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Dielectric behaviour of 1, 3-butanediol - 1, 4-dioxane mixtures

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Abstract

The TDR method was used to investigate the complex dielectric permittivity spectra of a mixture of 1,3-butanediol (1,3-BD) and 1,4-dioxane(1,4-DX) across a high-frequency range from 10 MHz to 30 GHz, which showsCole-Davidson type relaxation. The static dielectric constant was used to calculate Kirkwood correlation factor, which were used to study the H-bonding interactions in the mixture.Thedielectric parameters,Bruggeman factor,thermodynamic parameters and excess dielectric properties were also determined.

Keywords:TDR, Kirkwood correlation factor, complex permittivity spectra, Bruggeman factor, Molecular parameters.

1. Introduction

The dielectric permittivity data of the liquid is required to investigate hydrogen bond molecular interactionsas well as the structural rearrangement of molecules in theliquid state [1-5]. Organic alcoholsand liquid diols are extensively utilized in the chemicalindustry for a variety of applications such as reagents, solvents [6-7], or chemical intermediates [8] and exhibit a number of conformational characteristics due to their molecular flexibility [9]. 1,3-butanediol (1,3-BD) is a colorless liquid, and the hydroxyl groups are present at the first and third positions of the carbon chain.A network structure is created in 1,3-BDliquid because of two OH groups [10-11]. Because of the two OH groups, intermolecular interactions between dipoles and hydrogen bonds have a significant impact on the dielectric properties of 1,3-BD compounds. However, as the OH groups get closer together, on one molecule, as in the liquid, the capacity to make H-bond with other molecules reduces [12]. Measurements ofthedielectric permittivity of diols have been the subject of extensive research up to this point [13-14]. Due to its importance in industry and useas a food flavouring agentas well as a co-monomer in specific polyesters, numerous dielectric measurements of 1,3-BD and their solutionshave been performed [15-18].

This article reports the dielectric behaviour of1, 3-BD+1, 4-dioxane (1,4DX) mixtureusing the time domain reflectometry technique (TDR). The dielectric parameters, Bruggeman factor, Kirkwood correlation factor, thermodynamic and excess dielectric parameters werecomputed.

2. Experimental details

2.1. Chemicals

The chemicalspurchased commercially 1,3-BD fromMerck Specialities Private Ltd.and 1,4-DX from SigmaAldrich Chemicals Private Ltd.with 99% purity.

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2.2. Experimental

TDR (Model no.DSA8300) was used to examine the complex dielectric permittivity spectra (CPS) of 1, 3-BD+1, 4-DX at various temperatures.The detailed experimental setup and calibration of the instrument are done accordingly, as mentioned in the references [19, 20].

3. Results and Discussion

Figures.1 and 2 represents the Cole-Cole (ε'vs. ε'') plot and frequency dependent CPSfor various concentrations of 1,3-BD+1,4-DXmixtures. The spectra show the systematically varyingdielectric permittivity (ε') and dielectric loss (ε''). The $\varepsilon'$of mixture decreases with frequency increase, including 1, 3-BD, but the variation is not significant for pure 1, 4-DX due to its low dipole moment. To determine dielectric parameters the experimentally obtained complex dielectric permittivity $\varepsilon^*(\omega)$ data were fitted intothe Harviliak-Negami expression Eq.1 [21] using the method of non-linear least squares fit (LSF).

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

Whereτ , ε_∞, ε_s ,α and β are the fitting parameters. The Cole-Davidson equation describes the dielectric loss spectra of polyalcohols, which generally have an asymmetric shape. The parameter, $\alpha = 0$ and β varies from 0 to 1. β denotes the loss peak's asymmetric broadness.It can be seen from Figs. 1 and 2 and is confirmed by the fitting parameter, that theCole-Davidson relaxation can be used to represent dielectric relaxation in these mixtures [22]. The dielectric parameters (ε_s,τ)for the binary mixture of 1,3-BD+1,4-DX at various temperatures are reported in Table 1 andare good finding with those reported in the literature [15-18,23-24]. Thechange in β value indicates a change in molecular structure of the system.

