physical properties of pure liquids DMF and EE used for calculation are listed in **Table 1**.

Table 1: Literature values of Physical properties of DMF and EE

Name	Mol. Formula	Mol. Wt.	Density ρ gcm^{-3}	R I (n_D)	Dipole moment μ
DMF	C_3H_7NO	73.094	0.944255	1.430520	3.86 D
EE	$C_4H_{10}O_2$	90.121	0.925235	1.405425	2.19 D

**Source: Hand book of Chemistry and Physics David R Lide 84th Edition CRC Press**

(i) Permittivity and Relaxation Time:

The evaluated values of ε_s, τ as a function of mole fraction of EE at four different temperatures are given in **Table 2**. A graphical representation of ε_s, and τ is shown in **Graphs 2 and 3** respectively.

Table 2: Temperature dependent dielectric parameters for binary mixture of DMF+EE

Mole Fraction of EE	278K		288K		298K		308K	
	ε_s	τ (ps)	ε_s	τ (ps)	ε_s	τ (ps)	ε_s	τ (ps)
0.0000	45.0	25.2	41.1	19.3	39.4	11.1	34.7	8.4
0.1658	38.8	30.2	35.3	25.3	34.3	22.1	32.1	16.8
0.3463	33.2	40.4	32.2	34.5	30.7	30.2	27.1	27.3
0.4428	25.2	64.7	21.8	60.3	19.2	57.0	17.8	50.1
0.5438	29.4	58.6	4.4	54.4	22.7	48.6	19.0	46.6
0.7607	38.6	56.4	34.5	48.9	27.7	41.9	23.5	36.2
1.0000	17.5	55.8	16.5	46.5	15.7	38.6	14.2	34.5

Graph 2: Variation of static dielectric constant (ε_s) as a function of mole fraction of EE at different temperatures.
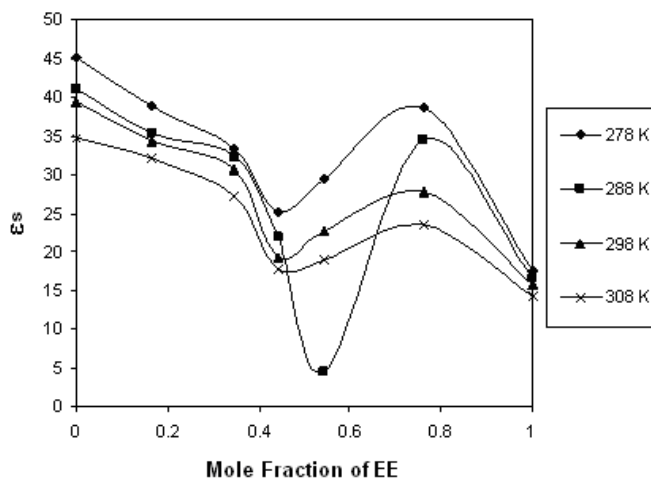
Graph 3: Variation of static relaxation time (τ_s) as a function of mole fraction of EE at different temperatures.
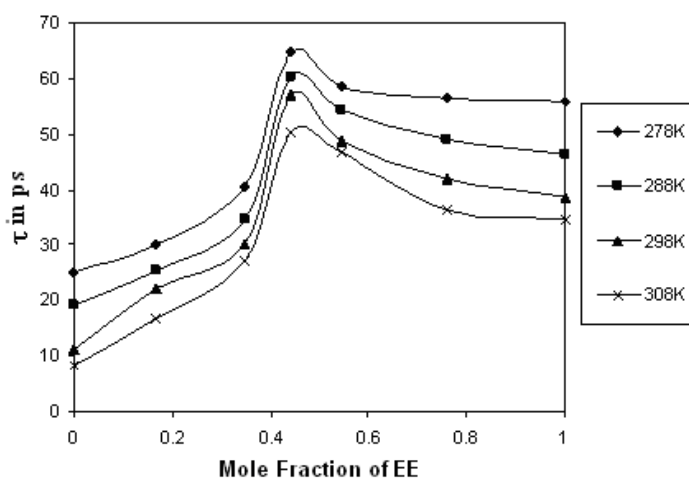
(ii) Excess Permittivity and Excess Inverse Relaxation Time:

The excess permittivity, ε_s^E at various concentrations is calculated using the equation 3.

$$\varepsilon_s^E = (\varepsilon_s)_m - [(\varepsilon_s)_A \, X_A + (\varepsilon_s)_B \, X_B] \text{-------(3)}$$

Where X is the mole fraction and subscripts m, A and B represent the binary mixtures and components DMF and EE of the binary mixture respectively.

