



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

KRISHNA H. FATTEPUR^{*1}, JAGADISH G. BARAGI,²
B.V.NARENDRA³ AND R.H.FATTEPUR⁴

¹ Department of Physics, The National Degree College, Basavanagudi Bangalore-560004, India.

² Department of Chemistry, J.S.S. College, Vidyagiri, Dharwad-580 004, India

³ Department of Physics, The National Degree College, Basavanagudi Bangalore-560004, India

⁴ Department of Physics, Basaveshwar Science College, Bagalkot, Karnataka-587101, India

ABSTRACT

The work reported in this paper is intended to study the intermolecular interactions in the binary mixture of Dimethyl Acetamide (DMAc) with Ethoxy Ethanol (EE) by computing parameters like dielectric permittivity ϵ_s and relaxation time τ in the temperature range 278K to 308K in steps of 10K using time domain reflectometry in the frequency range 10 MHz to 20GHz. The evaluated values of ϵ_s and τ are helped to calculate Kirkwood correlation factor (g^{eff}). Arrhenius plot $\ln(\tau T)$ against reciprocal of temperature for different mole fractions of EE enables to calculate the change in enthalpy (ΔH) and change in entropy (ΔS). The evaluated values of entropy indicate environment of the system is cooperative and stable for all temperature range and for all mole fractions of EE.

KEYWORDS: Dielectric Relaxation, Kirkwood Correlation factor, Enthalpy, Entropy, Dimethyl Acetamide, Ethoxy Ethanol,



KRISHNA H. FATTEPUR

Department of Physics, The National Degree College,
Basavanagudi Bangalore-560004, India.

INTRODUCTION

Studies on frequency dependent dielectric relaxation of binary mixture of DMAc with aqueous solutions have been reported¹⁻² to understand the microdynamics and hydrogen bond structure. The hydrogen bonding causes a significant effect upon the structure as well as thermodynamic properties like change in enthalpy (ΔH^*) and change in entropy (ΔS^*). Referring work of Gestblom and J. Sjolom³⁻⁴ 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 mixtures⁵⁻⁷. The present paper aims at systematic investigation of Kirkwood correlation factor

and thermodynamic properties. 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 Dimethyle Acetamide (DMAc) 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 DMAc and EE at room temperature. The mole fraction of components DMAc (1) and EE (2) is calculated using equation (1)⁷⁻⁸.

$$X_1 = \frac{\frac{V_A \rho_A}{M_A}}{\frac{V_A \rho_A}{M_A} + \frac{V_B \rho_B}{M_B}} \quad \text{and} \quad X_2 = \frac{\frac{V_B \rho_B}{M_B}}{\frac{V_A \rho_A}{M_A} + \frac{V_B \rho_B}{M_B}} \quad \text{-----(1)}$$

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 $\epsilon_{\infty m}$ 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 °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 $R1(t)$ 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 transformation⁹⁻¹⁰ 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 $\epsilon' - j\epsilon''$, 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 frequency dependent complex permittivity $\varepsilon^* = \varepsilon' - j\varepsilon''$ data was obtained by using

dielectric parameters of raw data. The static dielectric constant (ε_s) and relaxation time (τ) of the binary mixture are obtained by fitting the data to Havriliak – Negami equation (2)¹¹.

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{[1 + (j\omega\tau)^{1-\alpha}]^\beta} \quad \text{----- (2)}$$

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 ($\beta=1$),¹² Davidson–Cole ($\alpha=0$)¹³ and Debye ($\alpha=0, \beta=1$)¹⁴ relaxation models.

RESULTS

The Physical properties of pure liquids DMAc and EE used for calculation are listed in table 1.

Table 1
Literature values of Physical properties of DMAc and EE

Name	Mol. Formula	Mol. Wt.	Density ρ gcm ³	R I (n _D)	Dipole moment μ
DMAc	C ₄ H ₉ NO	87.120	0.937225	1.434125	3.72 D
EE	C ₄ H 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 and τ as a function of mole fraction of EE at four different temperatures are given in table 2.

