Dielectric Study of Lorazepam-Methanol Mixture using TDR Method at 288K

A. K. Dongare[1], S. B. Sayyed[2]

[1]Department of physics, Vasantdada Patil College, Patoda, Maharashtra, India

[2]Department of physics, Milliya College, Beed, Maharashtra, India

ABSTRACT

The dielectric parameters have been determined for mixture of lorazepam-methanol, with concentration of 0, 20, 40, 60, 80 & 100% in the frequency range of 10MHz to 50GHz at temperature of 288K by time domain reflectometry (TDR). The static permittivity and relaxation time have been used to obtain the excess permittivity, excess inverse relaxation time, Bruggeman factor, Kirkwood factor and thermodynamic parameters. A variation of dielectric constant and relaxation time, with volume fraction of methanol confirms structural formation due to the intermolecular interaction between methanol and lorazepam. The variation of different factors for different mole fraction of methanol in the binary mixture reported in the paper.

Keywords : Excess Permittivity, Excess Inverse Relaxation Time, Bruggeman Factor, Kirkwood factor

I. INTRODUCTION

Dielectric studies have been carried out extensively to understand intermolecular interaction and dynamics of the liquid mixture [1-4] using time domain reflectometry. The present study reveals molecular interaction between same functional group [-OH] of the normal alcohol with different molecular size (carbon chain), on the basis of evaluation of static permittivity, relaxation time, Bruggeman factor and thermodynamic parameters [5].

II. Experimental

Material

The chemical used in the present work is lorazepam and methanol is of spectroscopic grade, obtained commercially with 99% purity and used without further purification. The solutions were prepared at six different compositions in steps of 20 % by volume. Lorazepam ($C_{15}H_{10}Cl_2N_2O_2$), is a medicine sold under the brand name. It is used to treat anxiety disorders, trouble sleeping. It is also used, along with other treatments, for acute coronary syndrome due to cocaine use. It is available as a generic medication [6]. Methanol (CH_3OH) is a clear, colorless liquid. It has an alcoholic or repulsive odor, flammable. Methanol

mixes easily with water. It occurs naturally in humans, animals and plants. Many fruits, vegetables, fermented drinks and soda sweetened with aspartame provide a source of methanol in the diet. Methanol is an important commercial chemical. It is used as a solvent [7]. Above binary systems are studied for 06 different concentrations (0, 20, 40, 60, 80 and 100%) over the frequency range of 10 MHz to 50 GHz. Temperature dependent variations in dielectric parameters at temperature 288K also reported for the systems.

The volume fractions are converted to mole fractions for further calculations. Using this volume percentage the weight fraction is calculated [8] as

$$X_A = \frac{V_A \rho_A}{[(V_A \rho_A) + (V_B \rho_B)]} \qquad (1)$$

where, V_A and V_B are the volume and ρ_A and ρ_B is the density of liquid A(Lorazepam) and B (Methanol) respectively.