The excess permittivity provides qualitative information about structural aspects of the mixture.

If ε_s^E = 0 indicates the liquids A and B do not interact at all.

If ε_s^E < 0 indicates the liquids A and B interact in such a way that the total effective dipole gets reduced. This shows that liquids A and B may form multimers leading less effective dipoles or there is a tendency of dipoles to align in anti-parallel direction.

If ε_s^E > 0 indicates the liquids A and B interact in such a way that the total effective dipole moment increases. There is a tendency of dipole aligned in parallel direction.

The excess parameter $\left(\dfrac{1}{\tau}\right)^E$ at various concentrations is calculated using the **Equation 4**.

$$(1/\tau)^E = (1/\tau)_m - [(1/\tau)_A \, X_A + (1/\tau)_B \, X_B] \text{--------(4)}$$

Where X is the mole fraction and subscripts m, A and B represent the binary mixtures and components DMF and EE of the binary mixture respectively.

It provides the qualitative information about the formation of multimers and monomers in the following way –

$(1/\tau)^E$ = 0: Indicates there was no change in the dynamics of liquids A and B.

$(1/\tau)^E$ < 0: Indicates liquids A and B interaction produced a field such that the effective dipole rotated slowly.

$(1/\tau)^E$ > 0: Indicates liquids A and B interaction produced a field such that the effective dipoles rotated rapidly.

The evaluated ε_s^E and $\left(\dfrac{1}{\tau}\right)^E$ values of the DMF-EE binary mixture are given in **Table 3**.

Table 3: Excess permittivity ε_s^E and excess inverse relaxation time $(1/\tau)^E$ of DMF+EE

Mole Fraction of EE	278K		288K		298K		308K	
	ε_s^E	$(1/\tau)^E$	ε_s^E	$(1/\tau)^E$	ε_s^E	$(1/\tau)^E$	ε_s^E	$(1/\tau)^E$
0	0	0.0000	0	0.0000	0	0.0000	0	0.0000
0.1658	-1.6419	-0.0030	-1.7225	-0.0073	-1.172	-0.0342	0.7979	-0.0446
0.3463	-2.2760	-0.0074	-0.3803	-0.0123	-0.492	-0.0347	-0.5	-0.0512
0.4428	-7.6227	-0.0136	-8.4068	-0.0218	-9.705	-0.0441	-7.822	-0.0592
0.5438	-0.6451	-0.0108	-23.322	-0.0169	-3.812	-0.0346	-4.552	-0.0486
0.7607	14.5190	-0.0054	12.1133	-0.0083	6.3287	-0.0174	4.3944	-0.0229
1	0	0.0000	0	0.0000	0	0.0000	0	0.0000

A graphical representation of excess permittivity and excess inverse relaxation time against mole fraction of EE for four different temperatures are shown in **Graphs 4 and 5** respectively.