The static dielectric constant (ε_s) of liquids is affected by nature of the intermolecular forces,their dipole moment,the angular correlation of the dipoles to a neighbouring dipole,numberof carbon atoms in the molecules andtemperature.Fig. 3shows the $\varepsilon_s$versus V_{DX} for the 1,3BD+1,4DX. The ε_s for all binary mixtures decreased monotonically withincreasing concentrations of 1, 4 DX. This suggeststhat the electric dipole number density decreased within the mixture and caused a net change in polarization. An effect of temperature on the ε_s was noticed for all concentrations, indicating an increase inH-bond strength and orientation polarization with decreasing temperature.
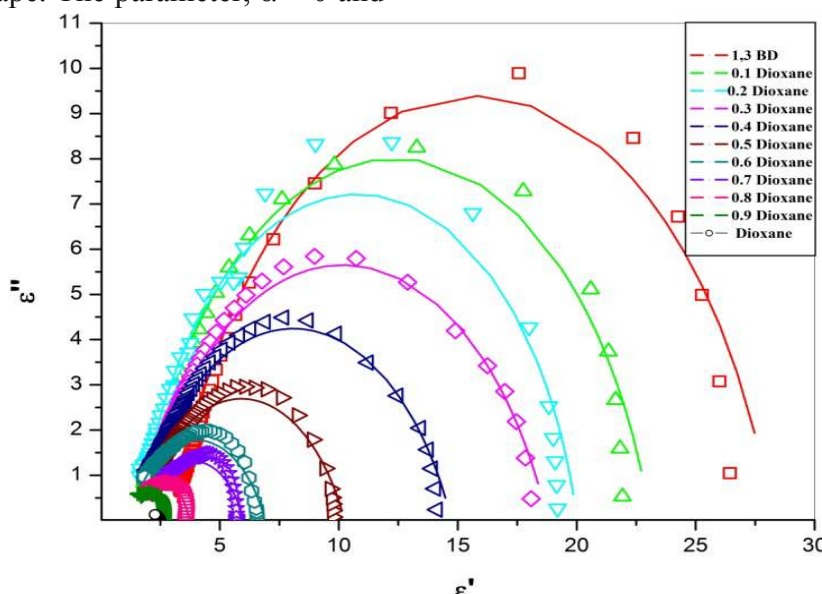

Fig. 1The Cole–Cole plot (ε' vs. ε'') for 1,3-BD+1,4-DX mixture at 25°C.
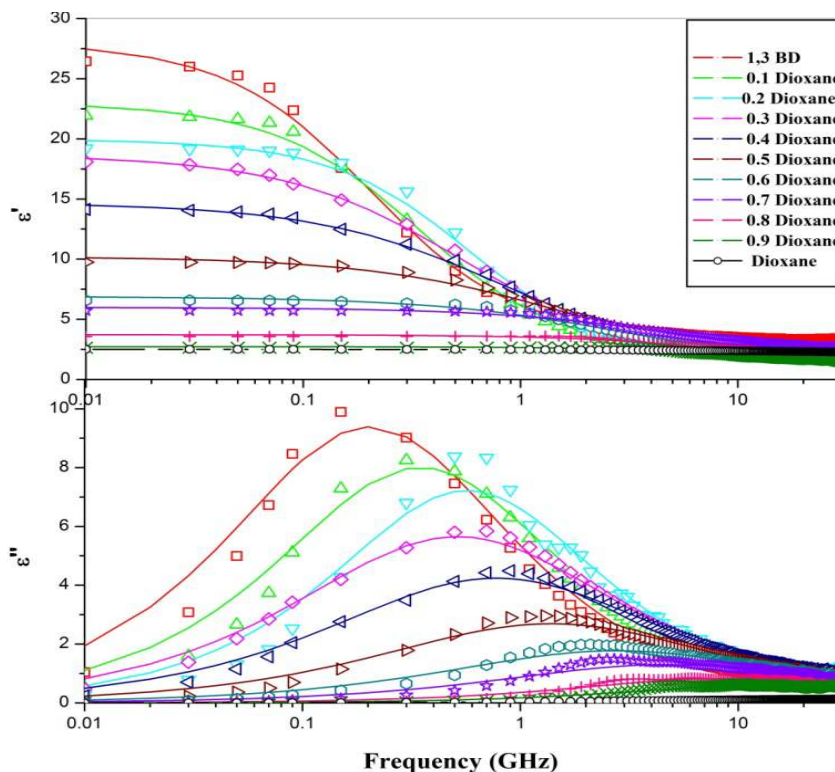
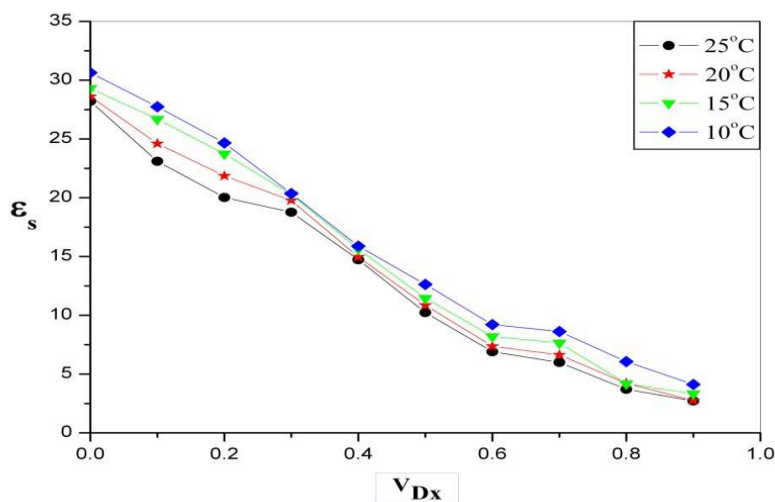*Fig. 2 The complex permittivity spectra (ε' and ε") of 1, 3BD+1,4DX system at 25°C.*

Fig.3 Static dielectric constant vs V_{DX} for the 1,3-BD+1,4DX system at various temperatures

3.1. Relaxation time

Fig. 4 represents the plot of relaxation time (τ) vs $V_{DX}$of the 1,3-BD+1,4-DX mixtures. With an increase in 1,4-DX concentration in 1,3-BD, the τ decreased. 1,4-DX reduces the hydrogen bonds in the 1,3-BD molecule.The change in $\tau$with 1,4-DX concentration isdue to the distribution of hydrogen bonds.The τrelieson functional groups,molecular size,and viscosity of the molecules. With increasing 1,4-DX concentration, the τ of the 1,3-BD-1,4-DX system decreased non-linearly.These decreases in values indicated a change in theorientational polarization configuration andchemical structure of themixture. With therise in temperature, theτ decreased;this is due to increase in effective length of dipoles with rising temperature.

