

Comparative Study of Dielectric parameters of Binary Mixture of Ethanol, Methanol and Propanol with Pharmaceutical Drug Diazepam using Time Domain Reflectometry

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Abstract:

The complex permittivity spectra in the frequency range of 10MHz to 50 GHz have been determined using time domain reflectometry technique for six different volume concentrations, at 10, 15, 20 and 25 °C. The values of static dielectric constant, relaxation time, the corresponding excess properties have been determined. It is observed that, in the dielectric relaxation study of binary mixture of Ethanol, Methanol and Propanol with Diazepam confirms the static dielectric constant represents strong interaction for all combinations and for all temperature studied.

Keywords: Static permittivity, Relaxation time, Excess permittivity, Excess inverse relaxation time.

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I. INTRODUCTION

Dielectric Relaxation Spectroscopy (DSR) technique is a powerful technique to study the intra and inter molecular interaction in hydrogen bonded system such as alcohols [1]. In Ethanol, Methanol and Propanol compounds the hydroxyl (-OH) group is attached. The Diazepam is a psychopharmaceutical drug that is under depressant category, which have the capacity to reduce the activity of central nervous system, it slowdown the reaction and reduces the strength of response[2]. The study reveals that the significant variation in dielectric parameter may be attributed to cellular concentration.

II. EXPERIMENTAL

The complex permittivity spectra is studied by using Time Domain Reflectometry. (TDR). The Tektronix Digital Serial Analyzer sampling Oscilloscope(DSA8200) with 80E08 TDR Module has been used. 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[3].

Table1 . Physical constant of pure liquids.

Sr. No.	Name of Compound	Molecular Formula	Permittivity Literature value (ϵ_s)	M.W. g/Mole	Density g/cm ³	Dipole Moment μ D	R. I.
1	Ethanol	C ₂ H ₅ OH	24.3	46.03	0.789	1.69	1.3617
2	Methanol	CH ₃ OH	32.7	32.04	0.792	1.69	1.3314
3	Propanol	C ₃ H ₈ O	20.1	60.09	0.803	1.68	1.3862
4	Diazepam	C ₁₆ H ₁₃ ClN ₂ O	N.A.	284.743	1.26	N.A.	1.5987

II.1. 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 [4,5] as

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

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 $j = \text{root}(-1)$. The complex

permittivity spectra [6] $\epsilon^*(\omega)$ were obtained from reflection coefficient spectra $\rho^*(\omega)$ by applying a bilinear calibration method. The experimental values of $\epsilon^*(\omega)$ are fitted by Debye equation [7].

$$\epsilon^*(\omega) = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{1 + j\omega\tau}$$

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 [8] used to determine the values of dielectric parameters.

In the present work excess dielectric properties are determined corresponding to static permittivity and inverse relaxation time. The inverse relaxation time is taken instead of relaxation time, as inverse relaxation time corresponds to broadening of spectral lines in resonant spectroscopy [9]. The broadening of two levels are additive for two energy levels. The analogy is taken from dielectric spectroscopy.

The excess permittivity (ϵ_0^E) is defined as [10]

$$\epsilon_0^E = (\epsilon_0)_m - [(\epsilon_0)_A X_A + (\epsilon_0)_B X_B] \tag{2.81}$$

Where, X is the mole fraction and the subscript m, A and B represent mixture, solute and solvent respectively. The excess permittivity provides qualitative information about multimer formation in the mixture as follows.

(i) $\epsilon^E=0$: indicates that liquid A and liquid B do not interact and do not change their individual structural properties in the presence of other liquid.

(ii) $\epsilon^E < 0$: indicates that liquid A and liquid B interact in such a way that the effective dipole get aligned in antiparallel direction resulting in effective dipole moment gets reduced. The solute and solvent may form multimers leading to less effective dipoles. In general the negative excess permittivity indicates the formation of multimers having small values of effective dipoles in the binary mixture.

(iii) $\epsilon^E > 0$: indicates liquid A and liquid B interact in such a way that the effective dipole moment increases. This may be due to breaking of multimer structure into monomer structure in the presence of other molecule.