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Graph 4: Variation of Excess permittivity ε_S^E as a function of mole fraction of EE at different temperatures
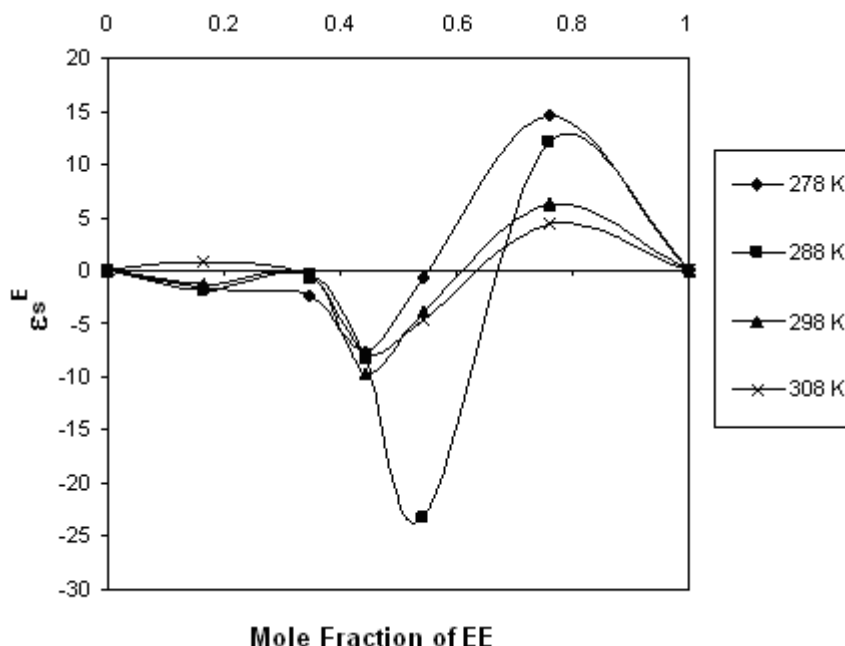
Graph 5: Variation of excess inverse relaxation time $(1/\tau)^E$ as a function of mole fraction of Ethoxy Ethanol at different temperatures.
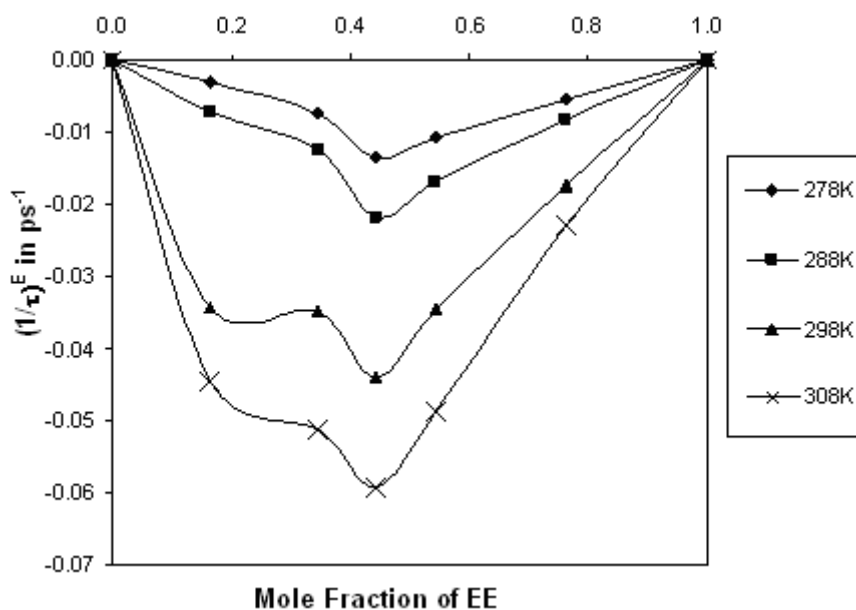
(iii) Bruggeman Factor (f_b):

The Bruggeman mixture formula can be used as first evidence of molecular interactions in binary mixture A and B respectively [15]. The equation for Bruggeman factor (f_B) is given by

$$ f_B = \frac{\varepsilon_{0m} - \varepsilon_{0B}}{\varepsilon_{0A} - \varepsilon_{0B}} \left(\frac{\varepsilon_{0A}}{\varepsilon_{0m}} \right)^{\frac{1}{3}} = 1 - V \quad \text{---------- (5)} $$

According to equation (5) a linear relation is expected between Bruggeman factor and mole fraction of EE. Any deviation from this linear relation indicates existence of intermolecular

interactions. Many similar observations have been reported in [16-17]. The evaluated values of Bruggeman factor f_B for binary mixture DMF+EE at four different temperatures are given in **Table 4**.

