OUR HERITAGE
ISSN: 0474-9030Vol-68, Special Issue-38
ONE DAY NATIONAL CONFERENCE ON RECENT ADVANCES IN SCIENCES
Held on: 13th February 2020.
Organized by: Department of PHYSICS, CHEMISTRY, MATHEMATICS, BOTANY & ZOOLOGY Shivaji Arts, Commerce and Science College Kannad. Dist: Aurangabad (MS)

Study of Molecular Interaction in Binary Mixture of Lorazepam with Methanol Using Bruggeman Model

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ABSTRACT

The dielectric relaxation parameters of Lorazepam with Ethanol in the microwave frequency range of 10MHz to 50MHz have been determined using time domain reflectometry technique. The Tektronix DSA8300 sampling oscilloscope sampling main frame with the dual channel sampling module 80E10B has been used for these measurements. The time dependent data is analyze to obtain complex reflection coefficient. The complex permittivity spectra obtained by applying bilinear calibration method. The Bruggeman parameters are obtained using static dielectric constant. It is observed that f_B shows a small deviation to upper side from the ideal Bruggeman behavior for every temperature studied of Lorazepam with Methanol as binary mixture.

KEYWORDS :-Lorazepam, Methanol, Time domain reflectometry, Dielectric relaxation, Bruggeman factor.

INTRODUCTION

The dielectric relaxation measurement at microwave frequencies have provided an effective means of studying mechanism of molecular process and intermolecular interaction between the binary mixtures of the organic compounds [1-5]. The Bruggeman parameter of binary polar liquids provides information regarding solute-solvent intermolecular interaction between the molecules.

Lorazepam, is a medicine sold under the brand name Ativan, Tavor, Temesta, among others. It is used to treat anxiety disorders, trouble sleeping. Lorazepam is also used, along with other

treatments, for acute coronary syndrome due to cocaine use [6]. Methanol 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 provide a source of methanol in the diet. Methanol is an important commercial chemical. It is used as a solvent [7].

In this work we report the dielectric study of Bruggeman factor of Lorazepam with Methanol binary mixture at 20% of volume fraction concentration and 283, 288, 293 and 298K temperature.

Table 1. Physical constant of pure liquids.

Name of Compound	Mol. Formula	Literature Value of ε_s	Mol. Wt. g/mol	Density in g/cm^3	Dipole Moment μ D	R.I.
Lorazepam	$C_{15}H_{10}Cl_2N_2O_2$	N.A.	321.2	1.52	N.A.	1.60
Methanol	CH_3OH	32.7	32.04	0.792	1.69	1.3314

EXPERIMENTAL

A. Chemical and sample preparation

The chemical used in the present work are 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. These volume fractions are converted to mole fractions for further calculations. Using this volume percentage the weight fraction is calculate [8] as

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

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

B. T.D.R. specification, Time domain reflectometry set up and data acquisition.

The Tektronix DSA8300 sampling oscilloscope sampling main frame with the dual channel sampling module 80E10B has been used for time domain reflectometry. The sampling

module provides 12ps incident and 15ps reflected rise time pulse. The coaxial cable used to feed pulse has 50 Ohm impedance, inner diameter of 0.28mm and outer diameter of 1.19mm. Sampling oscilloscope monitors changes in pulse after reflection from end of line. Reflected pulse without sample $R_1(t)$ and with sample $R_x(t)$ were recorded in time window of 5 ns and digitized in 2000 points. To minimize the signal to noise ratio the signal reflected is obtained from 512 samples after an optimum average of 100 times for each record. The subtraction [$p(t) = R_1(t) - R_x(t)$] and addition [$q(t) = R_1(t) + R_x(t)$] of these pulses are done in oscilloscope memory. These subtracted and added pulses are transferred to PC through compact disc for further analysis [9].

C. 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

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

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].

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

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.