With the addition of solute molecules, liquids undergo chemical modifications that control the dissociation and formation of solvent self-associations. Physical changes in our mixtureswere related to the dipole-dipole interactions [20].

Excess inverse relaxation time $(1/\tau)^E$is effective for detecting cooperative domains in mixtures and may confirm the creation of multimers as a result of molecular interaction.$(1/\tau)^E$is calculated as [20].

$$(1/\tau)^E=(1/\tau)_M-[(1/\tau)_{Dx}V_{Dx}+(1/\tau)_{BD}(1-V_{Dx})] \quad (2)$$
.

where M,BD,andDX, stand for mixture, 1,3-BD, and 1,4-DX respectively. Figure 5 depicts the relationship between $(1/\tau)^E$and theV_{DX}. Negative $(1/\tau)^E$values show that the rotation of dipoles in the mixture was slowed as a result of the interaction between a 1,3-BD and a 1,4-DXproduced by the H-bound structure, i.e., multimers, which provides a field that reduces the effective dipole moment as mentioned in ref. [20].The minimapeak values of $(1/\tau)^E$ for various temperatures were found to be around V $_{DX}\approx0.8$. The value of $(1/\tau)^E$ was negative for all temperature and concentrations.

Table 1: The dielectric parameters for 1,3-BD+1,4-DX mixture

Vol. frac. of 1,4-Dx	1,3-Butanediol-1,4-Dioxane							
	25ºC		20ºC		15ºC		10ºC	
	ε_s	τ (ps)	ε_s	τ (ps)	ε_s	τ (ps)	ε_s	τ (ps)
0	28.21(11)	778.4(94)	28.62(14)	917.1(13)	29.30(14)	1104.5(15)	30.63(23)	1206.8(28)
0.1	23.10(8)	460.8(49)	24.60(9)	573.7(69)	26.68(11)	777.5(99)	27.74(14)	930.1(14)
0.2	20.02(9)	380.1(37)	21.85(7)	421.6(43)	23.74(9)	546.1(72)	24.66(27)	747.0(29)
0.3	18.77(4)	310.2(26)	19.77(4)	366.1(30)	20.29(6)	387.4(44)	20.35(7)	421.2(57)
0.4	14.73(3)	205.7(18)	14.96(3)	223.6(18)	15.63(5)	235.3(29)	15.88(6)	247.7(37)
0.5	10.23(3)	115.0(12)	10.86(4)	124.8(18)	11.45(4)	145.4(23)	12.63(4)	194.8(29)
0.6	6.90(2)	57.29(70)	7.36(2)	60.4(81)	8.20(2)	74.7(10)	9.21(5)	78.0(19)
0.7	5.99(2)	34.17(45)	6.63(3)	36.1(68)	7.65(4)	44.1(11)	8.62(4)	47.5(12)
0.8	3.71(01)	19.94(18)	4.22(1)	20.1(28)	4.18(1)	26.7(29)	6.06(2)	22.4(46)
0.9	2.72(1)	12.73(14)	2.75(1)	12.6(15)	3.33(1)	14.2(16)	4.12(1)	12.6(22)
1	2.50(3)	3.95(2)	2.52(1)	4.01(3)	2.53(2)	4.23(3)	2.55(1)	4.4(1)