Table 4: Bruggeman Factor, f_B of DMF+EE

Mole Fraction of EE	f_B				
	278K	**288K**	**298K**	**308K**	**Ideal**
0.0000	1	1	1	1	1
0.1658	0.81378	0.804	0.82192	0.8961	0.8342
0.3463	0.63182	0.6923	0.6878	0.6833	0.6537
0.4428	0.3397	0.2662	0.18767	0.2194	0.5572
0.7607	0.80753	0.7757	0.56943	0.5166	0.2393
1.0000	0	0	0	0	0

A graphical representation of f_B against mole fraction is shown in **Graph 6**.

Graph 6: Variation of Bruggeman Factor f_B as a function of mole fraction of Ethoxy Ethanol at different temperatures.
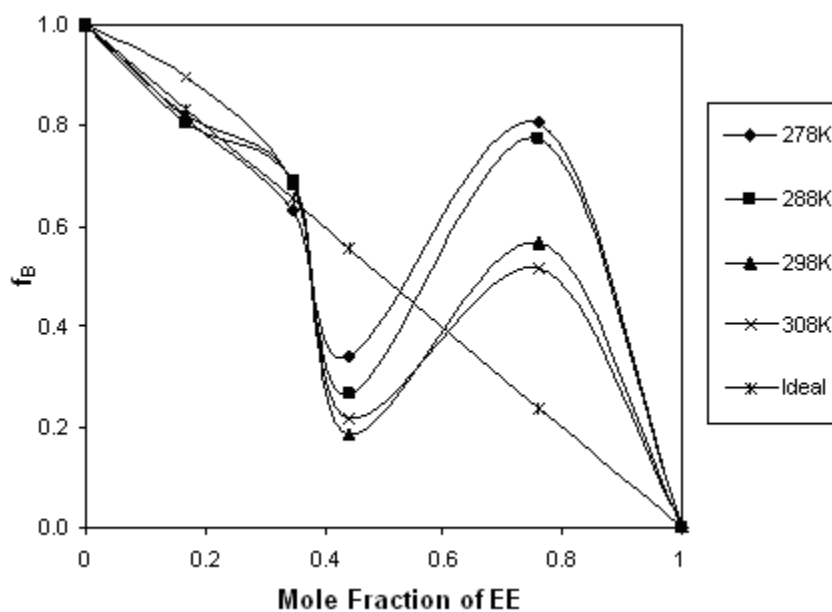
(iv) Effective Kirkwood Correlation Factor (g^{eff}):
The structural information about the liquids from the dielectric relaxation parameter may be obtained using the effective Kirkwood correlation factor, g^{eff} [17]. This factor is also a parameter for obtaining information regarding orientation of electric dipoles in polar liquids.
The Kirkwood equation for the binary mixture can be expressed as [18-19]

$$\frac{4\pi N}{KT}\left(\frac{\mu_A^2 \rho_A}{M_A}X_A + \frac{\mu_B^2 \rho_B}{M_B}X_B\right)g^{eff} = \frac{(\varepsilon_{sm}-\varepsilon_{\infty m})(2\varepsilon_{sm}+\varepsilon_{\infty m})}{\varepsilon_{sm}(\varepsilon_{\infty m}+2)^2} \quad \text{-- (6)}$$

Where X_A and X_B are mole fractions liquids A and B respectively, ε_s is static permittivity, ε_∞ is permittivity at high frequency, μ is dipole moment, ρ is density at temperature T, M is molecular weight, K is Boltzmann's constant, N is Avogadro's number. The values of g^{eff} are evaluated for different concentrations at

different temperatures using equation 6. The evaluated values of g^{eff} as a function of mole fraction of EE at four different temperatures are given in **Table 5**.

Table 5: Kirkwood Correlation Factor g^{eff} of DMF + EE

Mole fraction Of EE	g^{eff}			
	278K	**288K**	**298K**	**308K**
0.0000	1.27	1.20	1.19	1.08
0.1658	1.25	1.18	1.18	1.14
0.3463	1.27	1.27	1.25	1.14
0.4428	1.06	0.94	0.85	0.81
0.5438	1.40	0.15	1.15	0.98
0.7607	2.57	2.37	1.95	1.70
1.0000	1.92	1.87	1.83	1.70

The graphical representation of variation of g^{eff} with mole fraction of EE are given in **Graph 7**.