Similarly, the excess inverse relaxation time defined as

$$\left(\frac{1}{\tau}\right)^E = \left(\frac{1}{\tau}\right)_m - \left[\left(\frac{1}{\tau}\right)_A X_A + \left(\frac{1}{\tau}\right)_B X_B\right]$$

Where, $\left(\frac{1}{\tau}\right)^E$ is the excess inverse relaxation times, which represent the average broadening of dielectric spectra. Information regarding the dynamics of solute solvent interaction obtained from this excess property is as [11]

(i) $\left(\frac{1}{\tau}\right)^E = 0$: there is no change in the dynamics of liquid A and liquid B interaction, so their dipolar rotational times do not change.

(ii) $\left(\frac{1}{\tau}\right)^E < 0$: liquid A and liquid B interaction produces a field such that the relaxation time effectively gets enhanced resulting dipoles rotate slowly.

(iii) $\left(\frac{1}{\tau}\right)^E > 0$: liquid A and liquid B interaction produces a field such that the effective dipole rotate quickly, the field cooperate in rotation of dipoles.

III. RESULT AND DISCUSSION

Table 2. Temperature dependent dielectric parameters of binary mixture of Ethanol and Diazepam.

Mole Fraction of Diazepam	283 K		288 K		293 K		298 K	
	ϵ_s	τ (ps)	ϵ_s	τ (ps)	ϵ_s	τ (ps)	ϵ_s	τ (ps)
0	25.71	175.2	24.39	157	23.74	142.7	23.8	142.5
0.0606	29.33	157.1	28.77	130.3	27.74	119.6	26.25	104.2
0.1468	33.14	131.3	31.76	97.93	30.9	91.92	30.74	86.77
0.2791	39.04	130.5	36.97	97.5	35.88	92.33	35.43	85.93
0.5080	46.4	123.5	44.39	91.25	43.35	85.99	42.88	82.46
1	57.28	106.1	55.27	74.53	54.74	68.09	53.97	64.81

Table 3. Temperature dependent dielectric parameters of binary mixture of Methanol and Diazepam.

Mole Fraction of Diazepam	283K		288K		293K		298K	
	ϵ_s	τ (ps)	ϵ_s	τ (ps)	ϵ_s	τ (ps)	ϵ_s	τ (ps)
0	21.57	57.63	23.09	54.9	23.09	47.48	26.7	45.72
0.0428	42.16	63.81	41.99	60.61	41.99	59.58	40.62	58.32
0.1066	49.12	91.75	44.04	64.58	44.04	61.49	42.78	61.17
0.2117	51.02	92.08	44.79	70.14	44.79	64.24	43.22	62.93

0.4173	52.5	103.6	44.86	99.39	44.86	79.23	44.51	66.25
1	57.28	110.1	55.27	104.5	55.27	98.09	47.97	86.81

Table 4. Temperature dependent dielectric parameters of binary mixture of Diazepam and Propanol.

Mole Fraction of Diazepam	283K		288K		293K		298K	
	ϵ_s	τ (ps)	ϵ_s	τ (ps)	ϵ_s	τ (ps)	ϵ_s	τ (ps)
0	20.65	315.9	21.61	315.9	20.79	316.2	20.1	263.4
0.0765	19.85	200.3	19.52	199.4	19.52	199.4	19.06	159.7
0.1808	23.28	175	23.08	159.3	23.14	144.7	22.82	144.8
0.3319	29.51	131.3	28.59	96.98	28.33	86.23	28.19	81.85
0.5698	36.02	99.72	37.66	92.79	36.87	87.28	35.96	82.57
1	57.28	80.1	55.27	75.5	54.74	68.09	47.97	64.81