The bracketed term denotes error e.g.
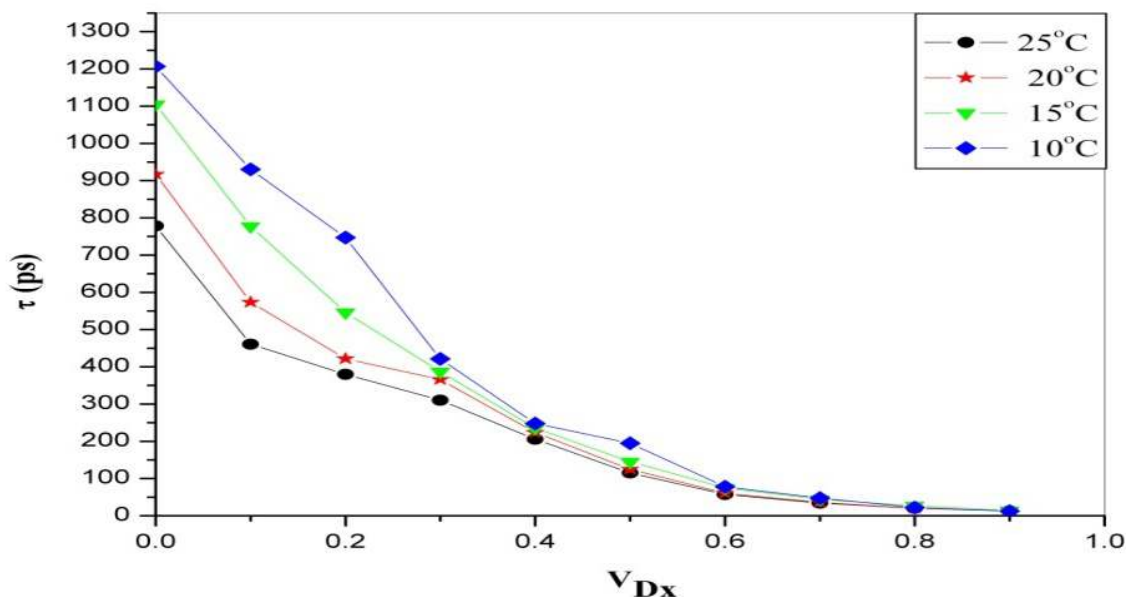28.62(14) means28.62±0. 14; 778.4(94) means 778.4± 9.4

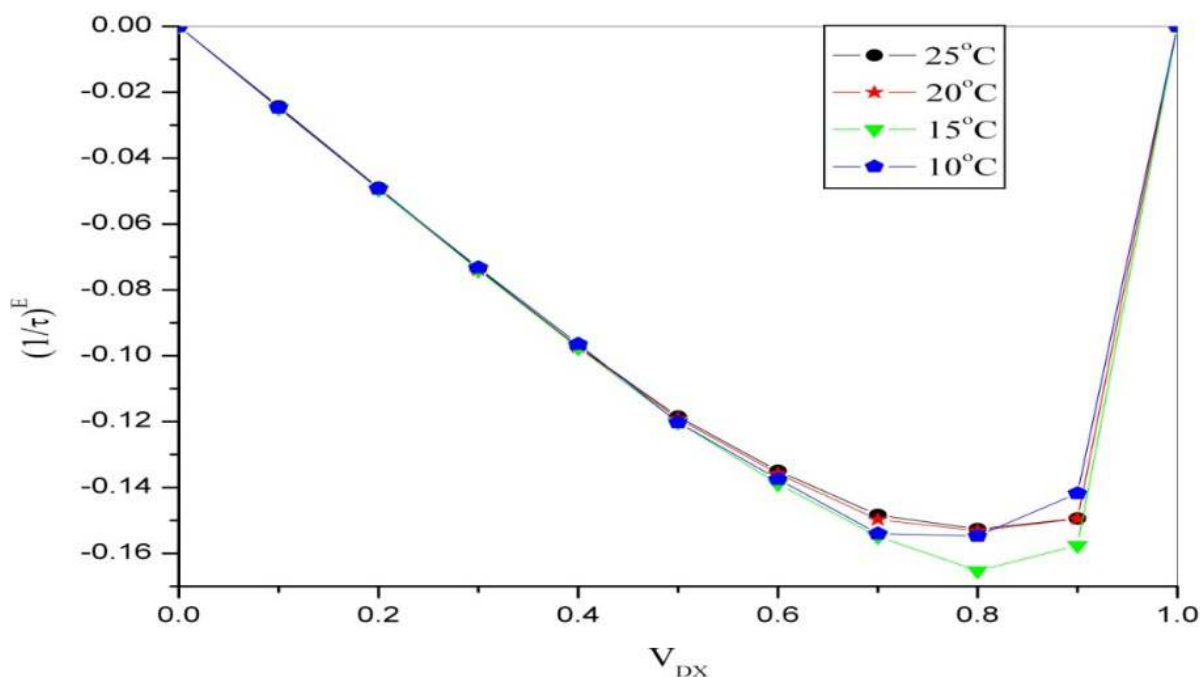*Fig. 4 Relaxation time vs V_{DX} for 1,3-BD+1,4DX system at different temperatures.*

Fig. 5 $(1/\tau)^E$ vs. V_{DX} for the 1,3-BD+1,4DX system at various temperatures.

3.2. Thermodynamic parameters

An Arrhenius plot for the 1,3-BD-1,4-DXmixtures studied is shown in Fig. 6. The slope of Arrhenius plot gives enthalpy of activation(ΔH_τ)foreach system. The activation energy,entropy ΔS andenthalpy ΔH were derived using the Eyring rate equation [25].

$$\tau = \frac{h}{kT} exp \frac{\Delta H - T\Delta S}{RT} \qquad (3)$$

Where h = Planck's constant, k = Boltzmann's constant, T = temperature (K), τ = relaxation time, and R = gas constant. Figure 7 shows the activation enthalpy