RESULT AND DISCUSSION

The static permittivity of two component mixture must lie somewhere between two extremes corresponding to static permittivity of two liquids. In order to understand the dipole interaction in the mixture of two liquids, a various mixture formulae have been proposed [15,

16]. Bruggeman mixture formulae [16-18] can be used as first evidence of molecular interactions in binary mixture. This formula states that static permittivity of binary mixture (εsm), solute A (εsA) and solvent B (εsB) can be related to volume fraction of solvent (V) in mixture as $f_B = 1\ V$

$$f_B = \left(\frac{\varepsilon_{sm}-\varepsilon_{sB}}{\varepsilon_{sA}-\varepsilon_{sB}}\right)\left(\frac{\varepsilon_{sA}}{\varepsilon_{sm}}\right)^{1/3} = 1 - V$$

According to above equation linear relationship is expected in Bruggeman factor f_B and (V). Any deviation from this linear relation indicates molecular interactions. Experimentally, it was found that the Bruggeman factor deviates from the linear behavior. It was proposed to modify the model as follows [19]

$$f_B = \left(\frac{\varepsilon_{sm}-\varepsilon_{sB}}{\varepsilon_{sA}-\varepsilon_{sB}}\right)\left(\frac{\varepsilon_{sA}}{\varepsilon_{sm}}\right)^{1/3} = 1 - [a - (a-1)V]V$$

In this model, it is assumed that the volume fraction V is modified by a factor a-(a-1)V in the mixture due to solute – solvent interaction. The value of a=1 corresponds to the Bruggeman's equations. The value of a can be determined by statistical technique of least square fit method [20].

Table: 2. Temperature dependent dielectric parameters for binary mixture of Lorazepam with Methanol.

Mole Fraction of Lorazepam	283K		288K		293K		298K	
	ε_s	τ (ps)	ε_s	τ (ps)	ε_s	τ (ps)	ε_s	τ (ps)
0	33.27	56.25	32.03	51.7	31.69	49.94	32.12	48.81
0.046	34.46	64.87	33.85	57.24	33.58	53.14	33.52	52.94
0.113	38.14	68.59	36.14	60	34.32	55.59	34.14	54.51
0.223	40.58	78.1	38.96	67.71	38.45	57.55	37.35	57.59
0.434	45.87	77.36	43.76	70.07	41.98	58.33	41.42	53.6
1	58.96	81.78	53.47	71.66	52.58	67.13	48.43	59.27

The Bruggemen factor which is the ratio of theoretical value of static dielectric constant computed from Bruggemen mixture formulae and practically obtained values has been obtained [21]. A linear relationship has been expected from the Bruggemen factor values, which gives a straight line when f_B plotted against volume fraction. However the experimental values of f_B were found to deviate from the linear relationship. The nonlinear relationship of Lorazepam with Methanol system suggest an intermolecular interaction takes place in the mixed components. It is assume that volume fraction in the mixture is modified by a factor [a-(a-1)φ]. This modification may be due to the structural rearrangement of solute molecules in the mixture. The value of 'a' contain information regarding the change in orientation of solute molecules in the mixture. The value of 'a' determined from the least square fit method, for all the studied system. The value of 'a' = 1 corresponds to ideal Bruggemen mixture formulae. The deviation from unity relates to corresponding mixture interaction [22]. The parameter 'a' in the modified Bruggemen model also provide information regarding nature of molecular interaction as [23]

1. The straight line from (0,1) to (1,0) represents noninteraction between solute – solvent system. In such case, the value of parameter 'a' will be 1.
2. The deviation to the upper part of the straight line indicates that effective volume of the solvents gets enhanced in presence of solute. The value of 'a' becomes less than one in such case.
3. The deviation to the lower part of the straight line indicates reduction of effective volume and value of the parameter 'a' gets larger than one.

