

Dielectric relaxation and hydrogen bonding studies of 1,3-propanediol–dioxane mixtures using time domain reflectometry technique

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MS received 13 September 2010; revised 25 January 2011; accepted 26 August 2011

Abstract. The complex permittivity, static dielectric constant and relaxation time for 1,3-propanediol, 1,4-dioxane and their mixtures have been studied using time domain reflectometry (TDR). The excess permittivity, excess inverse relaxation time and Kirkwood correlation factor have also been determined at various concentrations of dioxane. Hydrogen bonded theory was applied to compute the correlation terms for the mixtures. The Bruggeman model for the nonlinear case has been fitted to the dielectric data for mixtures.

Keywords. Hydrogen bond; aliphatic alcohols; time domain reflectometry.

PACS No. 77.22.Gm

1. Introduction

1,3-propanediol is an aliphatic dihydric alcohol which is a useful industrial solvent having an electric dipole moment around 2.5 D. The hydroxyl groups of 1,3-propanediol are on the carbon atoms at both terminals. 1,3-propanediol is used in the pharmaceutical industry and clinically for curing many diseases. The self-association network in the 1,3-propanediol is formed due to hydrogen bonding. Hydrogen bonding plays a great role in physics and chemistry and is one of the most important intermolecular interactions. It plays a huge role in various chemical and biological processes [1–3]. The intermolecular interaction of 1,3-propanediol in various chemical processes is greatly effected by the solvent. The local structure of hydrogen bonding of 1,3-propanediol is complicated due to molecular clusters and network structures through hydrogen bonds. Many methods have been used to study the hydrogen bonding behaviour in 1,3-propanediol. Hydrogen bonding cooperativity factor for alcohol has been investigated by infrared spectroscopy and nuclear magnetic resonance spectroscopy methods [4–16]. Hydrogen

bonding in pure aliphatic alcohol is also investigated using a calorimetric approach [17]. Lampre *et al* reported the absorption spectra of the solvated electron in 1,3-propanediol (1,3-DL) at different temperatures [18]. Excess molar volumes and partial molar volumes were determined for dilute aqueous solutions of 1,3-propanediol by Romero *et al* [19].

The pioneering work by Cole and others has given long-standing attention to dielectric spectrometry of associating liquids. To find hydrogen bond concentration, dielectric relaxation studies have been performed on alcohol–alcohol mixtures and on mixtures of alcohols with water [20–37]. Crossely [38] had studied the dielectric permittivity and loss for a series of diols and concluded that the relaxation times for the diols are almost independent of alkyl chain length. Hanna *et al* [28] had studied dielectric relaxation of diol mixtures and also dielectric spectra of binary mixtures of propanediamine and propanediol using time domain reflectometry method. The observed dielectric relaxation time has a maximum at around 0.7 mole fraction of 1,3-propanediol.

This work reports the dielectric relaxation study of 1,3-propanediol–dioxane 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-propanediol–dioxane mixture have been determined.

2. Experimental procedure

1,3-propanediol (1,3-DL) and 1,4-dioxane (1,4-Dx) are purchased from Aldrich Chemicals and used without purification. The complex permittivity of the solutions was measured in the frequency range of 10 MHz to 20 GHz at 25°C using time domain reflectometry (TDR) method [33,39]. The Tektronix DSA8200 sampling oscilloscope with 30 GHz bandwidth and TDR module 80E08 with step generator unit was used.

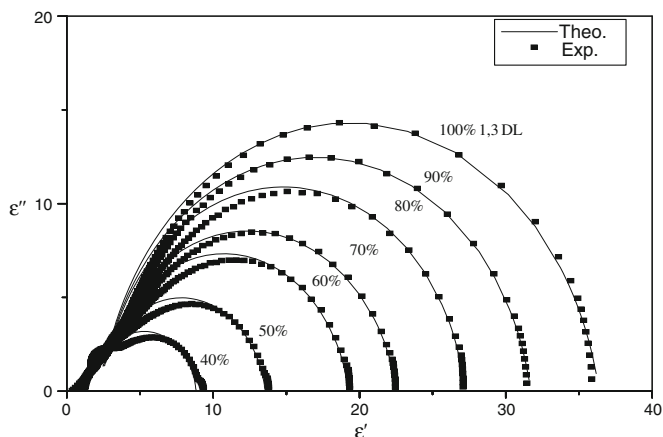


Figure 1. The Cole–Cole plot for 1,3-propanediol–Dx mixture at 25°C.