(ΔH), for all concentrations. A LSF method was used to obtain theactivation energies. For 1,3-butanediol, ΔH was 22.53kJ/mol, which states theamountof energy needed to break aH-bond. Figure 7 shows positive ΔHvalues which indicates during the molecular reorientation process, the heat energy was absorbed from the surrounding and formation of H-bonding in mixture when two species are combined. For binary mixtures, the higher values of ΔH in a region from 0 to 0.2 DX volume fraction regions indicate that high energy is required to achieve the group dipole orientation.
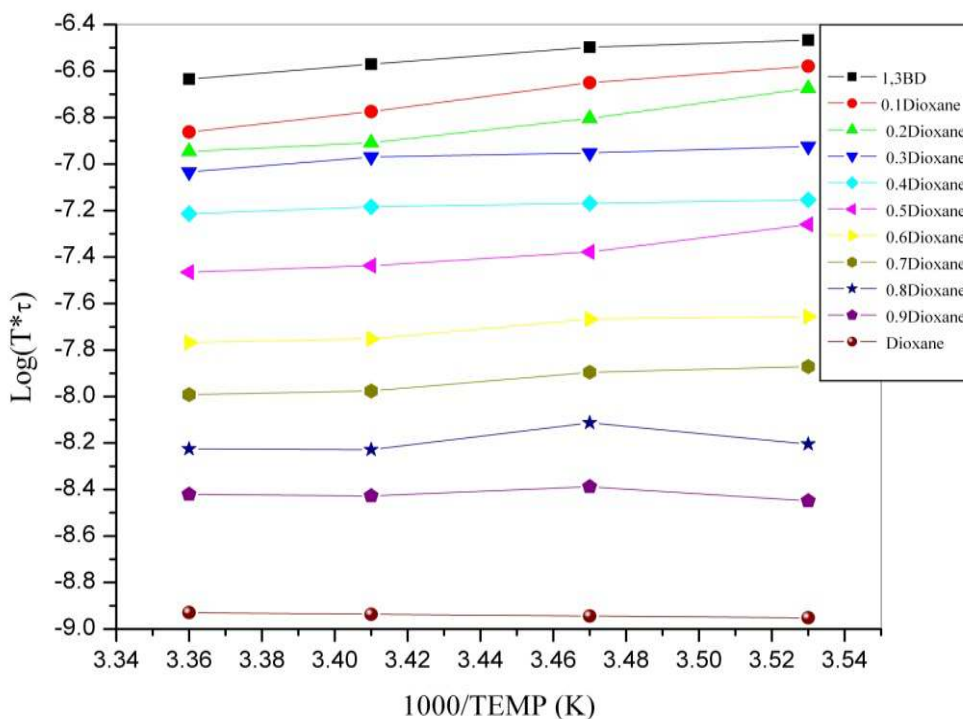

Fig.6 Arrhenius Plot of log(T ∗ τ) vs. reciprocal of temperature in Kelvin for various volume fraction of dioxane
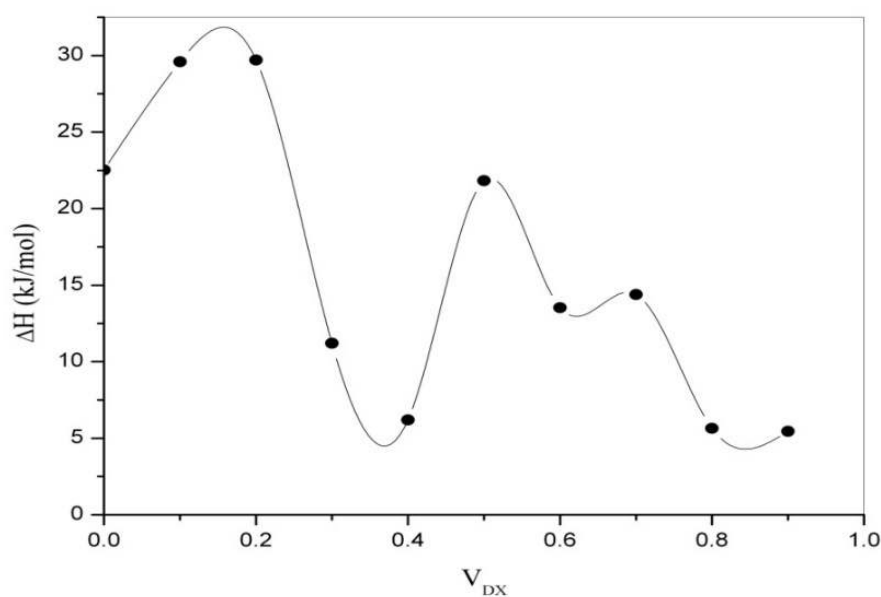

Fig. 7 Activation energy verses VDX.