Graph 7: Variation of Kirkwood correlation factor g^{eff} as a function of mole fraction of Ethoxy Ethanol at different temperatures.
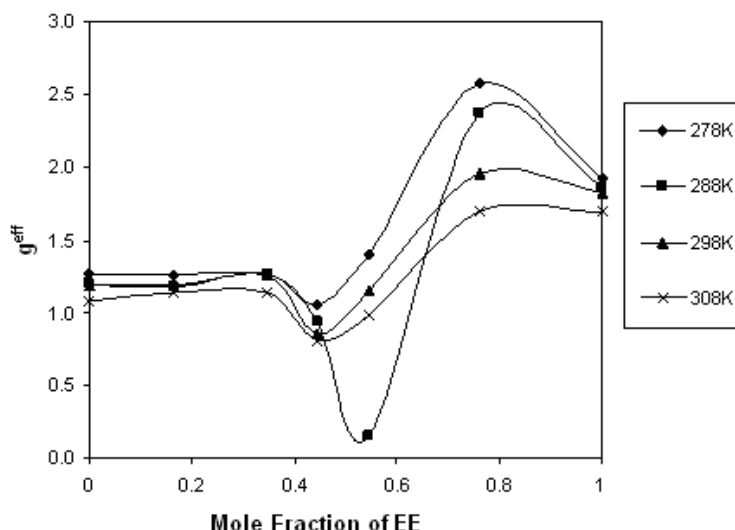
(v) Arrhenius Plot:

The thermodynamic parameters like molar enthalpy of activation ΔH^{*} and molar entropy of activation ΔS^{*} are calculated by Eyring's rate equation 7 using least square fit method. [20-21]

$$\tau = \frac{h}{KT} \exp^{\Delta G^{*}/RT}$$

--------- (7)

Where ΔG^{*} is molar free activation energy,

$$\Delta G^{*} = \Delta H^{*} - T\Delta S^{*}$$ ------ (8)

Equation 7 can also be written as

$$\ln(\tau T) = \ln\left(\frac{h}{K}\right) + \frac{\Delta H^{*} - T\Delta S^{*}}{RT}$$

$$\ln(\tau T) = \left[\ln\left(\frac{h}{K}\right) - \left(\frac{\Delta S^{*}}{R}\right)\right] + \left[\frac{\Delta H^{*}}{RT}\right]$$ ------- (9)

The slope of the linear plot between $\ln(\tau T)$ and (1/T) gives $\left(\dfrac{\Delta H}{R}\right)$.

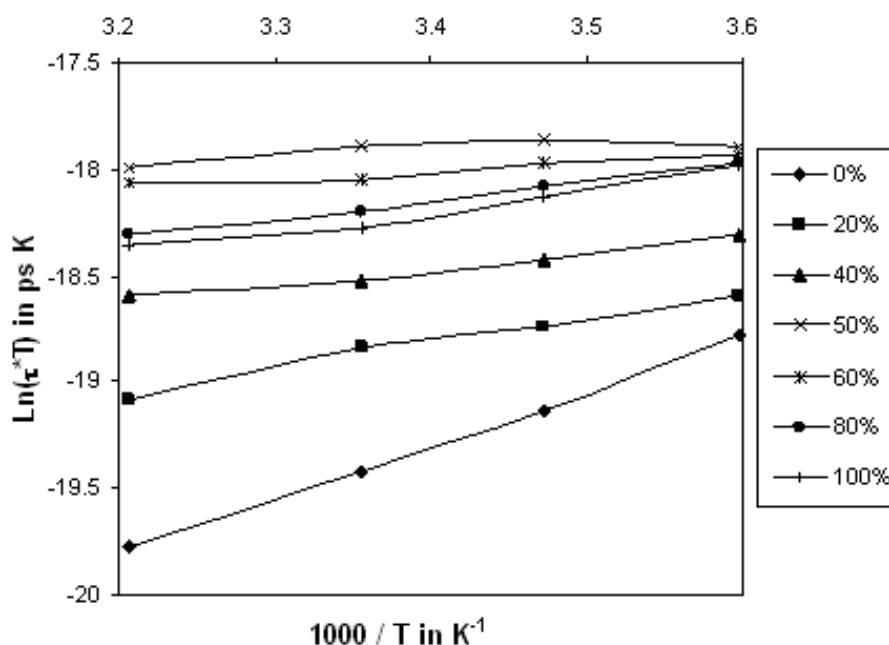Using values of molar enthalpy ΔH^* and molar entropy ΔS^*, molar free activation energy, ΔG^* can be calculated using equation 8. The evaluated values of $\ln(\tau T)$ and $(1/T)$ are tabulated in table 6 and the graphical representation of Arrhenius plot is shown in **Graph 8**.