3. Result and discussion

The Cole–Cole (ϵ' vs. ϵ'') plot for different concentrations of 1,3-propanediol in 1,3-DL–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 [40].

$$\epsilon^*(\omega) = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{[(1 + j\omega\tau)^{1-\alpha}]^\beta}, \quad (1)$$

where ϵ_0 , 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 Havriliak–Negami equation. Here these fitting parameters, α is kept to 0 and β is varied such that $0 \leq \beta \leq 1$. β indicates the asymmetrical broadness of the loss peak. Figure 2 shows β vs. conc. of 1,3-DL in which the value of β goes on decreasing on addition of dioxane in pure 1,3-DL. It can be seen from figure 2 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 alcohol.

Due to cooperative motion of solute–solute and solute–solvent molecules through hydrogen bond, the dielectric relaxation parameters of the primary process strongly depend on the 1,3-DL concentration in the whole concentration range. Change in static permittivity (ϵ_0) with the volume fraction of 1,3-DL in dioxane is shown in figure 3.

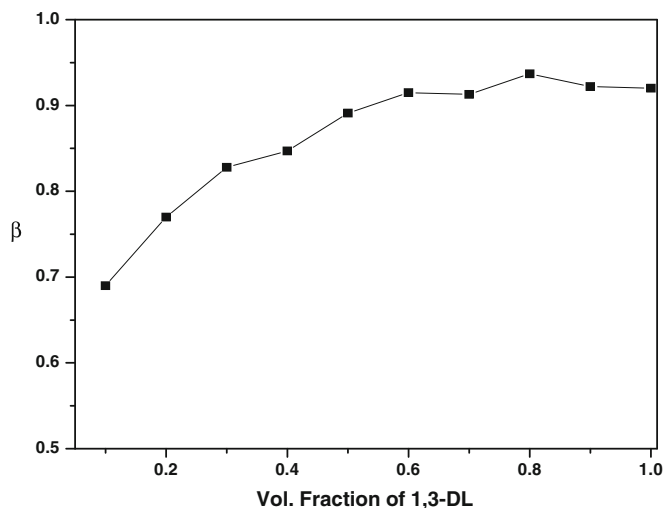


Figure 2. Plot of relaxation time distribution (β) of the Davidson–Cole function displayed as a function of volume fraction of 1,3-DL.

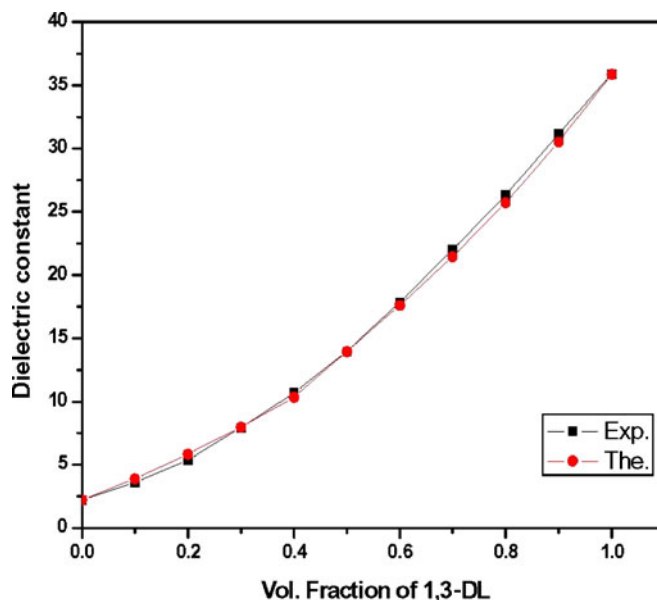


Figure 3. Plot of static dielectric constant vs. volume fraction of 1,3-DL.