Apparatus

The complex permittivity spectra are studied by using Time Domain Reflectometry. (T.D.R.). The Tektronix Digital Serial Analyzer sampling Oscilloscope (DSA8200) with 80E08 TDR Module has been used. Research work experimental part done at School of physics, Swami Ramanand Teerth Marathwada University. Nanded. Maharashtra. India. It generates a fast repetitive voltage pulse was fed through coaxial line system of impedance 50Ω. The time window used for the experiment is kept at 2 ns. The reflected pulse without sample and with sample are digitized in 2000 points and transferred to computer through USB device. TDR has up to 30GHz Bandwidth with 20ps reflected rise time and 18ps incident rise time [9].
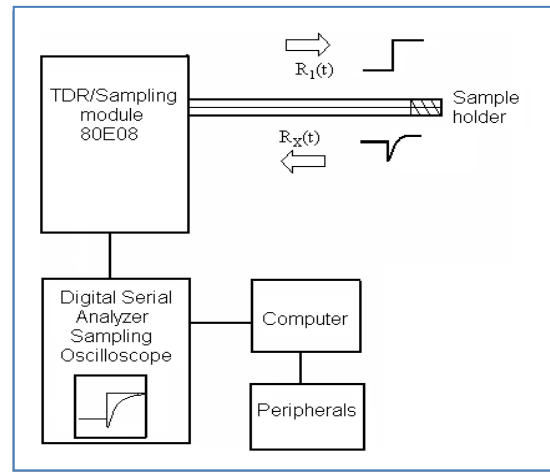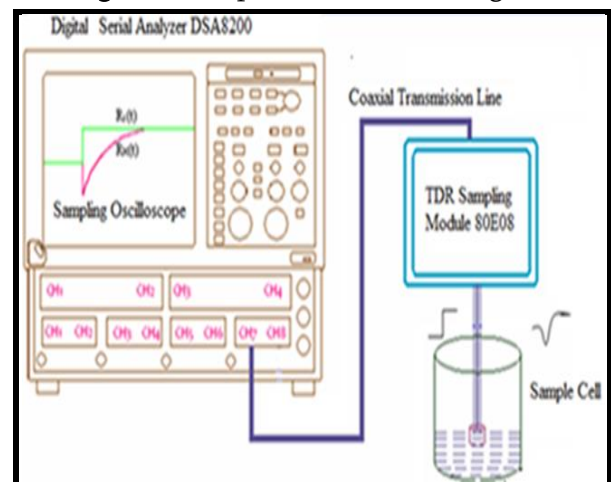

Fig.1 TDR Experimental block diagram

Fig.2 Experimental setup for TDR

Data analysis

The time dependent data were processed to obtain complex reflection coefficient spectra, $\rho^*(\omega)$ over the frequency range from 10 MHz to 50 GHz using Fourier transformation [10,11] as

$$\rho^*(\omega) = \left[\frac{c}{j\omega d}\right]\left[\frac{\rho(\omega)}{q(\omega)}\right] \qquad (2)$$

Where, $\rho(\omega)$ and $q(\omega)$ are Fourier transforms of [R_1 (t) - R_x (t)] and [R_1 (t) + R_x (t)], respectively. C is the velocity of light, ω is angular frequency and d is the effective pin length and j = root (-1). The complex permittivity spectra [12] $\varepsilon^*(\omega)$ were obtained from reflection coefficient spectra $\rho^*(\omega)$ by applying a bilinear calibration method. The experimental values of $\varepsilon^*(\omega)$ are fitted by Debye equation [13].

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + j\omega\tau} \qquad (3)$$

where, ε_0, ε_∞ and τ as fitting parameters. The value of ε_∞ was kept to be constant as the fitting parameters are not sensitive to ε_∞. A non-linear least squares fit method [14] used to determine the values of dielectric parameters.

III. RESULT AND DISCUSSION

Static Permittivity and Relaxation Time

Table 1. Temperature dependent dielectric parameters for binary mixture of Lorazepam + Methanol.

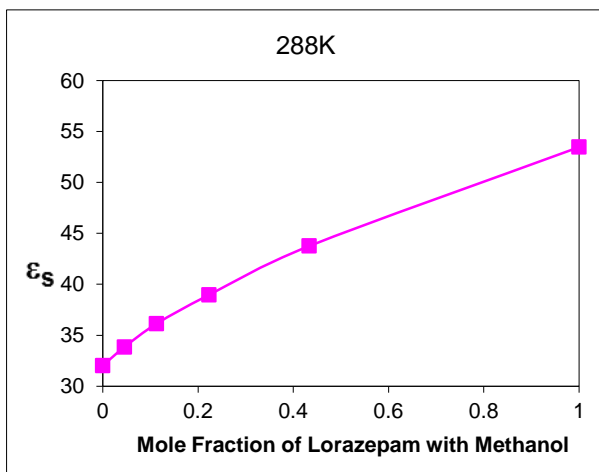| Mole Fraction of Lorazepam	288K	
	ε_s	τ (ps)
0	32.03	51.7
0.046	33.85	57.24
0.113	36.14	60
0.223	38.96	67.71
0.434	43.76	70.07
1	53.47	71.66

