

Dielectric and Structural Relaxation Studies Of 1,3-Butanediol-1,4-Dioxane Mixtures Using Time Domain Reflectometry Technique

Nitin Garad, Ashwini Gubre, Avadhut Deshmukh, A. C. Kumbharkhane*

*Department of Physical Sciences, Swami Ramanand Teerth Marathwada University, Nanded-431606, Maharashtra, India

ABSTRACT

The complex permittivity spectrum of 1,3-Butanediol in 1,4-Dioxane have been measured in the frequency range of $0.01 \leq \nu / \text{GHz} \leq 50$, over the entire concentration range using time domain reflectometry technique at 25°C. The dielectric parameters such as static dielectric constant (ϵ_s) and relaxation time (τ in ps) are obtained from the complex permittivity spectra using nonlinear least square fit method. The 1,3-Butanediol-1,4-Dioxane mixture shows the Cole-Davidson type relaxation process. The molecular interactions among 1,3-Butanediol-1,4-Dioxane mixture have been studied using excess dielectric constant, excess inverse relaxation time and Bruggeman factor.

Keywords: Complex Permittivity Spectra, Dielectric relaxation, Time domain reflectometry Excess inverse relaxation, Bruggeman factor.

I. INTRODUCTION

Dielectric relaxation spectroscopy of associating liquids offers valuable insights in the study of physicochemical properties. The time domain reflectometry (TDR) is a very useful technique to study the dielectric relaxation parameters of liquids. This technique covers a broadband of frequencies in a single measurement [1]. The measurement of dielectric relaxation is a good tool to study molecular interactions in hydrogen bonded liquids such as diols. In our laboratory the considerable dielectric work has been done on diol-dioxane mixtures using time domain reflectometry [2]. These molecules have an intrinsic electric dipole moment. Diols are the organic compounds which are most important in the field of organic chemistry and biochemistry. Due to the presence of two -OH groups in a diol molecule, the solution chemistry of these compounds can be strongly influenced by the intermolecular and intramolecular hydrogen bond formation. It also plays an important role in the physical properties of the molecules. Butanediols are four carbon diols that have many industrial and biological applications [3-5].

1,3-butanediol (1,3-BD) is the higher diol in diol family having structural formula $\text{OHCH}_2\text{CH}_2\text{CHOHCH}_3$. This colorless liquid is derived from butane alcohol in which hydroxyl groups are attached to first and third carbon atoms of the chain. 1,3-BD is commonly used as a solvent for food flavoring agents and is a co-monomer used in certain polyurethane and polyester resins. 1,3 BD is a highly effective humectants in pet foods, tobacco and

cosmetic formulations. Many workers [6-7] have reported dielectric relaxation studies of binary mixtures to understand hydrogen bonding and intramolecular interaction in the mixtures. Kadam *et al.* have studied dielectric properties of 1,3 butanediol-water mixture in frequency range of 10 MHz to 30 GHz using a time domain reflectometry (TDR) technique at 25°C temperature [8]. Shinde *et al.* have reported dielectric spectra of 1,3-propanediol-dioxane mixture in the frequency range 10 MHz to 30 GHz at 25°C using the method of time domain reflectometry [9].

In present paper, we have reported the dielectric relaxation study of 1,3-BD–1,4-Dioxane 1,4-Dx mixtures over a wide concentration and frequency range using time domain reflectometry technique. The static dielectric constant, relaxation time, excess properties, Kirkwood correlation factor and the number of hydrogen bonds for 1,3-BD–1,4-Dx mixture have been determined.

