



Dielectric Relaxation of 1,3-Butanediol-Water Mixture Using Time Domain Reflectometry

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Abstract:

The complex permittivity spectra of 1,3-Butanediol (1,3-BD) and water solutions have been obtained by time domain reflectometry (TDR) technique in the frequency range from 10 MHz to 30 GHz. The dielectric relaxation parameters such as static dielectric constant relaxation time were obtained by using non-linear least square fit method. The intermolecular hydrogen bonding of 1,3-Butanediol-water has been discussed using Kirkwood correlation factor.

Key words: Dielectric relaxation, Time Domain Reflectometry and 1,3-Butanediol.

Introduction

1,3-butanediol (1,3BD) is the organic compound having structural formula $\text{OHCH}_2\text{CH}_2\text{CHOHCH}_3$, this colorless liquid is derived from butane alcohol groups at first and third carbon of the chain and is commonly used as a solvent for food flavoring agents and is a co-monomer used in certain polyurethane and polyester resins. 1,3-Butanediol is a highly effective humectants in pet foods, tobacco and cosmetic formulations. The physical and chemical properties of the butanediols make them suitable as organic solvents and useful chemical intermediates in the manufacture of many chemical products. The associating behavior and the frequency dependences of complex permittivity for 1,3BD in water mixture are extensively studied through dielectric properties and cooperative domains [1]. The butanediols also have been studied with binary mixtures of non polar solvent like 1,4-dioxane and polar solvent such as 2-ethyl-1-hexanol [2]. The marked difference in the parameters between isomers of butanediols suggests a connection to the distance between the hydroxyl groups along the chains of the isomers. The main aim of the work is to study the temperature dependent dielectric properties 1,3-butanediol-water systems using Time domain reflectometry technique from 10MHz to 30GHz. The Static dielectric constant, relaxation time and Kirkwood correlation factor.

Experimental Method:

Materials

1,3-butanediol (1,3BD) was obtained commercially (Merck India Pvt. Ltd.) and used without further purification. The water used in the preparation of mixture was obtained by double distilled procedure.

Measurements

The dielectric spectra were obtained by the time domain reflectometry (TDR) technique [3-6]. The Tektronix model no DSA8200 Digital Serial Analyzer sampling mainframe along with the sampling module 80E08 has been used for the time domain reflectometry (TDR). A repetitive fast rising voltage pulse with 20ps incident rise time was fed through coaxial line system of impedance 50 Ohm. The reflected pulse without sample $R_1(t)$ and with sample $R_x(t)$ were recorded in time window of 5ns the recorded pulses $p(t)$, $q(t)$ and data analysis were done earlier to determine complex permittivity spectra $\epsilon^*(\omega)$ using non linear least square fit method [3,6].

$$p(t) = [R_1(t) - R_x(t)] \quad 1$$

$$q(t) = [R_1(t) + R_x(t)] \quad 2$$

Results and Discussion

The complex permittivity spectra of aqueous solution are fitted to the Havriliak-Negami (HN) equation [8,9]. The non linear least square fit method is used to calculate the dielectric relaxation parameters by the following equation [7-9].

$$\epsilon^*(\omega) = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{[1 + (j\omega\tau)^{1-\alpha}]^\beta} \quad 3$$

where ϵ_0 is the static dielectric constant, ϵ_∞ is the permittivity at high frequency, τ the relaxation time, α and β are the distribution parameters. The temperature dependant dielectric parameters for aqueous solution of 1,3BD at 25°C.

Table:1 Dielectric relaxation parameters for 1,3- Butanediol-water mixtures at 25°C.

System	Vol.% of BD	ϵ_0	τ (ps)	ϵ_∞	β
1,3-BD+water	0	78.32(2)	8.21(10)	2.00(1)	1.00
	10	72.24(7)	13.62(0)	2.82(5)	0.95
	20	69.46(5)	16.67(7)	2.24(4)	1.00
	30	66.63(4)	21.86(1)	2.32(3)	0.94
	40	62.42(3)	29.15(9)	3.43(2)	0.90

50	55.98(3)	45.57(13)	3.06(1)	0.87
60	48.18(7)	70.3(46)	2.69(2)	0.82
70	44.3(6)	112.58(68)	3.01(1)	0.81
80	40.83(7)	197.19(112)	3.13(1)	0.82
90	36.91(8)	398.04(214)	2.96(1)	0.81
100	28.23(7)	546.37(858)	2.49(1)	0.85

Numbers in the bracket denotes uncertainties in the last significant digit obtained by least square fit method e.g 78.32(2) means 0.02.