Figure 3. Variation of static dielectric constant (ε_s) as a function of mole fraction of Lorazepam at temperature 288K.
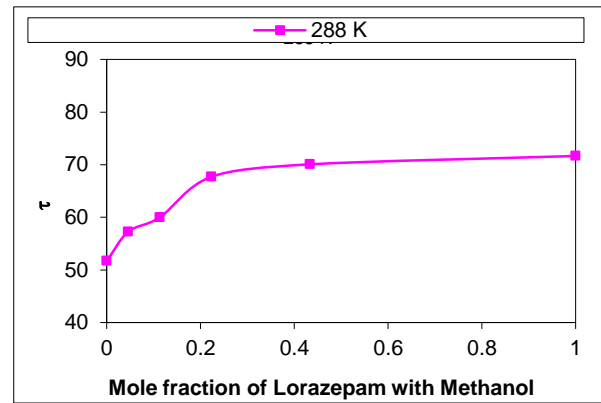

Figure 4. Variation of relaxation time (τ) as a function of mole fraction of Lorazepam at temperature 288K.

The static dielectric constant (ε_s)and relaxation time (τ) obtained by fitting experimental data with the Debye equation are listed in Table 1 It can be seen that there is almost linear relationship between the values of static dielectric constant (ε_s) and concentration of Lorazepam in the mixtures. The ε_s increases with increase in mole fraction of Lorazepam. This suggests that there is strong intermolecular interaction between the molecules of mixture. The relaxation time (τ) increases with increase in mole fraction of Lorazepam. This suggests strong intermolecular interaction between Lorazepam and Methanol molecules [15]. The static permittivity and relaxation time increases with increase in mole fraction and temperature of the system studied, indicating molecules rotate easily [16].
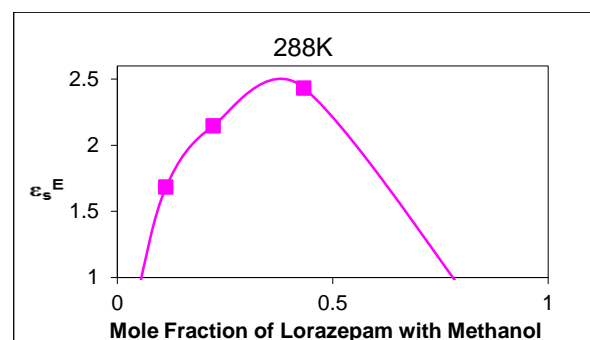
Excess Parameters

Figure 5. Variation of excess permittivity (ε_s^E) as a function of mole fraction (x_2) of Lorazepam at temperature 288K.
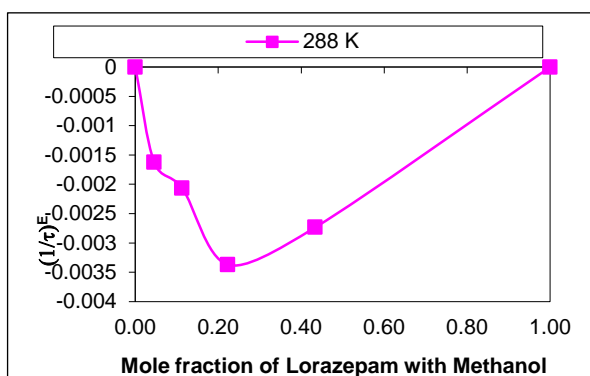
Figure 6. Variation of excess inverse relaxation time $(1/\tau)^E$, as a function of mole fraction (x_2) of Lorazepam at temperature 288K.