II. EXPERIMENTAL PROCEDURE

1,3 BD and 1,4-dioxane (1,4-Dx) are purchased from Merck-Chemicals and used without purification. Complex permittivity spectra for 1,3-butanediol and 1,4-dioxane (1,4-Dx) binary mixture at temperature 25°C was recorded over the frequency range $0.01 \leq \nu/\text{GHz} \leq 50$ using Time Domain Reflectometry. Tektronix Digital serial analyzer (DSA 8300) sampling main frame oscilloscope having dual channel sampling module 80E10B has been used. A sampling module provides 12 ps incident and 15 ps reflected rise time pulse produced by tunnel diode was fed through a coaxial line system having 50 Ω impedance. The inner and outer diameters of used coaxial cable were 0.28 mm and 1.19 mm respectively. Sampling oscilloscope records the changes in step pulse after reflection from the end of line. The reflected pulse without sample $R_1(t)$ and with sample $R_x(t)$ were recorded in the time window of 5 ns and digitized in 2000 points. The subtraction [$q(t) = R_1(t) - R_x(t)$] and addition [$p(t) = R_1(t) + R_x(t)$] of these pulses are done and stored in oscilloscope memory. Fourier transformation has been used for the conversion of time domain data to frequency domain data in the frequency range $0.01 \leq \nu/\text{GHz} \leq 50$. Calibration of TDR was done according to guidelines of manufacturers and using solvents with known dielectric constant [2, 10-11].

III. RESULT AND DISCUSSION

The Cole–Cole (ϵ'' vs. ϵ'') plot for different concentrations of 1,3-BD–1,4-Dx mixture is shown in **Figure 1**. To calculate static dielectric constant (ϵ_0), relaxation time (τ) and distribution parameters (α and β) the complex permittivity $\epsilon^*(\omega)$ data were fitted by the non-linear least squares fit method to the Havriliak–Negami expression [12] $\epsilon^*(\omega) = \epsilon_\infty + \frac{\epsilon_s - \epsilon_\infty}{[1 + (j\omega\tau)^{1-\alpha}]^\beta}$ (1)

where ϵ_s , ϵ_∞ , τ , α and β are the fitting parameters. The Havriliak–Negami function includes the Cole–Cole ($\beta = 1$), Davidson–Cole ($\alpha = 0$) and Debye ($\alpha = 0$, $\beta = 1$) relaxation spectral functions in the limiting form. In general, the dielectric loss spectrum of polyalcohol is an asymmetric shape, and it is described by Cole–Davidson equation. Here these fitting parameters, α is kept to 0 and β varies in between 1 to 0. β indicates the asymmetrical broadness of the loss peak.

It can be seen from **Figure 1** that the dielectric relaxation in these mixtures can be represented by Cole–Davidson relaxation. The change in β values may reflect a variation in the relaxing species or a perturbation of the molecular structure of the system. The decreases of β suggest that the structure of the mixtures deviates significantly from that of pure diol.

