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Picosecond time domain studies on hydrogen bonded binary mixture of Butyl alcohol in water

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Abstract

The dielectric relaxation study for the hydrogen bonded binary system of polar liquid Butyl alcohol in water has been carried out, using the Time domain Reflectometry technique, at 20°C and volume in different fractions. The dielectric parameters static permittivity, excess permittivity, Bruggemann parameter, relaxation time, excess inverse relaxation time and Kirkwood correlation factor have been obtained. The dielectric parameters show systematic change with concentrations. Variation in linear relation in Bruggemann factor suggests the presence of intermolecular interaction in the binary mixtures. The Kirkwood correlation factor confirms the parallel and antiparallel orientation of the dipoles in the mixtures.

Keywords

Dielectric relaxation, Bruggemann factor, Relaxation time, Hydrogen bond

1. Introduction

Water behaves as hydrogen bonded liquid because strong intermolecular hydrogen bonds exist between its molecules. These bonds are responsible for many unique physical and chemical properties of water. Butyl alcohol is an organic liquid used in chemical and electrical studies because it behaves as a moderately polar dielectric medium. The binary mixture of Water and Butyl alcohol is important in physical chemistry, dielectric studies, and solution chemistry and physics.

Dielectric relaxation studies are useful to investigate molecular and intra-molecular motions, solute–solute inter actions and solute–solvent interactions [1]. Early dielectric studies [2–8] were centered at a single component system either in pure state or in non-polar solvents. Dielectric investigation of binary polar liquid mixtures consisting of one associative and other non-associative liquids, provide valuable information regarding molecular complex formation in solution. Alcohols are strongly associated in solution because of dipole–dipole interaction and hydrogen bonding. Hydrogen bonding is complex in liquid state because of the

uncertainty in identifying the particular bonds and the number of molecules involved. Molecular mixtures bring about changes in physical properties like refractive index, dielectric permittivity, density, molar volume and also in thermodynamic properties like activation free energy, enthalpy, entropy, etc. [9].

2. Experimental details

Materials: - The chemicals utilized for the present investigation having 99% purity and used without further purification.

Methodology:-

Samples were prepared by mixing the volume fractions of Butyl alcohol in water. Measurements were taken by placing the sample in electronically temperature controller bath with an accuracy of ± 0.1 °C. The Tektronix DSA8300 sampling main frame oscilloscope sampling with the dual channel sampling module 80E10B has been used for time domain reflectometry. Sampling oscilloscope monitors changes in pulse after reflection from the 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. The addition [$q(t) = R_1(t) + R_x(t)$]] and subtraction [$p(t) = R_1(t) - R_x(t)$] of these pulses are done in oscilloscope memory. These subtracted and added pulses are transferred to PC for further analysis. The Fourier transformations of the pulse and data analysis were done earlier to determine complex permittivity spectra ε*(ω) using non linear least square fit method [10, 11].

Frequency dependent complex permittivity spectra for Butyl alcohol-water mixture oButyl alcoholined in the frequency region 10 MHz -30 GHz at room temperature are shown in Figure 1. The values of ε' and ε" for all the studied solvents were observed to be decreased with decreasing Polarity Index) towards high frequency. Complex permittivity spectra are described by Havriliak-Negami equation [12] given as:

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

where, ε_0 is static permittivity, ε_∞ is permittivity at high frequency, τ is relaxation time, α and β are the empirical parameters for the distribution of relaxation time between 0 and 1. The Havriliak-Negami function includes the Cole-Cole [13] (β=1), Cole-Davidson [14] (α=0) and Debye [15] (α=0, β=1) relaxation spectral function in limiting form. The complex permittivity spectra have been fitted in Debye type model using nonlinear least squares fit method to determine the dielectric relaxation parameters.