From figure 5 it can be seen that $(\varepsilon_s)^E$ is positive for all concentration of Lorazepam in the mixture. This indicates that the molecules of mixture may form multimers structures in such a way that there is increase in number of effective dipoles [17-19]. This is due to the similar alignment (parallel) of the dipoles in the mixture. For all the concentration the curves are more deviated at Methanol rich region.

The behavior in $(1/\tau)^E$ is as shown from figure 6. The values are negative for all concentration. Negative value of $(1/\tau)^E$ indicates rotation of the dipoles of the system [20].
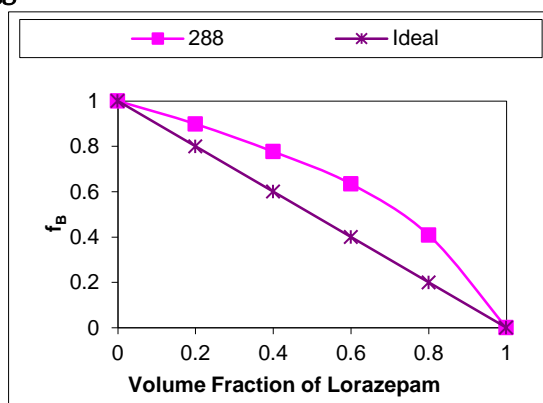
Bruggeman factor

Figure 7. The Bruggeman plot for binary mixture of lorazepam-methanol.

It can be seen from figure 7, f_B shows a deviation to upper side from the ideal Bruggeman behavior [21]. Indicate effective volume of solvent gets enhanced in the presence of solute. The effective volume value of Bruggeman parameter get less than

one. This confirms the strong intermolecular interaction in the mixture. Furthermore values of (f_B) decrease with increase in temperature, which shows temperature dependent nature of molecular interactions [22].
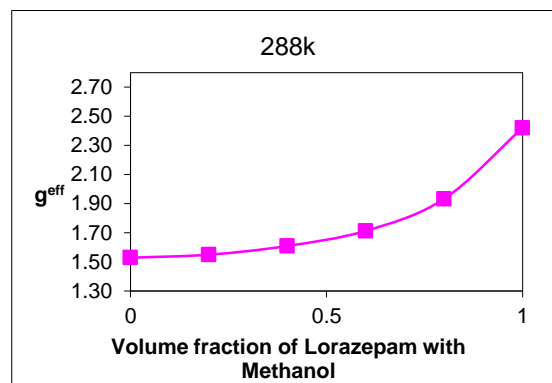
Kirkwood correlation factor

Figure 8. Variation of Kirkwood correlation factor 'g^eff ' with volume fraction of Lorazepam in Methanol at temperature 288K.
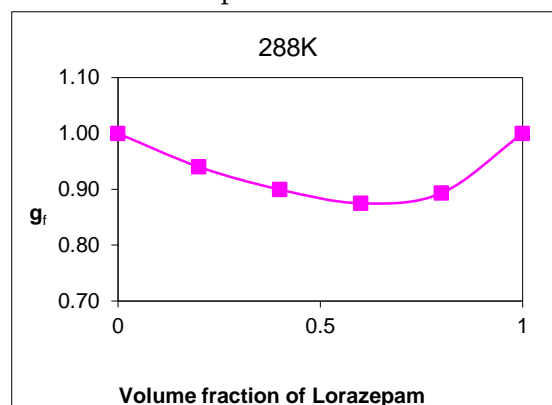

Figure 9. Variation of Kirkwood correlation factor g_f with variation of volume fraction of Lorazepam in Methanol at temperature 288K.

The values of g^{eff} are all positive and increases in the range from 1.5 to 2.6 at 288K temperature. The values confirm the formation of hydrogen bonding in pure Methanol system. These values are greater than unity suggesting effective dipole become larger as compare to pure liquid [23, 24]. Also indicate parallel orientation of electric dipoles. The corresponding values for Lorazepam are indicating weak dipole-dipole interaction resulting formation of antiparallel arrangement of dipoles in the pure system of Lorazepam [25].