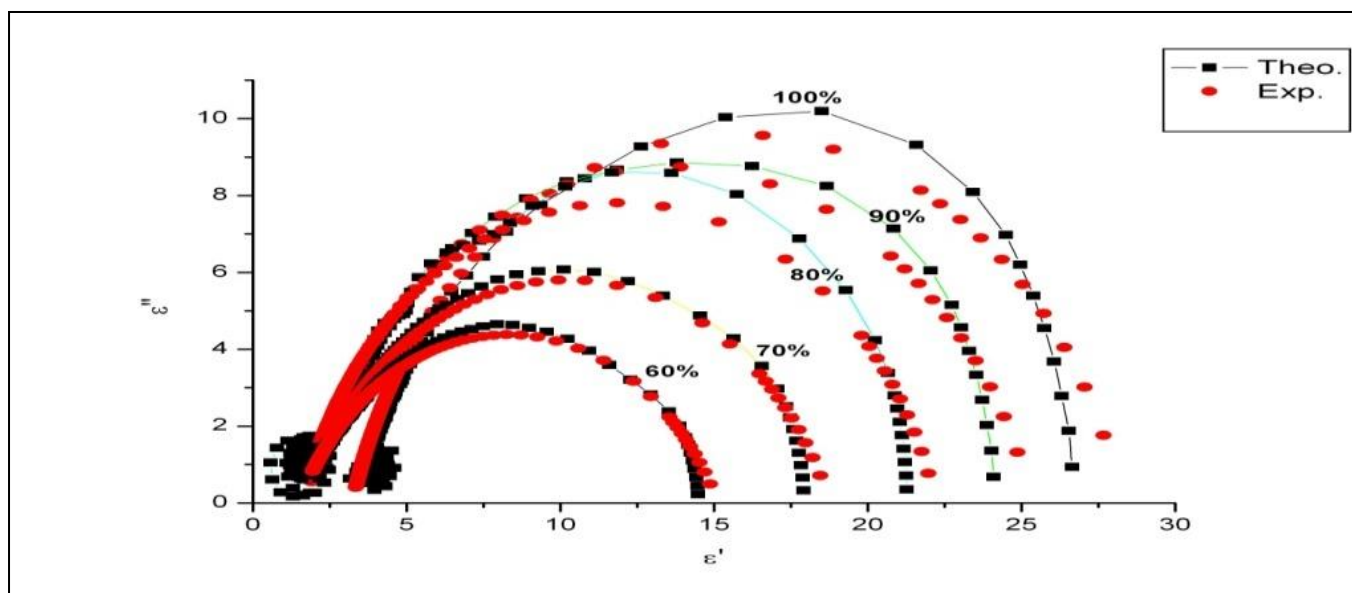


Figure 1. The Cole–Cole plot for 1,3-butanediol–Dx mixture at 25°C.

3.1 Complex Permittivity Spectra

Figure 2 shows the complex permittivity spectra (CSP) for 1,3-BD-1,4-Dx binary mixture in the frequency range $0.01 \leq \nu/\text{GHz} \leq 50$. This spectrum shows the systematic variation of dielectric permittivity ϵ' and dielectric loss ϵ'' . As frequency increases, dielectric permittivity of solution decreases for all concentrations including 1,3-BD but for pure 1,4-Dx variation is not significant due to its low dipole moment.

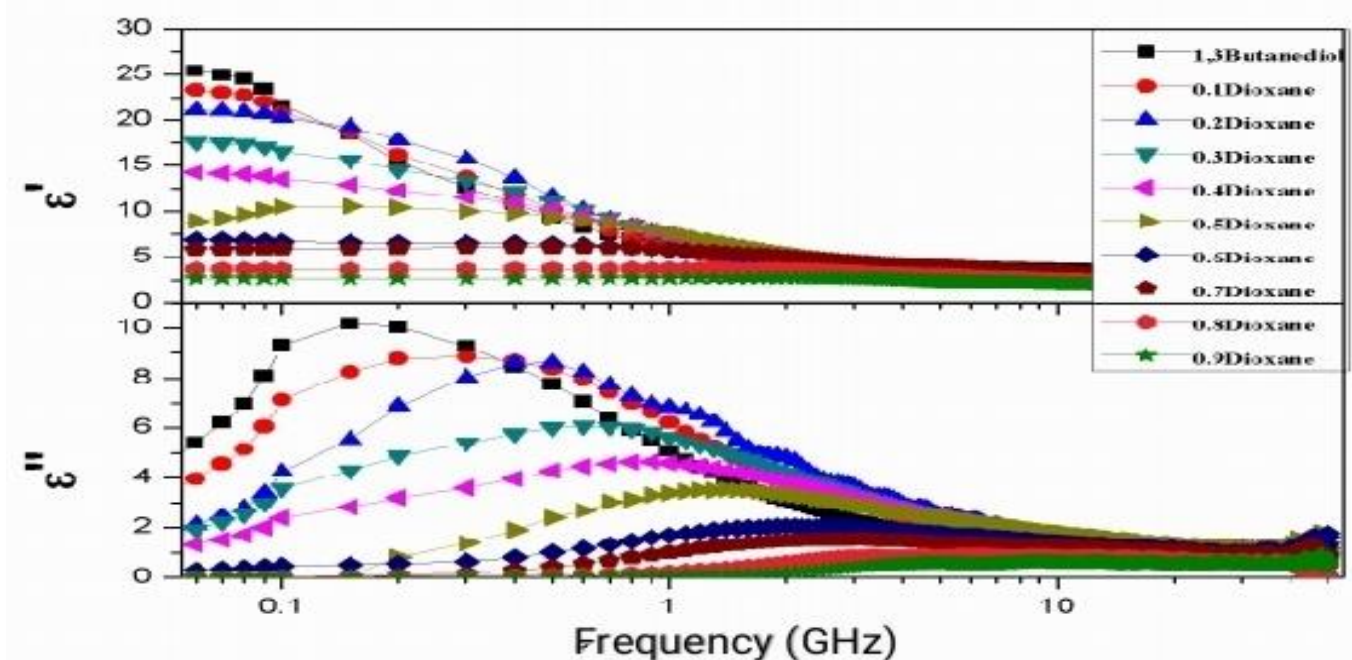


Figure2: Complex permittivity spectra for Butanediol - Dioxane binary mixture at 25°C.