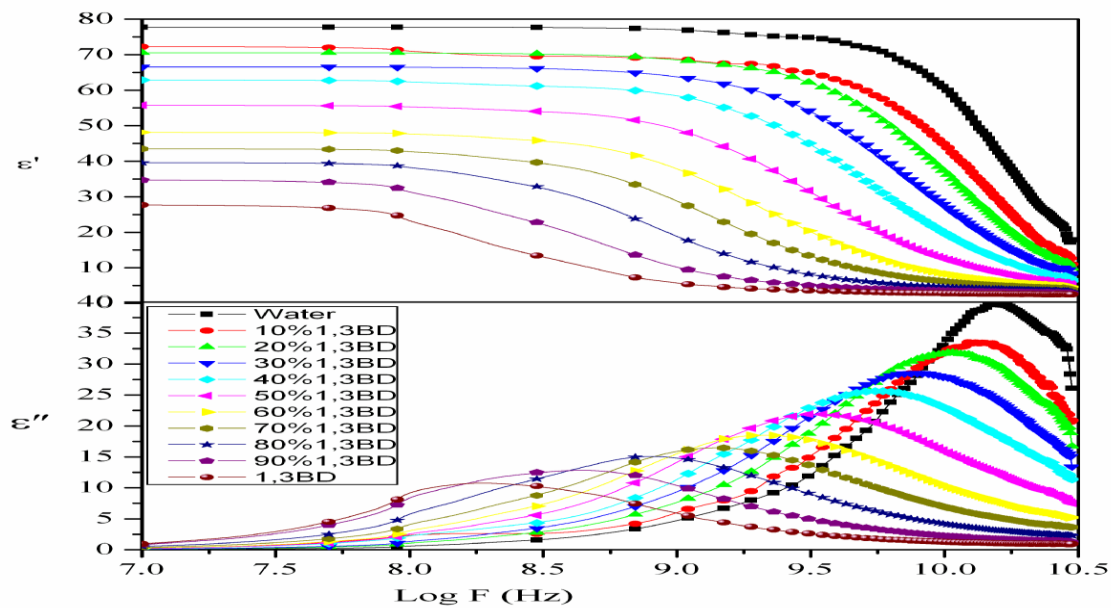


Fig.1 Frequency dependences of the (a) dielectric permittivity (ϵ') and (b) dielectric loss (ϵ'') for 1,3Butanediol-water mixtures at various concentrations at 25°C.

The static dielectric constant decreases and relaxation time increases with increase in volume fraction of solute with water concentration in 1,3BD as shown in fig 1. This may be due to water structure is modified by the hydrogen bond in alcohol so as to produce an increase in relaxation time and decrease in static dielectric constant in the mixture.[10]

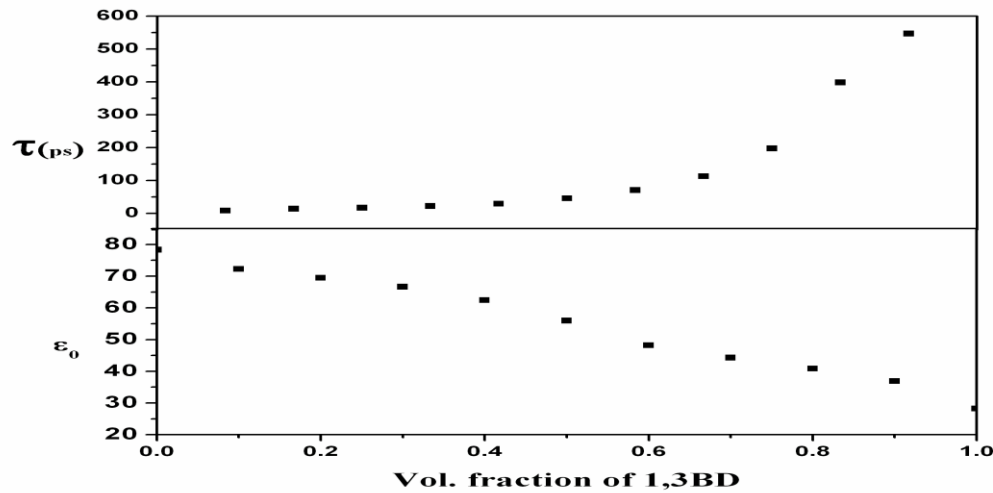


Fig.2 relaxation time (τ) and (ii) dielectric constant (ϵ_0) vs volume fraction of 1, 3 butanediol-water mixture at 25°C.