2. Results and discussion

2.1.Dielectric constant and relaxation time

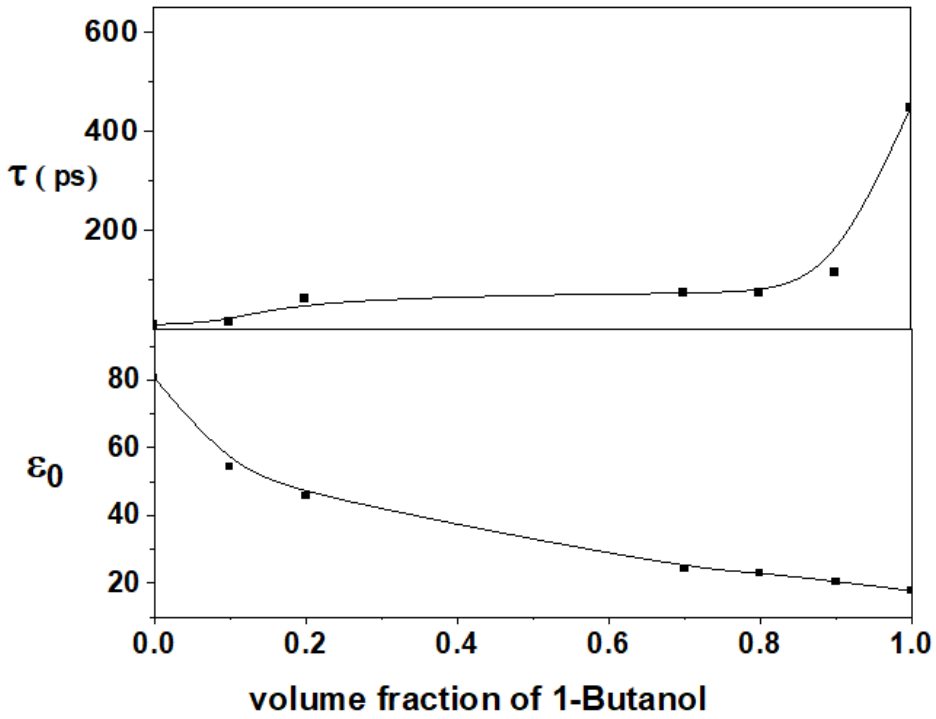

Figure 1: Dielectric parameters for Butyl alcohol and water binary mixture at 20ºC.

The frequency and temperature dependences of the complex dielectric spectra of Butyl alcohol-water binary mixtures were measured. The Butyl alcohol-water mixture dielectric spectra, at 20^{o}C, are shown in Figure 1. It can be seen that the mixture values of ε_0 start to decrease up to certain concentrations and then increase with increasing solute concentration, which may be due to the change in size and shape of the solute–solvent complexes [16]. This change reflects possible intermolecular interactions, including H-bonding and dipole–dipole interactions between unlike molecules in the mixtures [17]. In general, for ideal binary mixtures, the variation of ε_0 with solute volume fraction remains linear. As a result of associative interactions between the solute and solvent, deviations from ideal mixture behavior occurs. All the binary mixtures showed nonlinear variation of ε_0 with water, which indicates H-bonding formation between water and Butyl alcohol molecules. The pure Butyl alcohol has high relaxation times that increase with increase of chain length of alcohols and changes in the position of the hydroxyl group. The polar hydroxyl group restricts the molecular rotation as a result of H-bonding.

2.2.Excess properties

2.2.1. Excess permittivity

The values of excess permittivity has been figured out using equation [18]

$$(\varepsilon_0)^E = (\varepsilon_0)_m - [(\varepsilon_0)_E X_E + (\varepsilon_0)_A (1 - X_E)] \qquad (2)$$

Where X_E represents the volume fraction of water. Subscripts m, E and A represents Mixture, water and solute Butyl alcohol respectively.