3.3 Kirkwood correlation factor (KCF)

In a liquid, knowledge about dipole alignment is provided by the KCF. The KCF deviation from unity measures the strength of intermolecular hydrogen bonding. The KCF is calculated for liquids using the Kirkwood-Frochlich equation [26].

$$\frac{(\varepsilon_s - \varepsilon_\infty)(2\varepsilon_s + \varepsilon_\infty)}{\varepsilon_s(\varepsilon_\infty + 2)^2} = g_i \mu^2 \frac{4\pi N\rho}{9kTM} \quad (4)$$

(i=1 represents 1,3-BD and i=2 represents 1,4-DX) where, g_i denotes the Kirkwood correlation factor, T = temperature, ρ = density, k = Boltzmann constant, M = molecular weight, μ= dipole moment and N= Avogadro's number. It is very challenging to interpret the dielectric constant for mixtures of associating compounds, considering the KCF [27]. without assuming anything it is difficult to distinguish between the average KCFg_1 and g_2 from single $\varepsilon_s$value [27]. Luzar proposed theoretical equations applicable to hydrogen-bonded mixtures using the theory of mean field approximation [27-28]. To calculate the average KCF g_1 and g_2 the following equations were used [27-28].

$$g_1 = 1 + Z_{11}\cos\varphi_{11} + Z_{12}\cos\varphi_{12}(\mu_2/\mu_1) \quad (5)$$

$$g_2 = 1 + Z_{21}\cos\varphi_{21}(\mu_1/\mu_2) \quad (6)$$

where the angles of the 1,3-BD and 1,4-DX neighboring dipoles are, respectively, $\varphi 11$, $\varphi 12$, and $\varphi 21$. $Z_{11} = 2\langle n_{HB}^{11}\rangle$, $Z_{12}= \langle n_{HB}^{12}\rangle$ and $Z_{21} = \langle n_{HB}^{21}\rangle V_{DX}/1 - V_{DX}$ represent the average number of H-bonds in between 1,3-BD-1,3-BD, 1,3-BD-1,4-DX, and 1,4- DX-1,3-BD pairs respectively [27-28]. The g_1 and g_2 values depends on V_{DX} in the 1,3-BD+1,4-DX mixtures, as shown in Fig

8. The average number of H-bonds $\langle n_{HB}^{11}\rangle$, $\langle n_{HB}^{12}\rangle$ and $\langle n_{HB}^{21}\rangle$ per 1,3-BD molecule were calculated by using the following relationship [27-28]

$$\langle n_{HB}^{1i}\rangle = n^{1i} \omega^{1i}/ n_1, \quad (7)$$

Where $\omega^{1i} = 1/(1+\alpha^{1i} e^{-\beta E1i})$ represent the bond formation probability of 1,3-BD and 1,4-DX. The n_1 is the number density of 1,4-DX. α^{1i} represent the ratio in between two statistical subvolumes of the phase space that correspond to the non-H-bonded and H-bonded pairs, the value of β is $\beta = 1/ kT$ [27]. These H-bonded 11 and 12 pairs possess two different energy levels, E^{11} and E^{12}. The $\langle n_{HB}^{11}\rangle$ and $\langle n_{HB}^{12}\rangle$ depends on the H-bonding pair density between 1,3-BD-1,4-DX n_{12} and 1,3-BD –1,3-BD molecule, i.e. $n_{11} = 2n_1 - n_{12}$ [28]. This can be determined when 1,3-BD –1,3-BD (pair 11) and 1,3-BD–1,4-DX (pair 12) was formed [27-28]. Fig. 9 represents the plot between average number of H-bonds between pair 11 and 12 vs. V_{DX}. The $\langle n_{HB}^{11}\rangle$ and $\langle n_{HB}^{12}\rangle$ values depend on the V_{DX} in the 1,3-BD–1,4-DX. The parameters taking into consideration while applying Luzar model [27-28] to compute the theoretical values are mentioned in table 2. The theoretical values of ε_s by Luzar model and the experimental values obtained using TDR techniques are compared in Fig. 10 and are found to be in good agreement.

The excess dielectric permittivity (ε_s^E) can given as [20]

$$\varepsilon_s^E = (\varepsilon_s)_M - [(\varepsilon_s)_{Dx}V_{Dx}+ (\varepsilon_s)_{BD}(1-V_{Dx})] \quad (8)$$

Figure 11 shows the plot of ε_s^E against the V_{DX}. Negative ε_s^E values indicate that the 1,4-DX molecules break the structure of the 1,3-BD as evidenced by the decrease in the dipole moment [20]. The minima of ε_s^E was found to be at around $V_{DX} \approx 0.6$.