Table 2
Temperature dependent dielectric parameters for binary mixtures of DMAc+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	44.9	35.1	42.9	27	39.9	18	35.4	15.2
0.1926	38.6	38.8	37.6	32.6	36.8	27.2	33.3	24.9
0.3888	32.6	56.9	32	51.5	30	42.9	28	37.7
0.4883	26.9	83.7	25.5	70.4	24.2	54.5	23.2	48
0.5887	22.8	94.7	22.4	76.6	21.3	61.1	20.1	56.7
0.7924	34.4	77.5	32.9	54.7	29.9	47.1	25.4	44.1
1	17.5	55.8	16.3	46.5	15.7	38.6	14.2	34.5

(ii) 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} ¹⁵. 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 as¹⁶⁻¹⁷

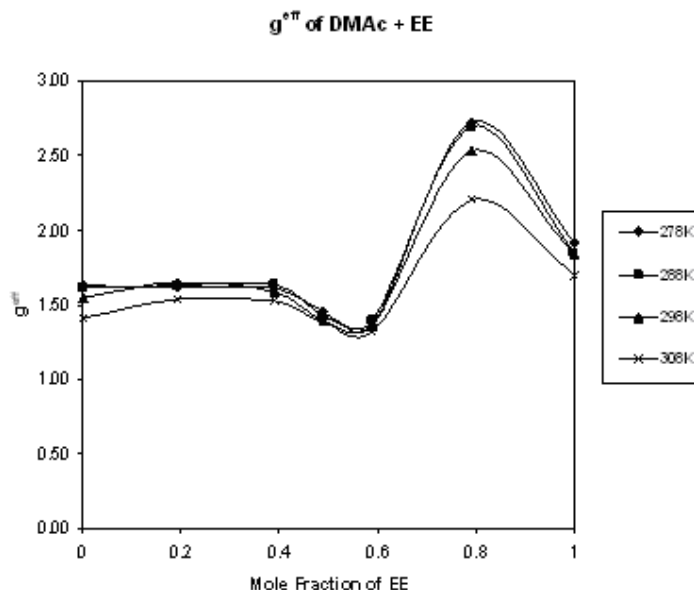
$$\frac{4\pi N}{KT} \left(\frac{\mu_A^2 \rho_A}{M_A} X_A + \frac{\mu_B^2 \rho_B}{M_B} X_B \right) g^{eff} = \frac{(\varepsilon_{sm} - \varepsilon_{\infty m})(2\varepsilon_{sm} + \varepsilon_{\infty m})}{\varepsilon_{sm}(\varepsilon_{\infty m} + 2)^2} \quad \text{----- (3)}$$

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 number. The values of g^{eff} are evaluated for different concentrations at different temperatures using equation (3). The evaluated values of g^{eff} as a function of mole fraction of EE at four different temperatures are given in table 3.

Table 3
Kirkwood Correlation Factor g^{eff} of DMAc + EE

Mole fraction of EE	g^{eff}			
	278K	288K	298K	308K
0.0000	1.63	1.61	1.55	1.42
0.1926	1.62	1.63	1.65	1.54
0.3888	1.61	1.64	1.58	1.52
0.4883	1.46	1.43	1.40	1.38
0.5887	1.37	1.39	1.36	1.32
0.7924	2.73	2.70	2.53	2.20
1.0000	1.92	1.84	1.83	1.70

Graph 1
The graphical representation of variation of g^{eff} with mole fraction of EE are presented in graph 1



Variation of Kirkwood correlation factor, g^{eff} as a function of mole fraction of Ethoxy Ethanol at different temperatures.