3.2 Dielectric constant and relaxation time:

The change in dielectric constant (ϵ_s) values for Butanediol-Dioxane system at 25°C temperature is shown in Figure 3. The ϵ_s values have been increasing linearly with increasing the volume fraction (V_w) of 1,3-BD in 1,4-

Dx, suggest the self-association, hydrogen bonding and aggregation of molecules changes from spherical to elongated aggregation in solutions [13].

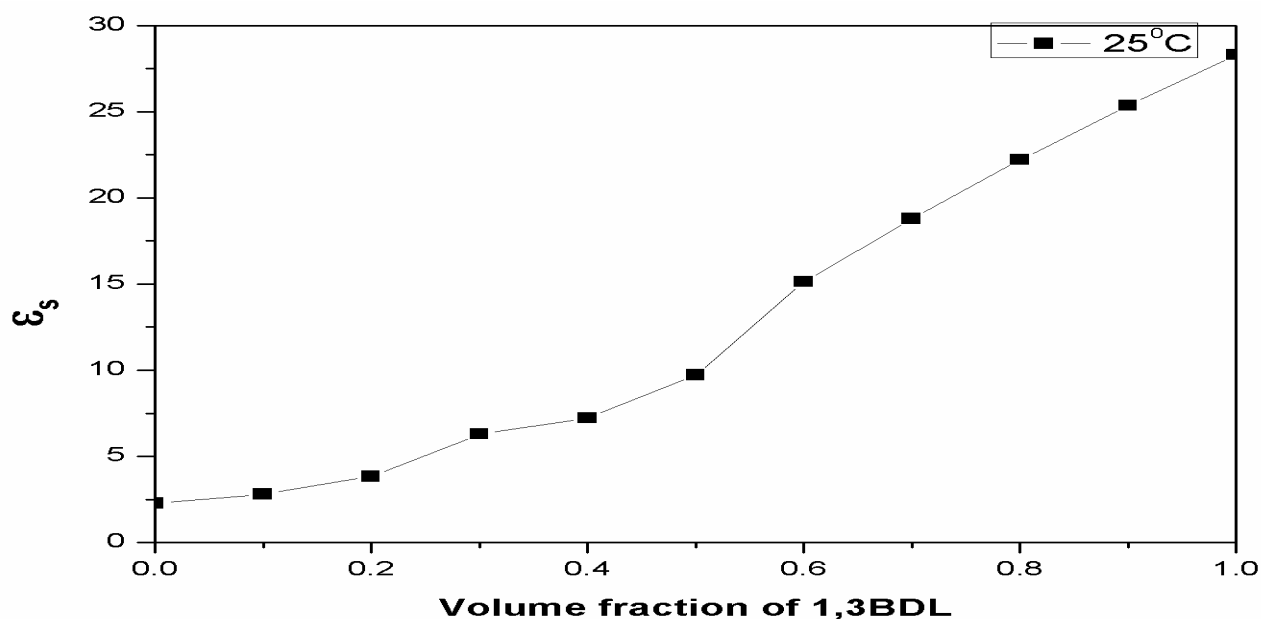


Figure3:static dielectric constant vs. volume fraction of 1,3-butenediol at 25°C.

Figure 4 shows the concentration dependence of relaxation time (τ) of 1,3-butenediol–dioxane mixtures. The relaxation time (τ) increases with increasing 1,3-BD concentration in dioxane. When dioxane is added to 1,3-BD, the number of hydrogen bonds decreases. The distribution of hydrogen bonds would affect the concentration dependence of the relaxation time. The relaxation time of alcohol–dioxane system increases non-linearly with increasing alcohol concentration. These values also suggest the net change in orientation polarization configuration in the mixture over entire concentration range [14].