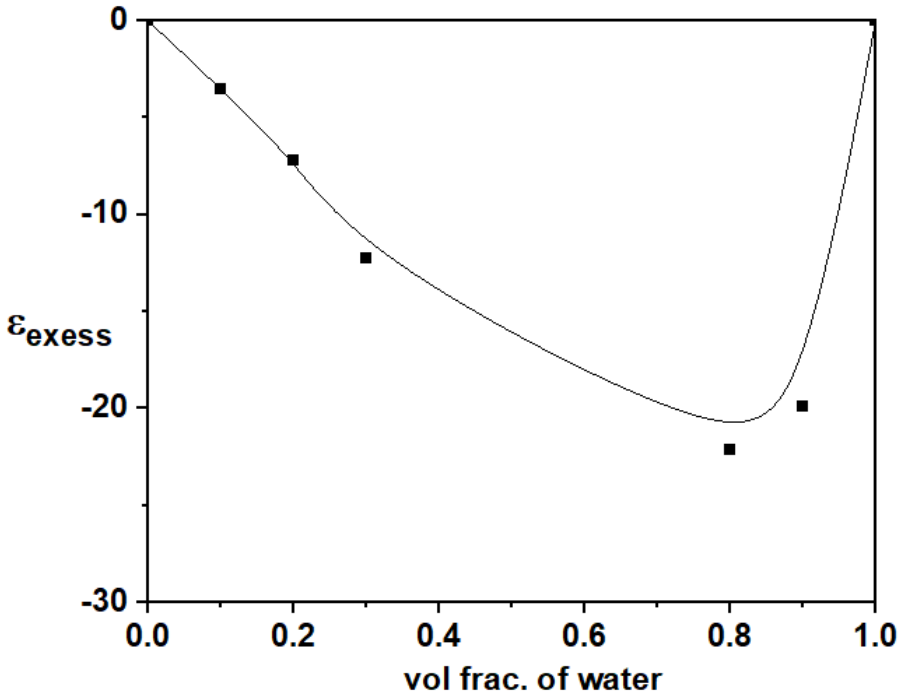

Figure 1: Excess permittivity (ε^E) vs volume fraction of water for Butyl alcohol and water binary mixtures at 20°C

The ε_0^E values for all binary liquid systems were evaluated using Eq. 2 and the variation of ε_0^E as a function of water concentration is shown in Figure 2. The deviation of ε_0^E from zero is evidence of the strength of the intermolecular interactions between water and Butyl alcohol molecules in the mixture. The ε_0^E values of water and Butyl alcohol mixtures are negative over the entire concentration range; this is due to anti-parallel alignment of dipoles in water and Butyl alcohol mixture molecules. This suggests that the change occurs as a result of charge transfer or dipole–dipole interaction or H-bonding between solute and solvent molecules.

2.2.2. Excess inverse relaxation time:-

The excess inverse relaxation time was found out using the relation

$$\left(\frac{1}{\tau}\right)^E = \left(\frac{1}{\tau}\right)_m - \left[\left(\frac{1}{\tau}\right)_A X_A + \left(\frac{1}{\tau}\right)_B X_B\right] \qquad (3)$$

Where $\left(\frac{1}{\tau}\right)^E$ is the excess inverse relaxation time which represents the average broadening of dielectric spectra [19]. The $\left(\frac{1}{\tau}\right)^E$ values provide evidence of molecular dynamics and rotational changes. The variation $\left(\frac{1}{\tau}\right)^E$ with volume fraction of water is calculated by using Eq. 3. The calculated $\left(\frac{1}{\tau}\right)^E$ with volume fraction of water for all concentrations are shown in Figure 3. The Butyl alcohol-water mixtures have negative $\left(\frac{1}{\tau}\right)^E$ values for water content, which reveals that the dissimilar molecule interactions produce the electric field and promote slower rotation of the effective dipoles.