The value of g_f is unity for an ideal mixture and deviation from unity may indicate interaction between two components of the mixture. The g_f value more than one indicates that the dipoles of mixture will be oriented in such a way that the effective dipole will be greater than the corresponding values of pure liquid [26-28].
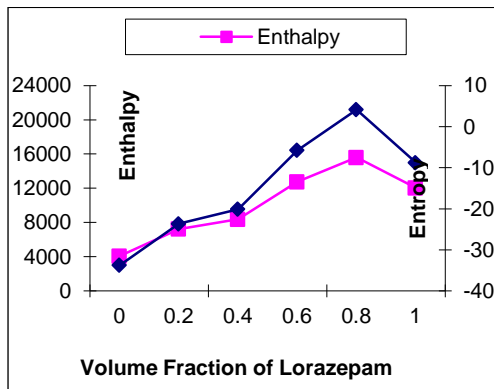
Thermodynamic Parameters

Figure 10. Enthalpy (ΔH) and Entropy (ΔS) of Lorazepam + Methanol Binary mixture.

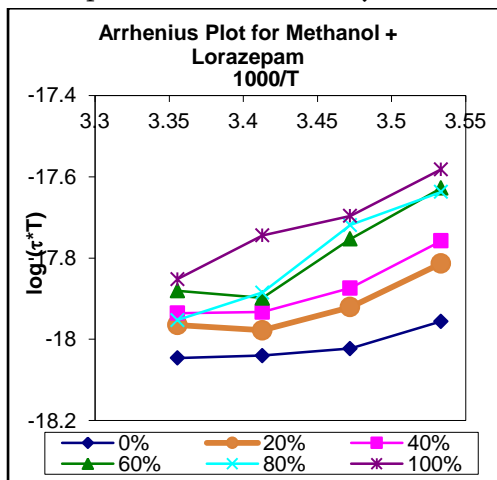**Figure 11.** Arrahenius plot of Lorazepam + Methanol Binary mixture.

From figure 10, it can be seen that the molar enthalpy of activation (ΔH) increases with increase in volume fraction of Lorazepam in Methanol from 4.069 KJ/mol up to 15.6KJ/mol, upto80% of Lorazepam in the mixture. Afterwards it will be decrease at12.05 KJ/mol (100% Lorazepam). This means that more energy is needed for group dipole reorientation up to 80% concentration of Lorazepam in the mixture. For 100% concentration of Lorazepam

in the mixture, less energy is needed for group dipole reorientation [29]. Negative values of molar entropy of activation (ΔS) with volume fraction of Lorazepam indicate relatively high ordered arrangement of molecules in the activated state [30-32].

Arrhenius plot for the system is shown in fig 11. The Arrhenius plot is almost linear for this system. The linear nature of Arrhenius plot shows that equivalent incremental change in temperature causes equivalent changes in values of activation enthalpy (ΔH) in temperature range under consideration. The slope of Arrhenius plot changes with concentration, which shows the change in activation energy of the system. The temperature dependence of relaxation time follows Arrhenius behavior [33, 34].

Conclusion

The static dielectric constant (ε_s) and relaxation time (τ) obtained by fitting experimental data with the Debye equation. The static permittivity and relaxation time increases with increase in mole fraction and temperature of the system studied, indicating strong intermolecular interaction and molecules rotate easily. $(\varepsilon_s)^E$ is positive for all .concentration indicate that there is increase in number of effective dipole and $(1/\tau)^E$ indicates rotation of the dipoles of the system. f_B shows a deviation to upper side from the ideal Bruggeman behavior indicate effective volume of solvent gets enhanced in the presence of solute. The g^{eff} values are greater than unity at all temperatures suggesting effective dipole become larger as compare to pure liquid. This means that more energy is needed for group dipole reorientation. The Arrhenius plot is almost linear for this system. The temperature dependence of relaxation time follows Arrhenius behavior.

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