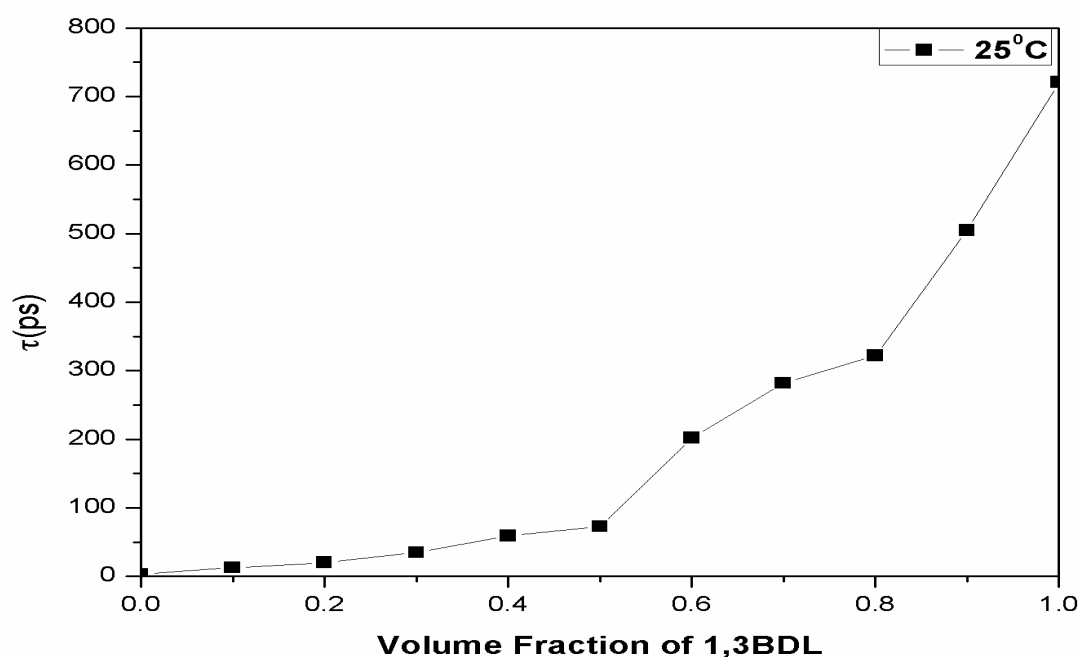


Figure4: Relaxation time vs. volume fraction of 1,3-butenediol at 25°C

3.3 Excess inverse relaxation:

The excess inverse relaxation property is useful for perception of cooperative domain in the mixture and may affirm the formation of multimers in mixture due to molecular interaction. The excess inverse relaxation time is defined as $(1/\tau)^E = (1/\tau)_M - [(1/\tau)_{Dx}X_{Dx} + (1/\tau)_{BD}(1-X_{Dx})]$ (2)

where the subscripts M, D and BD represents Mixture, 1,4-Dx and 1,3-BD respectively and X_{Dx} represents the volume fraction of 1,4-Dioxane in 1,3-BD. The plot of excess inverse relaxation time vs. volume fraction of 1,3-BD is shown in **Figure 5**. Negative values of excess inverse relaxation suggest that there is slower rotation of dipoles in mixture due to solute-solvent interaction form the hydrogen bonded structure i.e., multimer which produces a field in such a way that the effective dipole moment get reduced [2].