Figure 4 shows the concentration dependence of relaxation time (τ) of 1,3-propanediol–dioxane mixtures. The relaxation time (τ) increases with increasing 1,3-propanediol concentration in dioxane. When dioxane is added to 1,3-DL, the number of hydrogen bonds decreases. The distribution of hydrogen bonds would affect the

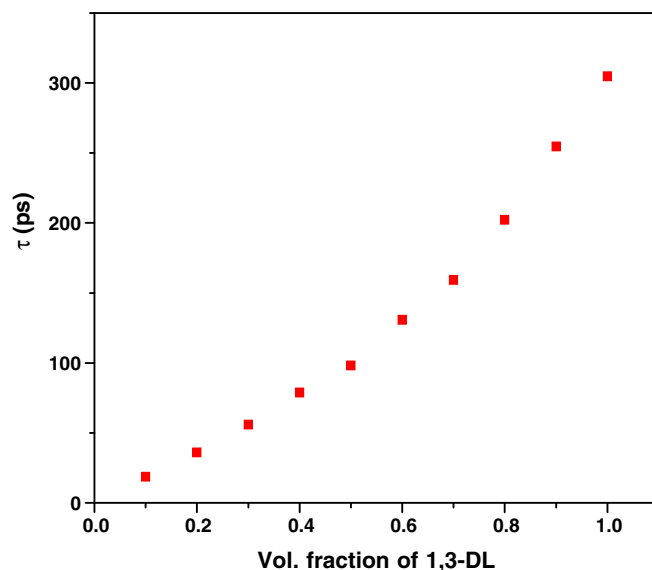


Figure 4. Relaxation time vs. volume fraction of 1,3-DL.

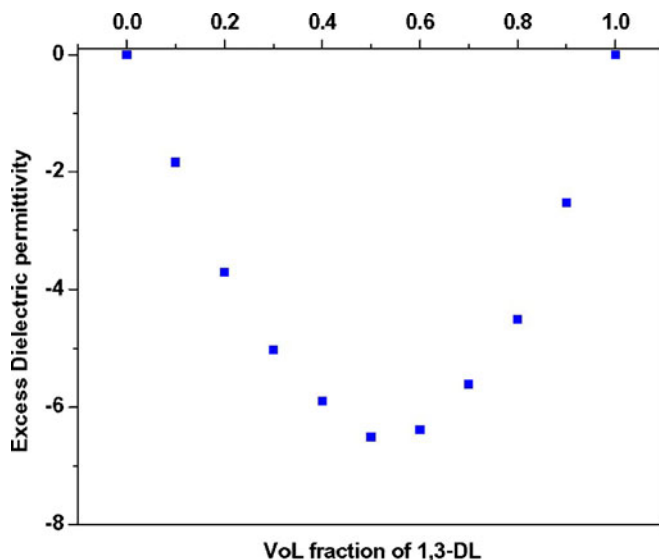


Figure 5. Excess dielectric permittivity for 1,3-propanediol + 1,4-dioxane mixture.

concentration dependence of the relaxation time. Sudo *et al* determined the dielectric relaxation time for various alcohols and water mixtures. The relaxation time of alcohol–water system increases monotonically with increasing alcohol concentration [41–44].

4. Excess dielectric permittivity

The excess permittivity (ϵ_0^E) may provide structural information. This is determined for the 1,3-DL–Dx solution as follows [43,45,46]:

$$(\epsilon_0^E) = (\epsilon_0)_m - [(\epsilon_0)_D X_D + (\epsilon_0)_A (1 - X_D)] \quad (2)$$

where $(\epsilon_0)_m$, $(\epsilon_0)_D$ and $(\epsilon_0)_A$ represent values of static dielectric constant corresponding to the mixture, 1,4-dioxane and 1,3-propanediol, respectively and X_D is the mole fraction of Dx. The resulting excess dielectric constants of Dx–1,3-DL mixture are as shown in figure 5. Negative values of excess permittivity are observed. Negative values of excess permittivity suggested that the addition of 1,3-propanediol to dioxane might create polymeric structure due to hydrogen bonding in the mixture.

5. Excess relaxation time

The information regarding the dynamics of liquid 1,3-DL and Dx can be obtained from the excess inverse relaxation time $(1/\tau)^E$ [44,47,48] as follows:

$$\left(\frac{1}{\tau}\right)^E = \left(\frac{1}{\tau}\right)_m - \left[\left(\frac{1}{\tau}\right)_D X_D + \left(\frac{1}{\tau}\right)_A (1 - X_D)\right], \quad (3)$$