(iii) Arrhenius Plot

The thermodynamic parameters like molar enthalpy of activation, ΔH^* and molar entropy of activation, ΔS^* are calculated by Eyring's rate equation (4) using least square fit method.¹⁸⁻¹⁹

$$\tau = \frac{h}{KT} \exp \frac{\Delta G^*}{RT} \quad \text{----- (4)}$$

Where ΔG^* is molar free activation energy, $\Delta G^* = \Delta H^* - T\Delta S^*$ ----- (5)
Equation 4 can also be written as

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

$$\ln(\tau T) = \left[\ln\left(\frac{h}{K}\right) - \left(\frac{\Delta S^*}{R}\right) \right] + \left[\frac{\Delta H^*}{RT} \right] \text{----- (6)}$$

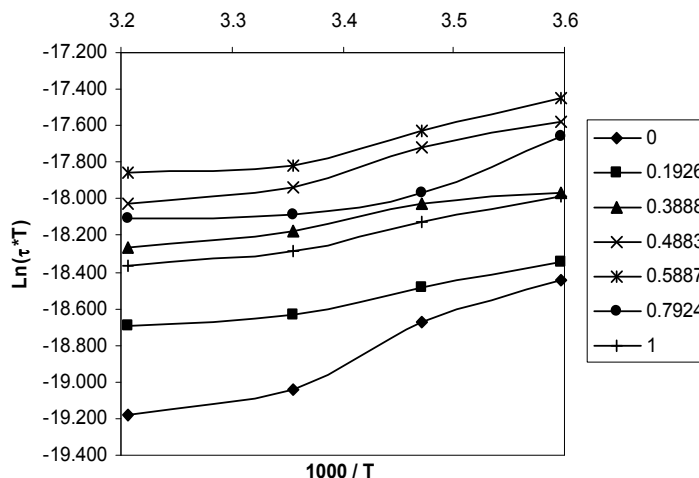
The slope of the linear plot between $\ln(\tau T)$ and $(1/T)$ gives $\left(\frac{\Delta H^*}{R}\right)$.

Using values of molar enthalpy ΔH^* and molar entropy ΔS^* , molar free activation energy, ΔG^* can be calculated using equation (5). The evaluated values of $\ln(\tau T)$ and $(1/T)$ are tabulated in table 4 and the graphical representation of Arrhenius plot is shown in graph 2.

Table 4
Arrhenius Plot for DMAc + EE

T in K	1000/T K ⁻¹	ln(τT)						
		Mole Fraction of EE						
		0	0.1926	0.3888	0.4883	0.5887	0.7924	1.000
278	3.597	-18.445	-18.345	-17.962	-17.576	-17.453	-17.653	-17.982
288	3.472	-18.672	-18.484	-18.026	-17.714	-17.629	-17.966	-18.129
298	3.356	-19.044	-18.631	-18.175	-17.936	-17.821	-18.082	-18.281
308	3.247	-19.180	-18.690	-18.270	-18.030	-17.860	-18.110	-18.360

Graph 2
Arrhenius plot to calculate thermodynamic parameters for different concentrations.



From graph 2 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 $\left(\frac{\Delta H^*}{R}\right)$