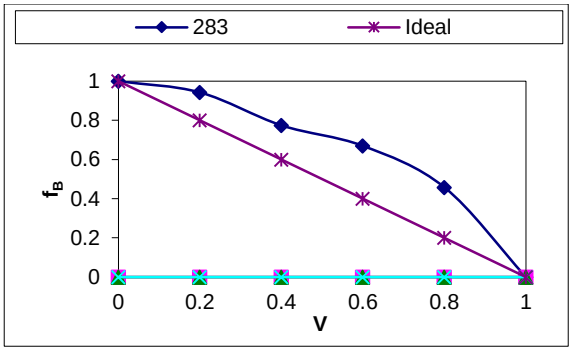

Figure 1: The Bruggeman plot for Lorazepam with Methanol at 283K

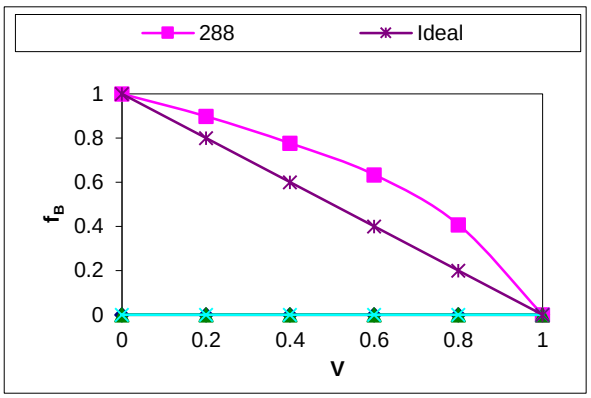

Figure 2: The Bruggeman plot for Lorazepam with Methanol at 288K

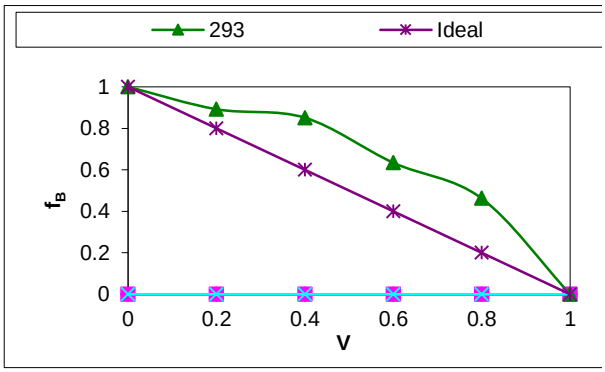

Figure 3: The Bruggeman plot for Lorazepam with Methanol at 293K

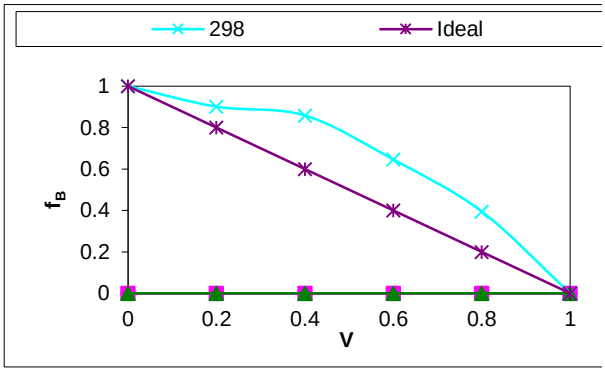

Figure 4: The Bruggeman plot for Lorazepam with Methanol at 298K

Figure shows the Bruggeman plot for Lorazepam with Methanol, volume fraction of Lorazepam (V) against Bruggeman factor f_B at particular temperature K. Linear line shows expected ideal behavior, small deviation line shows the experimental obtained behavior.

It can be seen from figure 1, 2, 3 and 4 f_B shows a small deviation to upper side from the ideal Bruggeman behavior [21]. Indicate that effective volume of the solvents gets enhanced in presence of solute. The value of 'a' becomes less than one in such case. This confirms the weak intermolecular interaction in the mixture. Furthermore values of (f_B) increase with increase in temperature and decrease in volume fraction of Diazepam, which shows temperature dependent nature of molecular interactions [24].

CONCLUSION

It can be concluded that f_B shows a small deviation to upper side from the ideal Bruggeman behavior of Lorazepam with Methanol in binary mixture. The interaction of the mixture is discussed using Bruggeman model at four different temperatures is weak and nature of molecular interactions is temperature dependent.

ACKNOWLEDGEMENT

The authors wish to acknowledge the Department of Physics Dr. Babasaheb Ambedkar Marathwada University Aurangabad, Department of Physics Swami Ramanand Teerth Marathwada University Nanded, Department of Physics Milliya Arts, Science and Management Science College Beed.

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