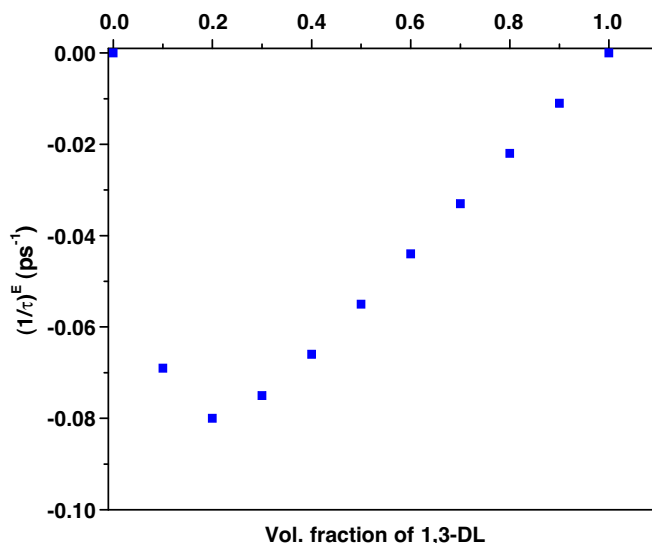


Figure 6. Excess inverse relaxation time for 1,3-propanediol + 1,4-dioxane mixture.

where m, D and A correspond to mixture, dioxane and 1,3-propanediol, respectively.

- (i) When $(1/\tau)^E = 0$ there is no change in the dynamics of liquid Dx and 1,3-DL interaction.
- (ii) When $(1/\tau)^E < 0$ the liquid Dx and 1,3-DL interaction produces a field such that the effective dipoles rotate slowly.
- (iii) When $(1/\tau)^E > 0$ the liquid Dx and 1,3-DL interaction produces a field such that the effective dipoles rotate faster, i.e. the field will cooperate in the rotation of dipoles.

Figure 6 gives the variation of excess inverse relaxation time with vol. fraction of 1,3-DL. The excess inverse relaxation has found to be maximum at 0.7 volume fraction of dioxane in 1,3-propanediol. This further confirmed that the distribution of hydrogen bonding in the 1,3-DL–Dx mixture is maximum.

6. Bruggeman dielectric theory

The static permittivity of a mixture with the volume fraction of solute is given by Bruggeman mixture formula [47–50]

$$f_B = \left[\frac{(\epsilon_{0m} - \epsilon_{02})}{(\epsilon_{01} - \epsilon_{02})} \right] \left(\frac{\epsilon_{01}}{\epsilon_{0m}} \right)^{1/3} = 1 - V_2, \quad (4)$$

where (f_B) is the Bruggeman dielectric factor. ϵ_{0m} , ϵ_{01} and ϵ_{02} are the static dielectric constants corresponding to the mixture, 1,3-propanediol and dioxane respectively and V_2

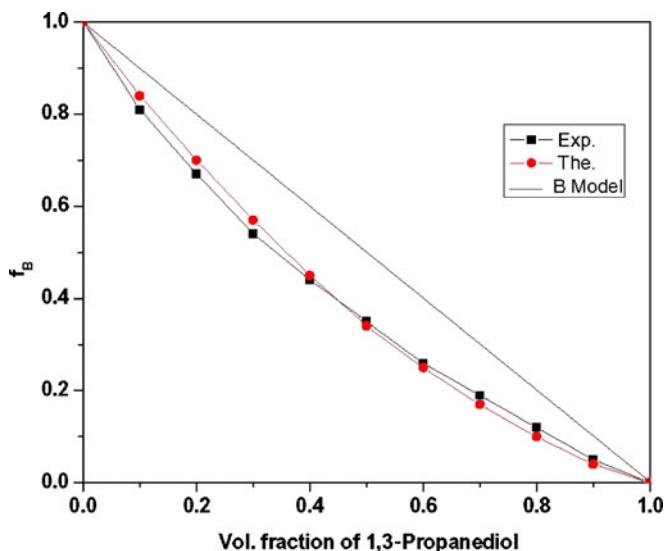


Figure 7. Plot of Bruggeman factor as a function of volume fraction of 1,3-propanediol.

is the volume fraction of dioxane. From the above equation, a linear relation is expected from a plot (f_B) vs. (V_2). From figure 7, it can be seen that f_B is not a linear of volume fraction of 1,3-DL as predicted by Bruggeman equation. The Bruggeman equation may be modified for binary liquids [47–50] as

$$f_B = \left[\frac{(\varepsilon_{0m} - \varepsilon_{02})}{(\varepsilon_{01} - \varepsilon_{02})} \right] \left(\frac{\varepsilon_{01}}{\varepsilon_{0m}} \right)^{1/3} = 1 - [a - (a - 1)V_2]V_2. \quad (5)$$

In this equation, volume fraction (V_2) is changed by a factor $[a - (a - 1)V_2]$ 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 1.60 and deviation of a from unity indicates the molecular interaction in the mixture.