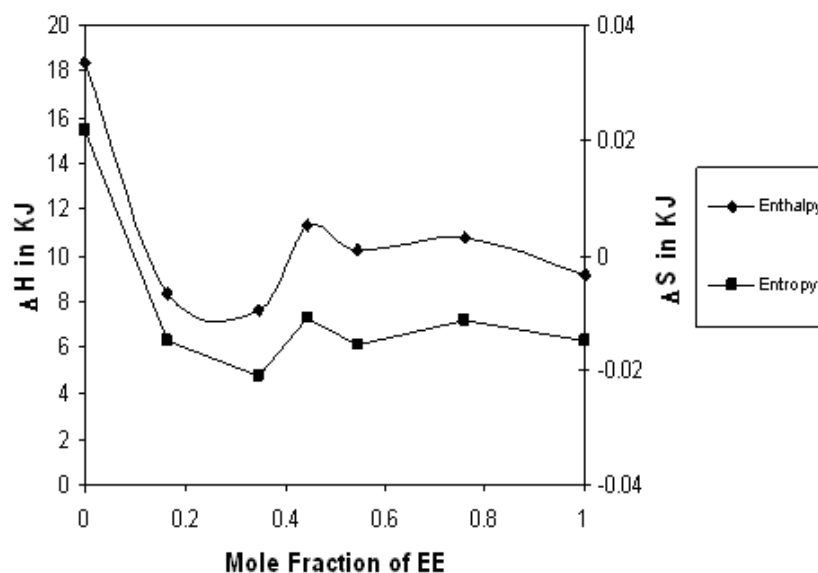
(iv) Molar Enthalpy and Molar Entropy

The evaluated values of molar enthalpy and molar entropy from Arrhenius plot for different molar concentrations are tabulated in table 5.

Table 5
Change in Enthalpy and Entropy of DMAc + EE

Mole Fraction of EE	ΔH^* in KJ	ΔS^* in KJ
0.0000	18.357582	0.0218
0.1926	8.3644862	-0.01484
0.3888	7.6386359	-0.020876
0.4883	11.278036	-0.010889
0.5887	10.190111	-0.015623
0.7924	10.803709	-0.011346
1.0000	9.1884923	-0.014922

Graph 3
The graphical representation of molar enthalpy and molar entropy are shown in graph 3.



Variation of molar enthalpy and molar entropy as a function of mole fractions (EE).

DISCUSSION

The static dielectric constant (ϵ_0) and relaxation time (τ) obtained by fitting experimental data with the Debye equation are listed in table 1. From Table 1 it is clearly shown that the value of permittivity and relaxation time decreases with increase in mole fraction of EE in the mixture. This is due to weak intermolecular interaction in the mixture. From graph 1, the value of g^{eff} is 1.63 at 278 K which decreases to 1.42 at 308K. The decrease in the values may be due to the formation of hydrogen bonding in pure EE system. The values of g^{eff} shows decreasing trend with increase in concentration of EE molecules in the mixture till mole fraction reaches a value of 0.5887. This trend suggests re-orientation of neighboring molecules of constituent polar molecules forming a tendency towards anti-parallel

alignment of dipoles. This conclusion is similar to that arrived from variation of dielectric constant with concentration. The maximum g^{eff} value is observed for all temperatures when mole fraction of EE is 0.7924 shows maximum inter molecular interaction within the system. From graph 2 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 0.3463 and then it increases. It means less energy is needed for group of dipole reorientation up to mole fraction of EE 0.3463. The entropy of the

system is the measure of the orderly nature of the system. If the environment of the system is cooperative for the activated process, then the change in entropy becomes negative. Where as positive values of the change in entropy for activated process indicates the non-cooperative environment of the system and the activated state is unstable. All negative value of change in entropy, ΔS^* for all mole fractions of EE except zero value of EE confirms relatively high ordered arrangement of molecules in the activated state.

CONCLUSION

The value of g^{eff} greater than 1 for all temperatures and all mole fractions of EE confirms parallel orientation of effective dipoles in the mixture. Highest value of g^{eff} for mole fraction 0.7924 of EE suggests that degree of parallel orientation is highest. Higher values of molar enthalpy shows more energy is required to change the state of orientation of dipoles and negative values of change in entropy (ΔS^*) indicates high ordered arrangement of molecules in the activated state.