Table 6: Arrhenius Plot for DMF + EE

T in K	1000/T K^{-1}	$\ln(\tau T)$ Mole Fraction of EE						
		0	0.1658	0.3463	0.4428	0.5438	0.7607	1.000
278	3.597	-18.777	-18.596	-18.305	-17.897	-17.933	-17.971	-17.980
288	3.472	-19.130	-18.737	-18.427	-17.869	-17.972	-18.078	-18.130
298	3.356	-19.420	-18.838	-18.526	-17.891	-18.050	-18.199	-18.280
308	3.247	-19.770	-19.080	-18.590	-17.99	-18.060	-18.310	-18.360

Graph 8: Arrhenius plot to calculate thermodynamic parameters for different concentrations.

From **Graph 8** linear nature of Arrhenius plot shows that equivalent changes in values of molar enthalpy of activation ΔH in the observed temperature range from 278 K to 308 K. The slope of Arrhenius plot changes with concentration, which shows the change in activation energy of the system.

6. Molar Enthalpy and Molar Entropy:

The evaluated values of molar enthalpy and molar entropy from Arrhenius plot for different molar concentrations are tabulated in **Table 7**.

Table 7: Change in Enthalpy and Entropy of DMF + EE

Mole Fraction of EE	ΔH in KJ	ΔS in KJ
0.0000	24.941395	0.047927
0.1658	11.000624	-0.003533
0.3463	6.908211	-0.020428
0.4428	2.0059208	-0.041773
0.5438	3.2762430	-0.036662
0.7607	8.1292074	-0.018940
1.0000	9.1884923	-0.014922

The graphical representation of molar enthalpy and molar entropy are shown in **Graph 9**.

Graph 9: Variation of molar enthalpy and molar entropy as a function of mole fractions (EE).
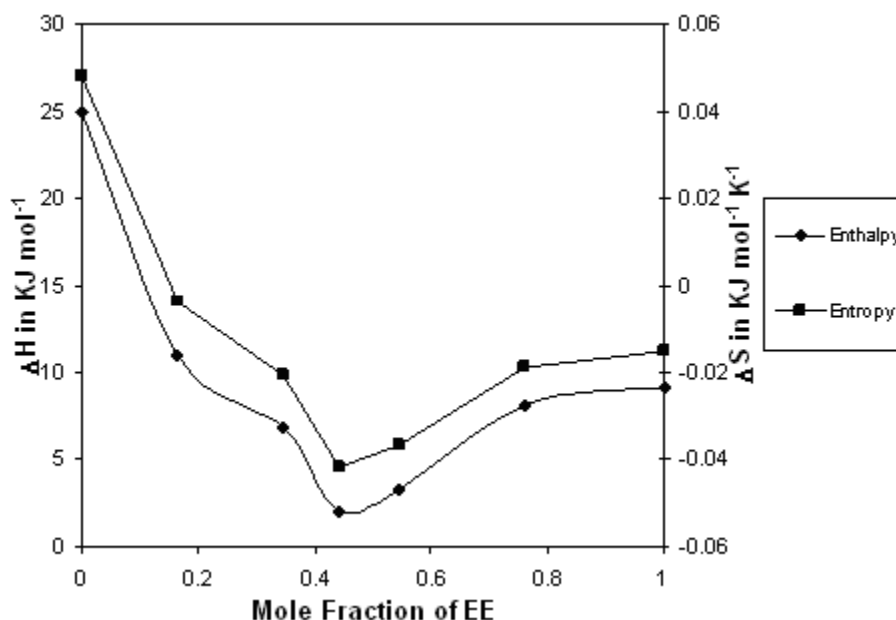
DISCUSSION