7. The Kirkwood correlation

The Kirkwood correlations factor g for a mixture, can be expressed as [39,43,46] follows:

$$\left[\frac{(\varepsilon_{0i} - \varepsilon_{\infty i})(2\varepsilon_{0i} + \varepsilon_{\infty i})}{9\varepsilon_{0i}} \right] = \frac{4\pi N \mu_i^2 \rho_i}{9kT M_i} g_i, \quad (6)$$

where $i = 1, 2$ represent 1,3-propanediol and dioxane, respectively; μ_i is the corresponding dipole moment in gas phase, ρ_i is the density, k is the Boltzmann constant, T is the temperature, ε_{0i} and $\varepsilon_{\infty i}$ are the static dielectric constant and dielectric constant at high frequency and g_i is the Kirkwood correlation factor for the i th liquid system.

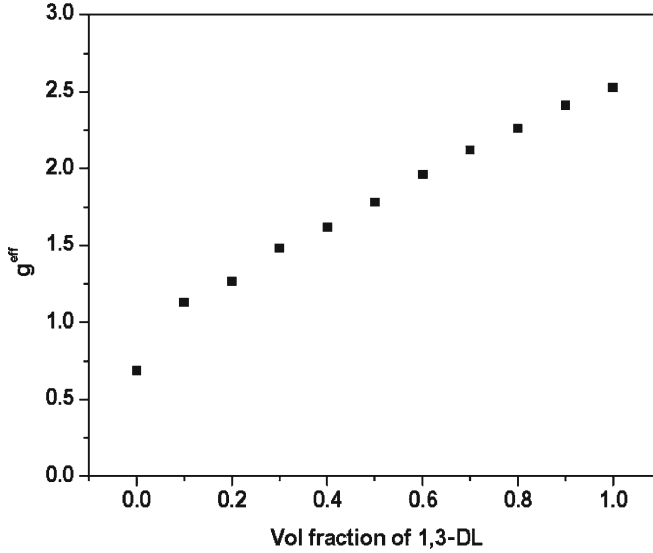


Figure 8. Plot of g^{eff} against volume fraction of 1,3-DL.

The interpretation of the dielectric phenomena in terms of the Kirkwood correlation factor is very difficult for a mixture of associating compounds. We have considered Kirkwood models as follows:

- (i) In the first model, we have assumed that the mixture can be represented by one correlation factor g^{eff} as follows [49]:

$$\left[\frac{(\varepsilon_{0i} - \varepsilon_{\infty i})(2\varepsilon_{0i} + \varepsilon_{\infty i})}{9\varepsilon_{0i}} \right] = \frac{4\pi N}{9kT} \left[\frac{\mu_A^2 \rho_A}{M_A} X_A + \frac{\mu_D^2 \rho_D}{M_D} (1 - X_A) \right] g^{\text{eff}}. \quad (7)$$

To calculate g^{eff} values, we have taken dipole moments of 1,3-propanediol and dioxane as 2.50 D [51] and 0.45 D [52], respectively. The value $(\varepsilon_{\infty i})$ is taken as the square of the refractive index (RI = 1.439) [51]. Figure 8 shows the g^{eff} values for 1,3-propanediol–dioxane systems. The value of $g^{\text{eff}} > 1$ indicates average parallel orientation of electric dipole in a molecule.

- (ii) In the second model, the Kirkwood correlation factors for individual species $i = 1, 2$ are modified by assuming for 1,3-propanediol–dioxane mixture, two kinds of intermolecular hydrogen bonds exist. One is the hydrogen bond between the 1,3-propanediol and 1,3-propanediol molecules; the other is the hydrogen bond between the 1,3-propanediol and dioxane molecules. These new correlations (g_1 and g_2) are described by the relation as follows [46]:

$$g_1 = 1 + Z_{11} \cos \phi_{11} + Z_{12} \cos \phi_{12} \left(\frac{\mu_2}{\mu_1} \right), \quad (8)$$

$$g_2 = 1 + Z_{21} \cos \phi_{21} \left(\frac{\mu_1}{\mu_2} \right), \quad (9)$$

where $Z_{11} = 2\langle n_{\text{HB}}^{11} \rangle$, $Z_{12} = 2\langle n_{\text{HB}}^{12} \rangle$ and $Z_{21} = 2\langle n_{\text{HB}}^{21} \rangle V_2 / (1 - V_2)$ are the average number of particles forming the hydrogen bond with 1,3-propanediol–1,3-propanediol and 1,3-propanediol–dioxane pairs, respectively. V_2 is the mole fraction of 1,3-propanediol. ϕ_{11} and ϕ_{21} are the angles between the neighbouring dipoles of 1,3-propanediol and dioxane molecules. The values of g_1 and g_2 depend on the concentration of dioxane in 1,3-propanediol–dioxane mixtures.