Table 2: The molecular parameters

Molecular Parameters	1,3-butanediol	1,4-dioxane
Polarizability (α_1, α_2) in A^{03}	9.96	2.79
Enthalpy (α_{11}, α_{12}) (KJ/mol)	40	30
Binding energy (E_{11}, E_{12}) (KJ/mol)	-16	-18.25
Density (g/cm^3)	1.001	1.028
Dipole moment (μ_1, μ_2) (Debye)	2.48	0.97
Molecular weight (g/mol)	90.12	88.11
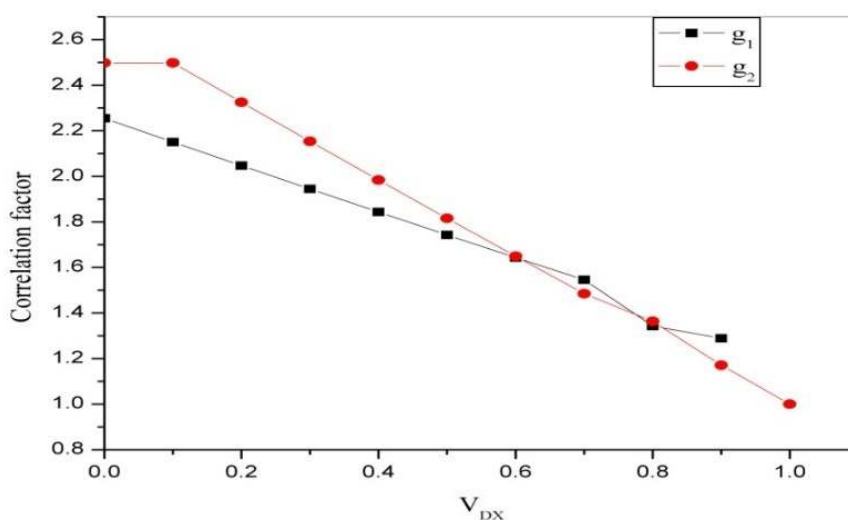
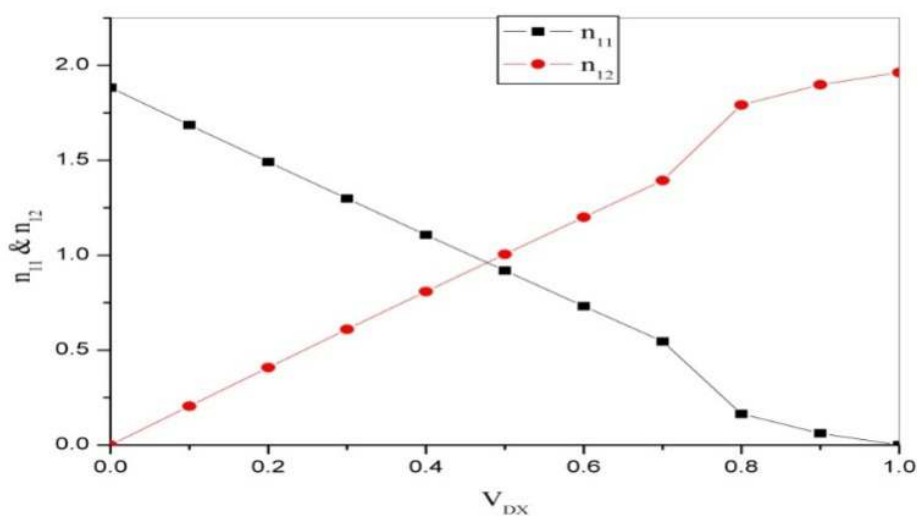Fig. 8 Correlation factors vs . V_{DX} for the 1,3-BD+1,4-DX system

Fig. 9 Plot of the average number of hydrogen bonds in 1,3-BD-1,3-BD(pair 11) and 1,3-BD-1,4-DX(pair 12) against V_{DX}.
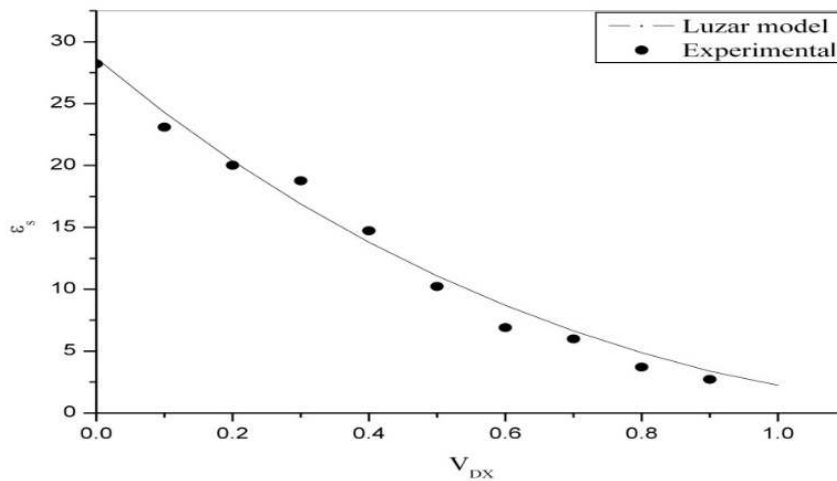
Fig. 10 Static dielectric constant vs . V_{DX} for the 1,3-BD+1,4-DX system at 25°C temperature.
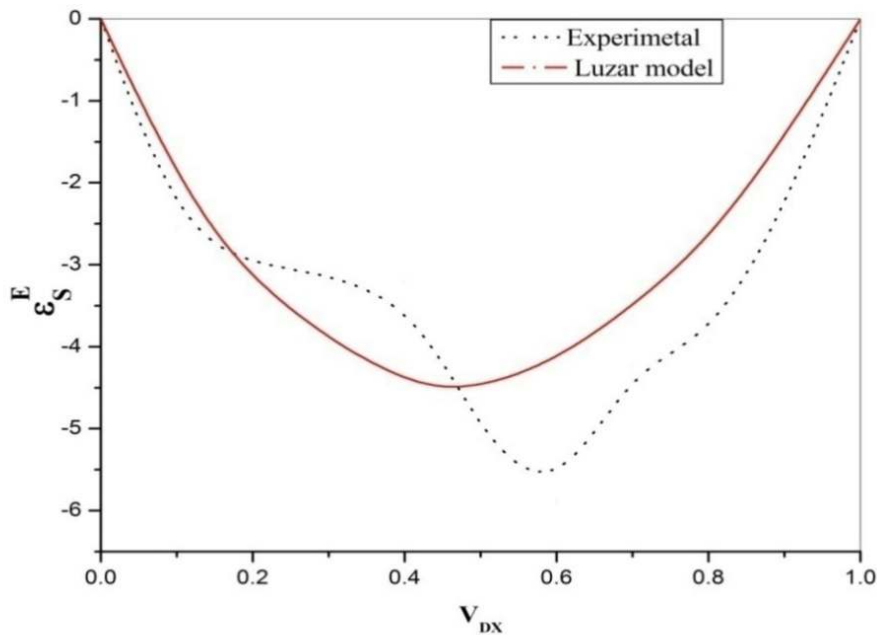