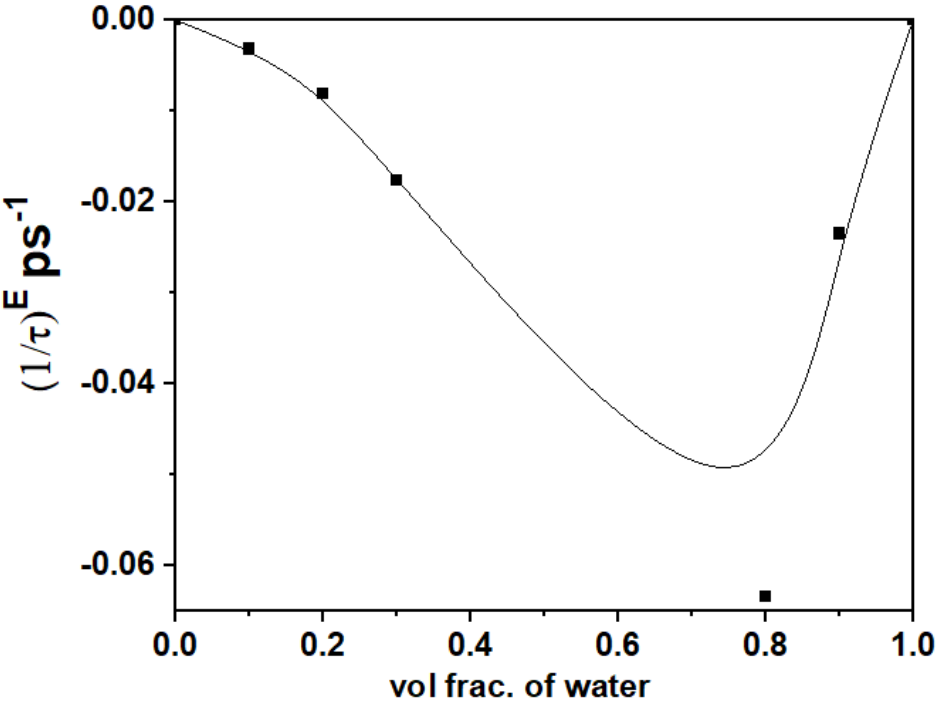

Figure 3: excess inverse relaxation time vs volume fraction of water for Butyl alcohol and water binary mixtures at 20°C

*2.3.*Kirkwood correlation factor

Static dielectric constant for the mixture can be explained using Kirkwood Frohlich equation as follows [20, 21].

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

Where μ, ρ and M indicates, dipole moment in gas phase ,density and molecular weight respectively, k is Boltzmann constant, T is the temperature, and N is the Avogadro's number.

Kirkwood correlation factor "g" calculated from dielectric constant yields significant information regarding collective orientation correlation between molecules. For the mixture of two polar liquids a and b equation (5) is a modified form of equation (4) as described earlier in the literature[22, 23] with the assumption that g for the binary mixture is expressed by an effective average correlation factor g^{eff} such that

$$\frac{4\pi N}{9KT}\left[\frac{\mu_E^2\rho_E}{M_E}V_E + \frac{\mu_A^2\rho_A}{M_A}(1 - V_E)\right] g^{eff}$$

$$= \frac{(\epsilon_{0m} - \epsilon_{\infty m})(2\,\epsilon_{0m} + \epsilon_{\infty m})}{\epsilon_{0m}\,(\epsilon_{\infty m} + 2)^2} \qquad (5)$$

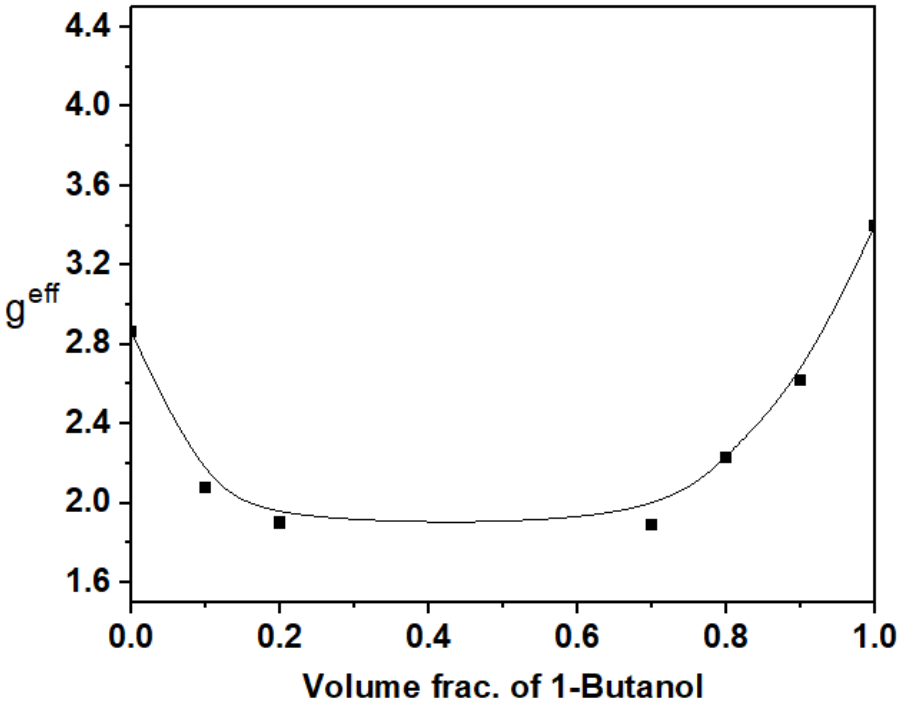

Figure 4: g^{eff} vs volume fraction of water for Butyl alcohol-water binary mixtures at 20°C