The average number of hydrogen bonds $\langle n_{\text{HB}}^{11} \rangle$, $\langle n_{\text{HB}}^{12} \rangle$ and $\langle n_{\text{HB}}^{21} \rangle$ per 1,3-propanediol molecule for $1i$ pairs ($i = 1, 2$) have been determined according to the following relation [46]:

$$\langle n_{\text{HB}}^{1i} \rangle = \frac{n_{1i} \omega^{1i}}{n_1}, \quad (10)$$

where $\omega^{1i} = 1 / (1 + \alpha^{1i} e^{-\beta E^{1i}})$ is the probability of bond formation between 1,3-propanediol and dioxane and n_1 is the number density of dioxane molecules. $\beta = 1/kT$ and α^{1i} is the ratio of the two subvolumes of the phase space, related to the non-hydrogen bonded and hydrogen bonded pairs. These hydrogen-bonded pairs have only two energy levels, E_{11} and E_{12} , for 1,3-propanediol–1,3-propanediol and 1,3-propanediol–dioxane pair formed bonds, respectively. The values of $\langle n_{\text{HB}}^{11} \rangle$ and $\langle n_{\text{HB}}^{12} \rangle$ depend on the number of densities of hydrogen bonding pairs between 1,3-propanediol–dioxane, n_{12} and those between 1,3-propanediol–1,3-propanediol molecule, i.e. $n_{11} = 2n_1 - n_{12}$. This can be calculated during 1,3-propanediol–1,3-propanediol (pair 11) and 1,3-propanediol–dioxane

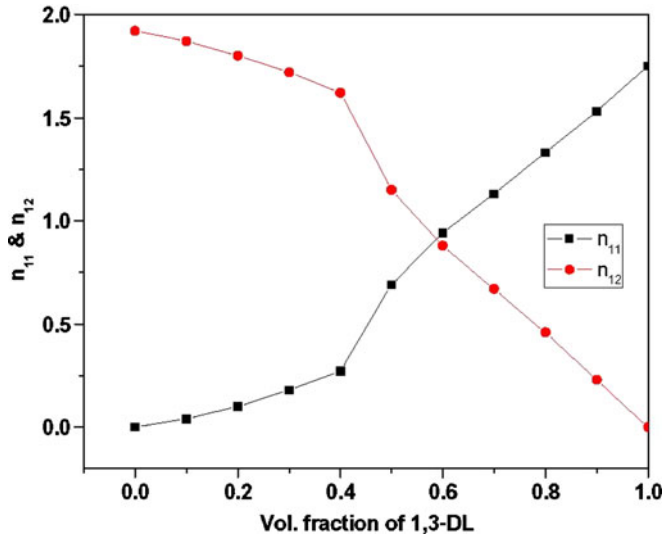


Figure 9. Plot of average number of hydrogen bonds in 1,3-propanediol–1,3-propanediol molecules (n_{11} pair) and 1,3-propanediol–dioxane (n_{12} pair) against volume fraction of 1,3-DL.

Table 1. Molecular parameters used in the computation of the static dielectric constant.

Molecular parameters	1,3-propanediol	1,4-dioxane
Dipole moment (μ_1, μ_2)	2.95 D	0.97 D
Polarizability (α_1, α_2)	4.94	2.79
Bonding energy (E_{11}, E_{12}) (kJ/mol)	-13.98	-16.25
Molecular weight (g/mol)	76.11	88.11
Density (g/cm ³)	1.049	1.028
Enthalpy (α_{11}, α_{12}) (kJ/mol)	40	28

11 – 1,3-propanediol pair, 12 – 1,3-propanediol–dioxane pair.

(pair 12) formation [46]. Figure 9 shows plot of the average number of hydrogen bonds between 1,3-propanediol and 1,3-propanediol molecules (11 pairs) and 1,3-propanediol and dioxane (12 pairs) against volume fraction of 1,3-propanediol.