Fig. 11 Excess dielectric permittivity vs. V_{DX} for the 1,3-BD+1,4-DX system.

3.4. Bruggeman dielectric theory

Bruggeman formula is used to find out the relationship between static dielectric permittivity with the V_{DX} is as follow [27]:

$$f_B = \left(\frac{\varepsilon_{sm}-\varepsilon_{DX}}{\varepsilon_{BD}-\varepsilon_{DX}}\right)\left(\frac{\varepsilon_{BD}}{\varepsilon_{sm}}\right)^{1/3} = 1 - V_{DX} \quad (9)$$

Where f_B stand for Bruggeman dielectric factor. ε_{BD}, ε_{Dx}, and ε_{sm} are static dielectric constants of 1,3-BD, 1,4-DX and the mixture, respectively. A linear relationship

(black line) is predicted by the above equation for a plot of (f_B) vs. (V_{Dx}). Figure 12 shows (red line) that f_B does not follow the Bruggeman equation's prediction that it is linear with V_{DX}. Thereforeto understand the curve's non-linear relationship the Bruggeman formula modified as.

The modified Bruggeman equation is as follows [29]:

$$f_B = \left(\frac{\varepsilon_{sm}-\varepsilon_{Dx}}{\varepsilon_{BD}-\varepsilon_{Dx}}\right)\left(\frac{\varepsilon_{BD}}{\varepsilon_{sm}}\right)^{1/3} = 1 - [a-(a-1)V_{Dx}]V_{Dx}$$

$$(10)$$

where $V_{Dx}$is modified by the mixture's *[a−(a−1) V_{Dx}]*factor. The Bruggeman equation shows that there is no interaction between in the mixturewhen "a" = 1.The value of "a" calculated by using aLSF method was found to be 1.30.
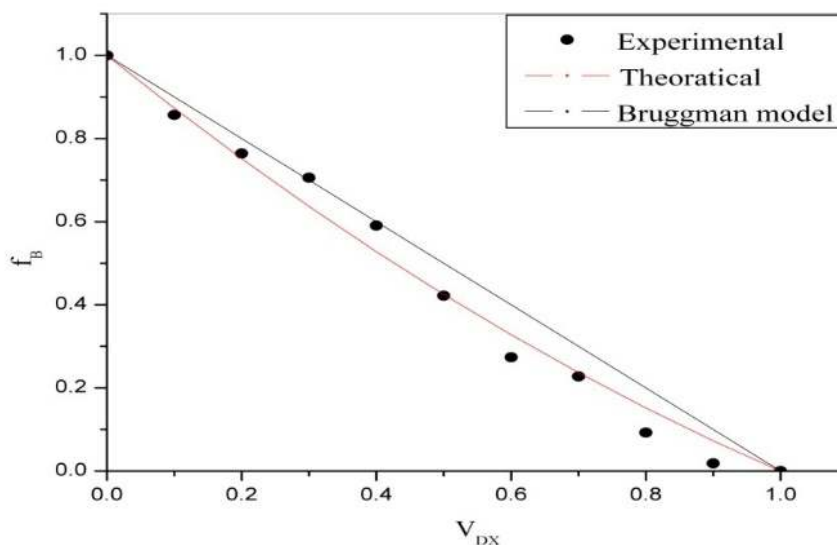

Fig. 12 Bruggeman factor vs V_{DX} for 1,3-BD+1,4-DX system at 25^oC temperature.

4. Conclusion

The CPS of the 1, 3-BD-1,4-DX mixturesshow Cole-Davidson type dielectric relaxation. The decrease indielectric parameters (ε_s,τ)with an increase in DX is due to the decrease in electric dipole density and the change orientation polarization configuration.The excess dielectric parameters and Kirkwood correlation factorsuggest a reduction in overall number of effective electrical dipoles in mixture. The number of H-bonds between the 1, 3-BD+1,4-DX mixtures suggests the formation and orientation of molecules occur cooperatively with electric dipole correlation and decrease with increasing 1,4-DX concentration. The Bruggeman factor and molecular parameters are also reported for the system.

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