III.1 STATIC PERMITTIVITY

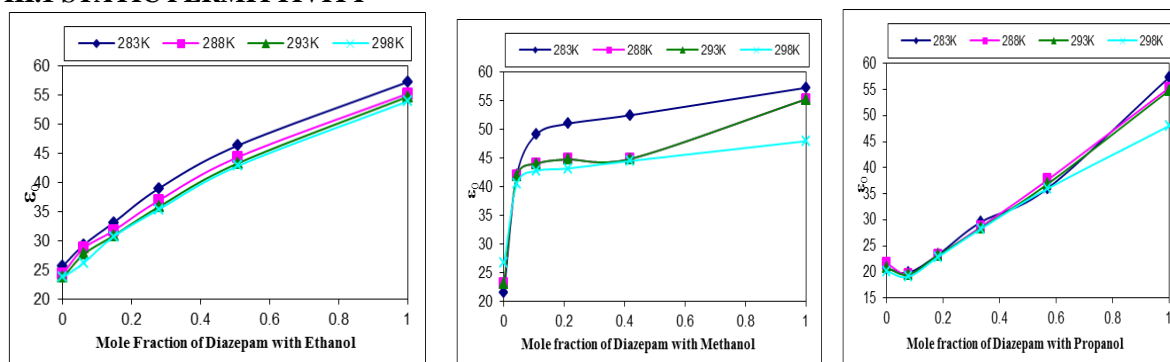


Figure 1. Variation of static dielectric constant (ϵ_s) as a function of mole fraction of Diazepam at temperatures 283, 288, 293 and 298K.

It can be seen that there is almost linear relationship between the values of static dielectric constant (ϵ_s) and concentration of Diazepam in the mixtures. The ϵ_s increases linear with increase in mole fraction of Diazepam. This suggests that there is strong intermolecular interaction between the molecules of mixture.

III.2 RELAXATION TIME

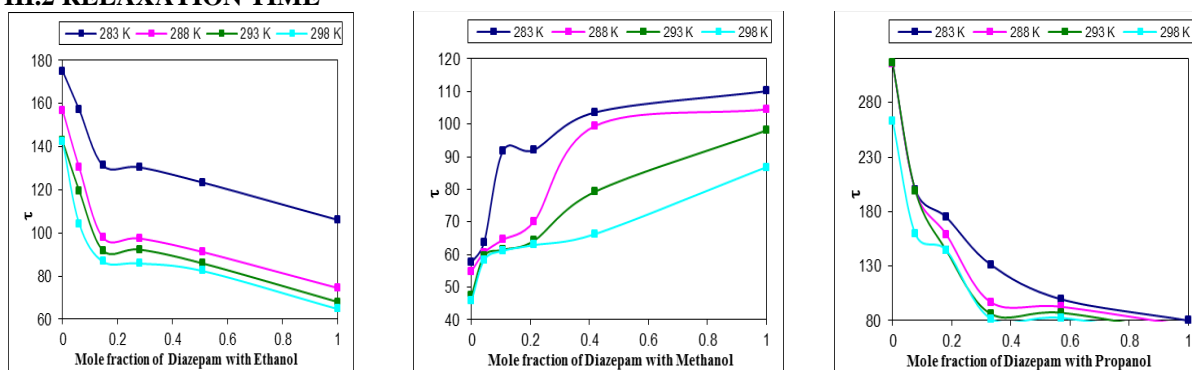


Figure 2. Variation of relaxation time (τ) as a function of mole fraction of Diazepam at temperatures 283, 288, 293 and 298K.

The relationship for the relaxation time (τ) is linear. It is observe that the value of τ decrease with increase in mole fraction of Diazepam with Ethanol and Propanol. This suggests strong intermolecular interaction between Diazepam with Ethanol and Propanol molecules, where as weak interaction with Methanol [12].

The static permittivity increases and relaxation time decreases with increase in mole fraction of Diazepam, as a combination result it indicate intermolecular interaction is less, the value of relaxation time becomes low [13].