It can be seen from figure 9 that the average number of hydrogen bonds increases in 1,3-propanediol–1,3-propanediol, whereas it decreases in 1,3-propanediol–dioxane as the concentration of 1,3-propanediol increases in dioxane. The Luzar model [46] gives a good qualitative account of the dielectric constant for 1,3-propanediol–dioxane mixture at 25°C. The different parameters required in the Luzar model [46] are dipole moments, polarizabilities, possible number of hydrogen bonds and angles between dipoles $\cos \phi_{11}$ and $\cos \phi_{12}$ for the 1,3-propanediol and dioxane. The best possible values of molecular parameters in our analysis for which static dielectric constant values are in reasonable agreement with the experimental values are given in table 1.

8. Conclusion

The complex permittivities for 1,3-propanediol–1,4-dioxane mixture are determined using TDR method. The dielectric constant for the mixtures can be explained using hydrogen-bonded model by assuming the formation of hydrogen bonds between 1,3-propanediol–1,3-propanediol and 1,3-propanediol–1,4-dioxane pairs. The orientation correlations between neighbouring molecules due to hydrogen bonding interaction are determined in terms of Kirkwood factors. The average number of hydrogen bonds in 1,3-propanediol–1,3-propanediol and 1,3-propanediol–1,4-dioxane molecules are also computed. The Bruggeman model for the nonlinear case has been fitted to the dielectric data for mixtures.

Acknowledgements

The financial support from the Department of Science and Technology, New Delhi is gratefully acknowledged (Project No. SR/S2/LOP-25/2007). RBT is thankful to Swami Ramanand Teerth Marathwada University, Nanded, for providing University Research Fellowship. PGH is thankful to DST for providing JRF. YSJ is thankful to UGC for providing FIP. The authors thank Prof. S C Mehrotra, Dr M K Patil and Dr A S Choudhari for discussion.

References

- [1] B N Solomonov, M A Varfolomeev and V B Novikov, *J. Phys. Org. Chem.* **19**, 263 (2006)
- [2] G A Jeffrey and W Saenger, *Hydrogen bonding in biological structures* (Springer-Verlag, New York, 1991)
- [3] T H Steiner, *Angew. Chem. Int. Ed.* **41**, 48 (2002)
- [4] B N Solomonov, M A Varfolomeev and D I Abaidullina, *Vibrational Spectroscopy* **43**, 380 (2007)
- [5] G S Denisov and L A Kuzina, *J. Mol. Struct.* **322**, 205 (1994)
- [6] N S Golubev and G S Denisov, *J. Mol. Struct.* **270**, 263 (1994)
- [7] N S Golubev, G S Denisov, L A Kuzina and S N Smirmov, *Zh. Obsch. Khim.* **64**, 1162 (1994) (in Russian)
- [8] F Huisken, E G Tarakanova, A A Vigasin and G V Yuhnevich, *Chem. Phys. Lett.* **245**, 319 (1995)
- [9] P L Huysken, *J. Am. Chem. Soc.* **99**, 2578 (1977)
- [10] H Kleeberg, G Heinje and W A P Luck, *J. Phys. Chem.* **90**, 4427 (1986)
- [11] H Kleeberg, D Klein and W A P Luck, *J. Phys. Chem.* **91**, 3200 (1987)
- [12] H Kleeberg and W A P Luck, *Z. Phys. Chem.* **270**, 613 (1989)
- [13] W A P Luck, *J. Mol. Struct.* **448**, 131 (1998)
- [14] M Akiyama and H Torii, *Spectrochim. Acta* **A56**, 137 (2000)
- [15] B N Solomonov, M A Varfolomeev, V B Novikov and A E Klimovitskii, *Spectrochim. Acta Part A* **64**, 397 (2006)
- [16] B N Solomonov, V B Novikov, M A Varfolomeev and N M Milesenko, *J. Phys. Org. Chem.* **18**, 49 (2005)
- [17] B N Solomonov, V B Novikov, M A Varfolomeev and A E Klimovitskii, *J. Phys. Org. Chem.* **18**, 1132 (2005)
- [18] I Lampre, M Lin, H He, Z Han, M Mostafavi and Y Katsumura, *Chem. Phys. Lett.* **402**, 192 (2005)
- [19] C M Romero and M S Paez, *J. Chem. Thermo.* **40**, 1645 (2008)
- [20] S Schwerdtfeger, F Kohler, R Pottel and U Kaatz, *J. Chem. Phys.* **115**, 4186 (2001)
- [21] P Petong, R Pottel and U Kaatz, *J. Chem. Phys.* **A104**, 7420 (2000)
- [22] T Sato, A Chiba and R Nozaki, *J. Chem. Phys.* **110**, 2508 (1999)
- [23] P Petong, R Pottel and U Kaatz, *J. Chem. Phys.* **A103**, 6114 (1999)
- [24] T Sato, A Chiba and R Nozaki, *J. Chem. Phys.* **112**, 2924 (2000)
- [25] A C Kumbharkhane, M N Shinde, S C Mehrotra, N Oshiki, N Shinyashiki, S Yagihara and S Sudo, *J. Phys. Chem.* **A113**, 10196 (2009)
- [26] R J Sengwa, S Sankhla and N Shinyashiki, *J. Sol. Chem.* **37**, 137 (2008)
- [27] R J Sengwa and S Sankhla, *J. Non-Cryst. Solids* **353**, 4570 (2007)
- [28] F F Hanna, B Gestblom and A Soliman, *Phys. Chem. Chem. Phys.* **2**, 5071 (2000)
- [29] M Tabellout, P Lanceleur, J R Emery, D Hayward and R Pethrick, *J. Chem. Soc. Faraday Trans.* **86**, 1493 (1990)
- [30] D Bertolini, M Casstari and G Salvetti, *J. Chem. Phys.* **78**, 365 (1983)
- [31] J P Perl, D T Wassan, I V Winsor and R H Cole, *J. Mol. Liquids* **28**, 103 (1984)
- [32] B Gestblom and J Sjoblom, *J. Acta Chem. Scand. Ser A* **38**, 47 (1984)
- [33] A C Kumbharkhane, S M Puranik and S C Mehrotra, *J. Chem. Soc. Faraday Trans.* **87(10)**, 1569 (1991)
- [34] S Yagihara, R Nozaki, S Mashimo and K Higasi, *Chem. Lett.* **1**, 137 (1985)
- [35] S Mashimo, N Miura, T Umehara, S Yagihara and K Higasi, *J. Chem. Phys.* **96**, 6358 (1992)
- [36] K S Kanse, S D Chavan, A C Kumbharkhane and S C Mehrotra, *J. Polym. Mater.* **23(1)**, 47 (2006)