From **Graph 2**, the nonlinear behavior of these parameters confirms the H-Bond complex function over the entire concentration range of DMF-EE mixture.

The maximum decrease in ε_s value is observed when mole fraction of EE is 0.4428 reveals that dipole interaction is minimum for all observed temperatures 278, 288, 298 and 308K.This suggests that weak intermolecular interaction due to shielded charge distribution in DMF. The maximum value of ε_s observed for temperatures 278, 298 and 308K when mole fraction of EE is 0.7607 reveals the dipole interaction between DMF-EE binary mixtures is maximum.

From graph 3, Relaxation time is found to be maximum for all temperatures when mole fraction of EE is 0.4428.

The Excess parameters related to ε_s and τ provide valuable information regarding interaction between polar-polar liquid mixtures. It also gives

the information of formation of multimers in the mixture due to intermolecular interaction.

From **Graph 4** it is observed that the maximum negative value of ε_S^E when mole fraction of EE is 0.4428 for all observed temperatures. It represents that effective value of dipole moment is get reduced due to anti-parallel alignments of dipoles in the mixture. Maximum negative value of ε_S^E at 288K confirms the formation of strong H-bond hetero molecular interactions in the mixture and these interactions are relatively stronger compare to other observed temperatures. Excess permittivity ε_S^E is maximum positive value is observed when mole fraction of EE is 0.7607. It indicates the molecular interaction of DMF & EE increases the effective dipole moment. There is a tendency of dipole aligned in parallel direction also it is maximum at temperature 278K. As temperature increases alignment of dipoles in parallel direction decreases.

From **Graph 5** it is observed that $\left(\dfrac{1}{\tau}\right)^E$ is negative for entire range of concentration and for all observed temperatures. The negative value of inverse relaxation time indicates molecular interaction produced hindering field making effective dipole rotation slowly. The maximum negative value is observed when mole fraction of EE is 0.4428 for all observed temperatures.

It is observed in **Graph 6**, that there is a non-linear relationship between f_B and mole fraction. The Bruggeman factor shows a positive deviation throughout from the ideal value. Maximum deviation from ideal value is observed when mole fraction of EE is 0.7607. This indicates the existence of inter molecular interaction in the mixture.

According to **Graph 7** the values of g^{eff} are greater than unity for all temperatures shows parallel orientation of electric dipoles. The maximum g^{eff} value is observed for all temperatures when mole fraction of EE is 0.7607 shows maximum inter molecular interaction within the system.

From graph 8 linear nature of Arrhenius plot shows that equivalent changes in values of molar enthalpy of activation ΔH in the observed temperature range from 278 K to 308 K. The slope of Arrhenius plot changes with concentration, which shows the change in activation energy of the system.

It is observed that molar enthalpy of activation ΔH decreases till mole fraction of EE is 0.4428 and then it increases. It means less energy is needed for group of dipole reorientation up to mole fraction of EE 0.4428. Negative value of entropy ΔS for all mole fractions of EE except zero value of EE confirms relatively high ordered arrangement of molecules in the system.

CONCLUSION

The dielectric parameters, Kirkwood correlation factor, Bruggeman factor, thermo dynamic parameters have been reported for DMF-EE binary mixture for different concentrations at various temperatures. The relaxation time of the mixture is found to be higher for mole fraction of EE is 0.4428. The maximum negative value of excess relaxation time $\left(\dfrac{1}{\tau}\right)^E$ indicates the slower rotation of effective dipoles of the system. The more deviation of Bruggeman factor from its ideal value for mole fraction of EE 0.7607 shows more energy is needed for group dipole reorientation.

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