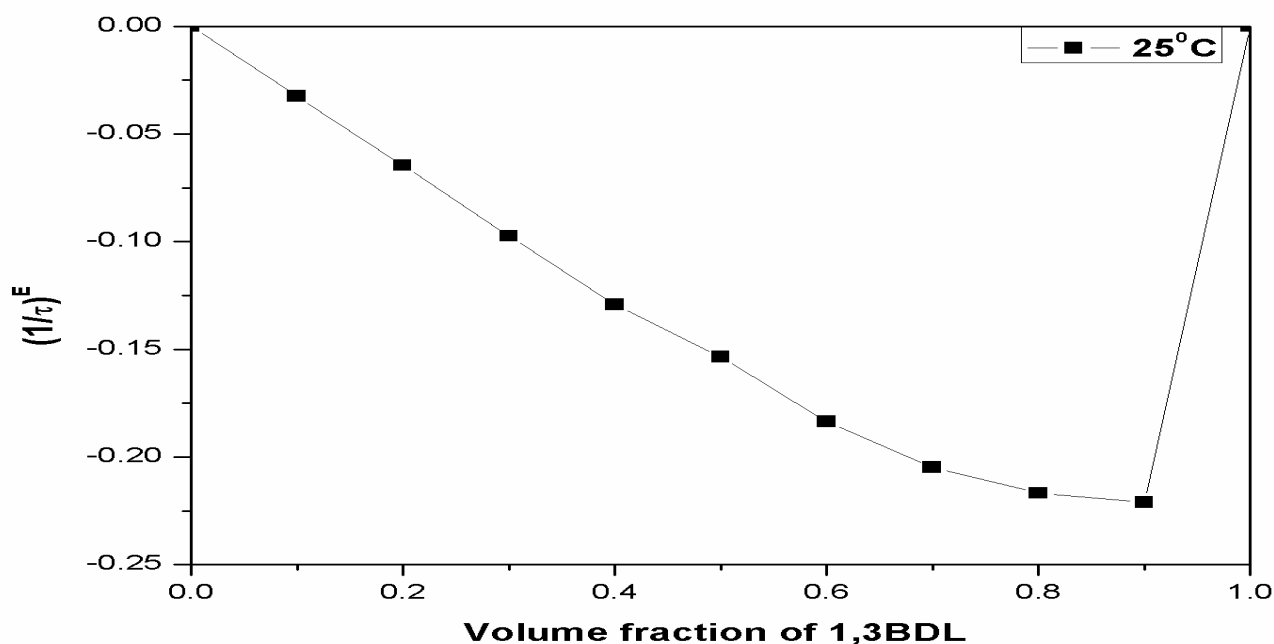


Figure 5. Excess inverse relaxation time $(1/\tau)^E$ versus volume fraction of butanediol at 25°C.

3.4 Excess dielectric permittivity:

The excess dielectric permittivity (ϵ_s^E) can be written as: $\epsilon_s^E = (\epsilon_s)_M - [(\epsilon_s)_{Dx}X_{Dx} + (\epsilon_s)_{BD}(1-X_{Dx})]$ (3)

where the subscripts M, Dx and BD represents Mixture, 1,4-Dioxane and 1,3-Butanediol respectively and X_{Dx} represents the volume fraction of dioxane in 1,3-Butanediol. The plot of ϵ_s^E vs volume fraction of butanediol is shown in **Figure 6**. The negative values of ϵ_s^E suggest that molecules of 1,3 Butanediol break the structure of Dioxane and the Butanediol- Dioxane molecules grow together which results into the formation of polymeric structure and decrease in total number of effective dipoles [2].