REFERENCES

1. Study Of Solute Solvent Interaction Through Dielectric Properties Of Allyl Chloride With Dimethyl Formamide Using Time Domain Reflectometry Technique - G.M. Dharne, A.P. Maharolkar, S.S.Patil, P.W.Khirade and S.C. Mehrotra. IJPBS V1 (2), (2010).
2. Dielectric characterization and molecular interaction behavior in binary mixtures of amides with dimethylsulphoxide and 1,4-dioxane - R.J. Sengwa, Sonu Sankhela, Vinita Khatri. J. Mol. Liq., 151, 17-22, (2010).
3. Dielectric relaxation and related studies of 4-ethylphenol-methanol mixtures using time domain reflectometry - R.H. Fattepur, M.T. Hosmani, D.K. Deshpande, R.L. Patil and S.C. Mehrotra. Pramana, Vol. 44 No.1, 33-44, (1995).
4. Dielectric Relaxation Study of Aqueous Methanol – Butanol Solutions. A comparison with Heigher Homologus - B.Gestblom and J. Sjoblom, J. Acta. Chem. Scan. A38, 575, (1984).
5. Microwave dielectric characterization of binary mixture of formamide with N, N - dimethyl amino ethanol - Prabhakar Undre, S.N.Helambe, S.B.Jagadale, P.W.Khirade & S.C.Mehrotra, Pramana J.Phys. Vol. 68, No 5, 851-861, (2007).
6. Temperature-Dependent Dielectric Relaxation of 2-Ethoxyethanol, Ethanol, and 1-Propanol in Dimethyl formamide Solution Using the Time-Domain Technique - P.W. Khirade, A.S. Chaudhari, J.B. Shinde, S.N. Helambe and S.C. Mehrotra, J. Soln, Chem. 28 (8), 1031-1043, (1999).
7. Dielectric Relaxation Study of Dimethylene Chloride with Ethanol Using Time Domain Reflectometry - V.P. Pawar and S.C. Mehrotra, J. Mol. Liq., 108/1-3, 95-105, (2003).
8. Dielectric Relaxation of Binary Mixtures of Alcohols with Acrylic Esters - K. Dharmalingam, K. Ramachandran, P. Shivgurunathan, B. Prabhakar Undre, P.W. Khirade, S.C. Mehrotra., J. Appl. Polym. Sci. Vol. 107 No.4, 2312-2316, (2008).
9. Communication in the Presence of Noise - C.E. Shanon, Proc. IRE, 37, 10, (1949).
10. Spectrum Analysis of Transient Response Curves - H.A. Samulan, Proc. IRE, 39, 175, (1951).
11. Results from an unbiased analysis of nearly 1000 sets of relaxation data - S. Havriliak and S.Negami, J. Polym, Sci. C14, 99, (1966).
12. Dispersion and Absorption in Dielectrics I. Alternating Current Characteristics - K.S. Cole, R.H. Cole, J. Chem Phys. 9, 341, (1941).
13. Dielectric Relaxation in Glycerine - D.W. Davidson, R.H.Cole, J. Chem. Phys. 18, 1484, (1950).
14. Polar molecules - P. Debye, Polar molecules, Chem. Catalog Co., New York, (1929).
15. The theory of rate process - M.I. Aralaguppi, T.M. Aminbhavi, R.H.

- Balundugi and S.S. Joshi, J. Phys. Chem. 95, 5299, (1991).
16. The Dielectric Polarization of Polar Liquids, - Kirkwood J.G., J.Chem. Phys., Vol7, pp. 911 – 919 (1939).
 17. Structural Study of Amide - Water Mixtures Using Dielectric Relaxation Technique, - A. C. Kumbharkhane, S. M. Puranik, and S. C. Mehrotra, J. Mol. Liq., Vol. 51, pp 261 – 277 (1992).
 18. Theory of rate Process - S. Glasstone, K.J. Laidler and H. Eyring, Mc Graw-Hill, New York, 541, (1941).
 19. Dielectric Study of Binary Mixtures of 2-Methoxyethanol in Nitrobenzene and Chlorobenzene Using Time Domain Reflectometry - R.H. Fattepur, S.B. Sayyad, N.H. Ayachit. P.W. Khirade and S.C. Mehrotra. Int.M.S. 9, (2010).