- [37] S Sudo, N Oshiki, N Shinyashiki, S Yagihara, A C Kumbharkhane and S C Mehrotra, *J. Phys. Chem.* **A111(16)**, 2993 (2007)
- [38] J Crossely, *Can. J. Chem.* **56**, 352 (1978)
- [39] A C Kumbharkhane, S N Helambe, S Doraiswamy and S C Mehrotra, *J. Chem. Phys.* **99(4)**, 2405 (1993)
- [40] S Havriliak and S Negami, *J. Polym. Sci.* **14**, 99 (1996)
- [41] S Sudo, N Shinyasiki, Y Kitsuki and S Yagihara, *J. Phys. Chem.* **A106**, 458 (2002)
- [42] F Wang, R Pottel and U Kaatz, *J. Phys. Chem.* **B101**, 922 (1997)
- [43] J B Hasted, *Aqueous dielectrics* (Chapman and Hall, London, 1973)
- [44] A C Kumbharkhane, S M Puranik and S C Mehrotra, *J. Sol. Chem.* **20(12)**, 1 (1991)
- [45] A C Kumbharkhane, S M Puranik and S C Mehrotra, *J. Mol. Liquid.* **51**, 261 (1992)
- [46] A Luzar, *J. Mol. Liq.* **46**, 221 (1990)
- [47] S M Puranik, A C Kumbharkhane and S C Mehrotra, *J. Mol. Liquid.* **59**, 173 (1994)
- [48] A Chaudhari and S C Mehrotra, *J. Mol. Phys.* **100(24)**, 3907 (2002)
- [49] A C Kumbharkhane, S M Puranik and S C Mehrotra, *J. Sol. Chem.* **22**, 219 (1993)
- [50] D A G Brugeman, *Ann. Phys. (Leipzig)* **5**, 636 (1935)
- [51] D R Lide (ed.), *CRC Handbook of chemistry and physics* (Taylor and Francis, Boca Raton, FL, 2007)
- [52] A L McClellan, *Tables of experimental dipole moments* (W H Freeman, San Francisco, California, 1963)