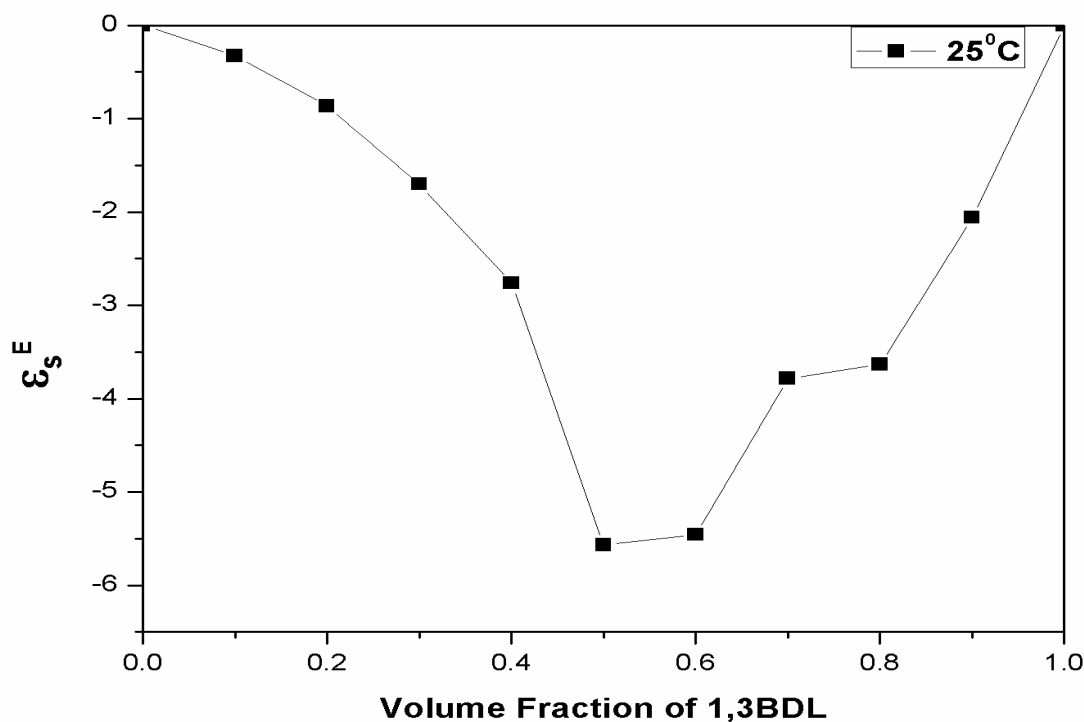


Figure 6. Excess static Dielectric Permittivity for 1,3-BD-1,4-Dx mixture.

3.5 Bruggeman dielectric theory

The static permittivity of a mixture with the volume fraction of solute is given by Bruggeman mixture formula [15]

$$f_B = \left(\frac{\epsilon_{sm} - \epsilon_{sDx}}{\epsilon_{sBD} - \epsilon_{sDx}} \right) \left(\frac{\epsilon_{sBD}}{\epsilon_{sm}} \right)^{1/3} = 1 - V_{Dx} \quad (4)$$

Where, f_B is the Bruggeman dielectric factor. ϵ_{sm} , ϵ_{sDx} and ϵ_{sBD} are the static dielectric constants corresponding to the mixture, 1,4-Dx and 1,3-BD respectively and V_{Dx} is the volume fraction of dioxane. From the above equation, a linear relation is expected from a plot of f_B vs. V_{Dx} . From **Figure 7**, it can be seen that f_B is not a linear function of volume fraction of 1,3-BD as predicted by Bruggeman equation. The Bruggeman equation may be modified for binary liquids as [7]

$$f_B = \left(\frac{\epsilon_{sm} - \epsilon_{sDx}}{\epsilon_{sBD} - \epsilon_{sDx}} \right) \left(\frac{\epsilon_{sBD}}{\epsilon_{sDx}} \right)^{1/3} = 1 - [a - (a - 1)V_{Dx}]V_{Dx} \quad (5)$$

In this equation, volume fraction V_{Dx} is changed by a factor $[a - (a - 1)V_{Dx}]$ of the mixture. Where $a = 1$ corresponds to Bruggeman equation. The value of a is determined by the least squares fit method and found to be 1.17 and deviation of a from unity indicates the molecular interaction in the mixture [9].