III.3 EXCESS PERMITTIVITY

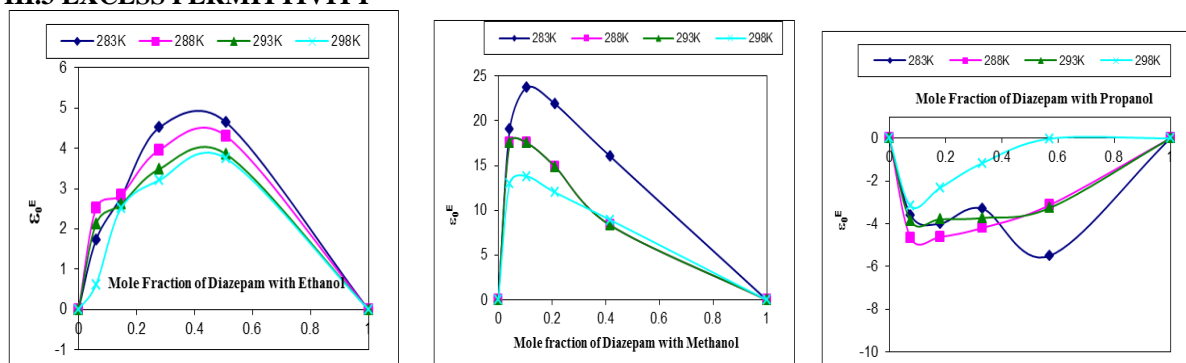


Figure 3. Variation of excess permittivity as a function of mole fraction of Diazepam at temperatures 283, 288, 293 and 298K.

It can be seen that $(\epsilon_s)^E$ is positive for all concentration of Diazepam in the mixture with Ethanol and Methanol, all temperature studied. This indicates that the molecules of mixture may form multimers structures in such a way that there is increase in number of effective dipoles where as with Propanol, effective dipole decreases [14-16].

III.4 EXCESS INVERSE RELAXATION TIME

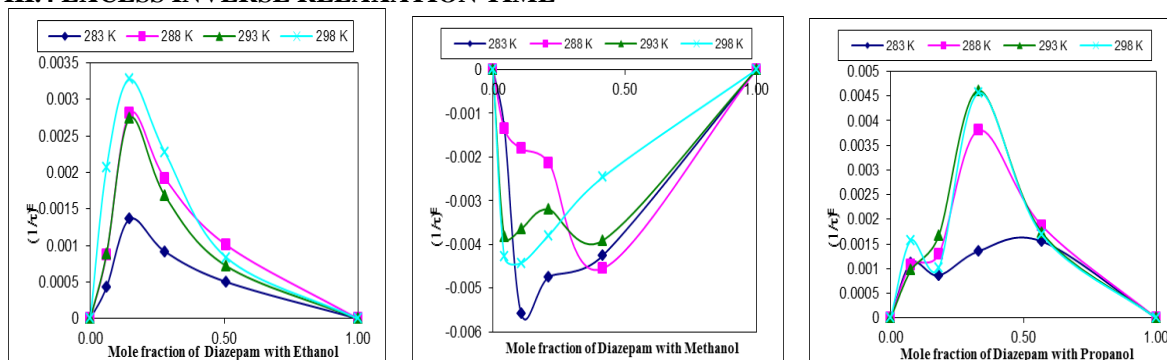


Figure 3. Variation of excess inverse relaxation time as a function of mole fraction of Diazepam at temperatures 283, 288, 293 and 298K.

The behavior in $(1/\tau)^E$ shows increase upto 40% with Ethanol and 60% with Propanol and then decrease with higher concentration, At all temperature $(1/\tau)^E$ are positive, this suggest that the molecular interaction produces a cooperative field and the effective dipoles have less freedom of rotation, molecules not rotate easily. Whereas with Methanol it shows negative values, molecules rotate easily [17].

IV. CONCLUSION

It is concluded that, in the dielectric relaxation study of binary mixture of Ethanol, Methanol and Propanol with Diazepam confirms the static dielectric constant represents strong interaction for all combinations and for all temperature studied. Relaxation time with Methanol is higher than Ethanol and Propanol, it may be due to more association through hydrogen bonding of OH group, excess permittivity positive for Ethanol and Methanol, inverse relaxation time is negative for Methanol.

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