Kirkwood correlation factor

The information regarding the orientation of dipole in case of pure liquids is described by the Kirkwood Frohlich equation. The departure of Kirkwood correlation factor “g” value from unity is measure of the extent of dipole orientation due to hydrogen bond interactions. It can be represented as [11].

$$\frac{(\epsilon_0 - \epsilon_\infty)(2\epsilon_0 + \epsilon_\infty)}{\epsilon_0(\epsilon_\infty + 2)^2} = g \mu^2 \frac{4\pi N \rho}{9kTM} \quad 4$$

where g is Kirkwood correlation factor, N is Avagadro’s number, μ is dipole moment of liquid, ρ the density of liquid, ϵ_0 the static dielectric constant, ϵ_∞ Dielectric constant at high frequency, k is the Boltzmann constant and T is the temperature. To calculate value of ‘g’, we have taken $\mu_{\text{wat}}=1.84$ D, $\mu_{13\text{BD}}=2.54$ D The information on dipole-dipole correlation in associating binary liquids can be determined from effective correlation factor (g^{eff}) in binary mixture by modified Kirkwood equation [12].

$$\frac{4\pi N}{9kT} \left[\frac{\mu_w^2 \rho_w}{M_w} X_w + \frac{\mu_E^2 \rho_E}{M_E} (1 - X_w) \right] g^{\text{eff}} = \frac{(\epsilon_{0m} - \epsilon_{\infty m})(2\epsilon_{0m} - \epsilon_{\infty m})}{\epsilon_{0m}(\epsilon_{\infty m} + 2)^2} \quad 5$$

The Kirkwood factor is a measure of order/molecular organization in liquid mixtures. Effective Kirkwood correlation factor increases in 1,3BD water mixture with increase in volume fraction of water as shown in table. It is observed that the effective Kirkwood correlation factor for water is larger than that of solute. As concentration of solute (13BD) increase in aqueous medium, there is an increase in the number of self associated groups formed by the hydrogen bonds.

Table:2 Kirkwood correlation factor (g^{eff}) for 1,3 &1,4-BD+water mixtures at 25⁰C.

1,3-Butanediol+water	
Vol.Fra.of 1,3BD	g^{eff}
0	2.81(15)
0.1	2.72(16)
0.2	2.75(16)
0.3	2.79(17)
0.4	2.79(17)
0.5	2.67(16)
0.6	2.58(15)
0.7	2.49(16)
0.8	2.52(17)
0.9	2.37(15)
1	2.22(12)

Conclusion

The complex permittivity spectra of 1,3-butanediol in aqueous solution have been studied using time domain reflectometry technique in the frequency range 10 MHz–30 GHz. The dielectric permittivity spectrum of 1,3-butanediol with water can be well described by Cole–Davidson model. The dielectric relaxation parameters are dependent on water concentration in the 1,3-butanediol –water mixture. The hydrogen bonding dynamics is well studied using the Kirkwood correlation factor.

References

- 1.S. Sudo, N. Shinyashiki, Y. Kitsuki and S. Yagihara, *J. Phys. Chem.* **A.106**, 458 (2002).
- 2.G. A. Ghanadzadeh, H. Ghanadzadeh, Kh. Bahrpaima and A. Ranjkesh, *J. Chem. Thermodyn.* **42(8)**, 967 (2010).
3. R H Cole, J G Berberian, S Mashimo, G Chryssikos, A Burns and E Tomabari *J. Appl. Phys.* **66** 739 (1989)
4. D Bertolini, M Cassettari, G Salvetti, E Tomabari and S Versoni *Rev. Sci. Instrum.* **61** 450 (1990)
5. U. Kaatz, *J. Mol. Liq.* **56**, 95 (1993).
6. S. D. Chavan, A. C. Kumbharkhane and S. C. Mehrotra, *J. Chin. Chem. Soc.* **54**, 1457 (2007).

7. A C Kumbharkhane, S M Puranik, S C Mehrotra *J. Chem Soc. Faraday Trans* **87** 1596 (1991)
8. U Kaatze *Radiat. Phys. Chem.* **45** 549 (1995)
9. S D Chavan, B D Watode, P G Hudge, D B Surywanshi, C G Akode, A C Kumbharkhane and S C Mehrotra *Indian J. Phys.* **84** 419 (2010)
10. F. Wang, R. Pottel and U. Kaatze, *J. Phys. Chem.* **B.101**, 922 (1997).
11. J G Kirkwood *J. Chem. Phys.* **7** 911 (1939)
12. A C Kumbharkhane, S M Puranik and S C Mehrotra *J. Sol. Chem.* **21** 201 (1992)