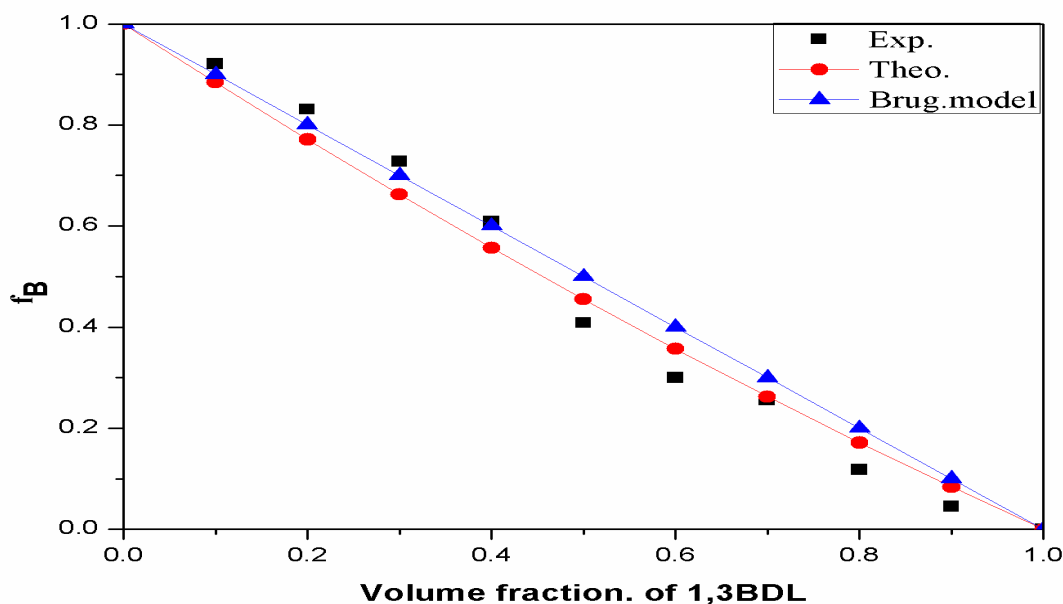


Figure 7. Plot of Bruggeman factor as a function of volume fraction of 1,3-BD

IV. CONCLUSIONS

The complex permittivity spectra of 1,3Butanediol with 1,4-Dioxane have been studied at 25°C, using TDR technique in the frequency range of $0.01 \leq \nu/\text{GHz} \leq 50$. The dielectric constant for the mixture can be explained by using Cole-Davidson's model. The relaxation time for 1,3-BD is found to be 750 ps which indicates there is excessive H-bond network formation in 1,3-BD. The excess dielectric properties and Bruggeman factor shows the molecular interaction in mixtures.

V. ACKNOWLEDGEMENTS

The financial support from the University Grant Commission (UGC), New Delhi is Thank fully acknowledged N.P. Garad thanks Swami Ramanand Teerth Marathwada University, Nanded & DST for making the laboratory & Instrument facility available.

VI. REFERENCES

- [1]. F. Kremer, Broadband dielectric spectroscopy 729 pages.
- [2]. SC Mehrotra, AC Kumbharkhane and AS Chaudhari, Binary Polar Liquids: Structural and Dynamic Characterization Using Spectroscopic Methods. 1st edition. (Elsevier, Amsterdam, 2017).
- [3]. U Kaatze, J. Mol. Liq. 56 95 (1993).
- [4]. SD Chavan, AC Kumbharkhane and SC Mehrotra, J. ChinChem. Soc. 54 1457 (2007).
- [5]. P Petong, R Pottel and U Kaatze, J. Phys. Chem. A 104 7420 (2000).
- [6]. T Sato, R Chiba and Nozaki J. Mol. Liq. 101 (1-3) 99 (2002).
- [7]. SMPuranik, AC Kumbharkhane and SC Mehrotra, 59, 173, (1994)

- [8] . SS Kadam, KS Kanse, YS Joshi, et al. Indian J Phys 92, 1367(2018).
- [9] . MN Shinde, RB Talware, PG Hudge, et al. Pramana - J Phys 78 297(2012)
- [10] . AR Deshmukh, RV Shinde, SA Ingole, AW Pathan, MP Lokhande, AV Sarode and AC Kumbharkhane Ind. J. Pure Appl. Phys. 56 346 (2018)
- [11] . R Buchner and J Barthel Ber. Bunsenges. Phys. Chem, 101509 (1997)
- [12] . S Havriliak and S Negami Journal of polymer science C14 99 (1966)
- [13] . S Mallick and M Malathi Indian J Phys. 92 1245 (2018)
- [14] . CP Smyth, Electrical Engineering, 975 (1950)
- [15] . DAG Bruggemmn, Ann. Phys. (Leipzig) 24 636 (1994)