The Kirkwood correlation factor (g^{eff}) for all the binary systems were calculated at 20°C. the g^{eff} value decreases non-linearly with the increase of Butyl alcohol concentration, which signifies the formation of a hydrogen bonded network structure between Butyl alcohols with water molecules in the binary mixtures. The decrease is also due to the addition of water molecule which leads to the breakup of parallel dipole orientation in alcohols and results in the formation of antiparallel alignments between alcohol dipoles with water dipoles in the binary mixtures. At a lower concentration of water the g^{eff} values are increased, due to the association of large numbers of alcohol molecules with the surrounding Butyl alcohol molecules, leading to the formation of aggregates of Butyl alcohol molecules with water molecules and a reduction of parallel dipole orientations.

2.4.Bruggemann factor

The Bruggemann equation [24] is another parameter which may be used as an indicator of solute solvent interaction. The Bruggemann factor (f_B) is given by,

$$f_B = \left[\frac{(\varepsilon_{0m} - \varepsilon_{02})}{(\varepsilon_{01} - \varepsilon_{02})}\right]\left(\frac{\varepsilon_{01}}{\varepsilon_{0m}}\right)^{\frac{1}{3}} = 1 - V \qquad (6)$$

Where ε_{0m}, ε_{01} and ε_{02} are the static dielectric constant corresponding to mixture, solute and solvent respectively; V- is the volume fraction of solvent (water). From above equation, the linear relation is expected from a plot f_B Vs Volume fraction of water. But in binary liquids, there is non-linear relationship. To explain non-linear relationship of the plot, above equation has been modified as [25],

$$f_B = \left[\frac{(\varepsilon_{0m} - \varepsilon_{02})}{(\varepsilon_{01} - \varepsilon_{02})}\right]\left(\frac{\varepsilon_{01}}{\varepsilon_{0m}}\right)^{\frac{1}{3}} = 1 - [a - (a-1)V]V \qquad (7)$$

In this equation, volume fraction (V) is changed by a factor ' a -(a -1) V' of the mixture.

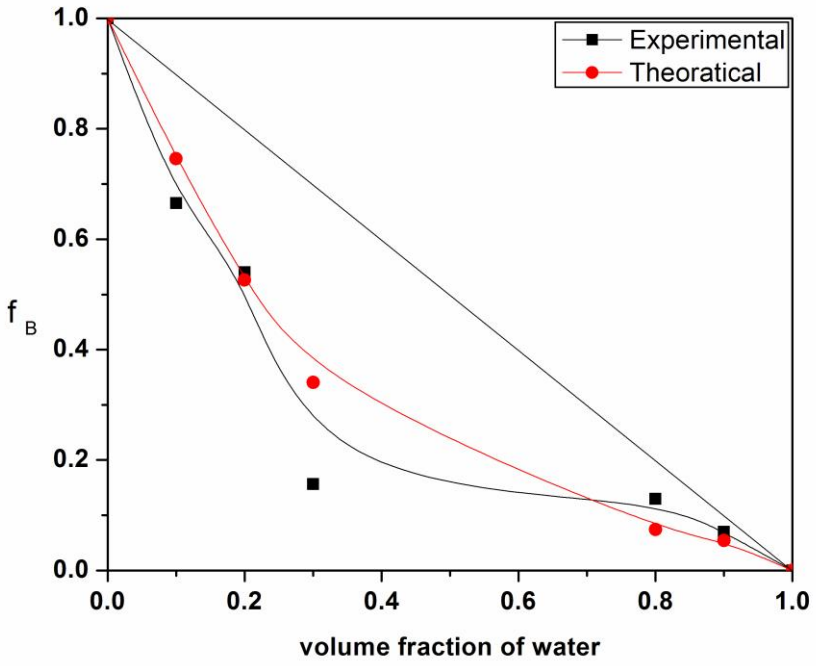

Figure 5: f_B vs volume fraction of water for butyl alcohol-water binary mixtures at 20°C

The Bruggemann f_B factor values of Butyl alcohol-water systems data shows that there is a deviation from the linear relation which gives the confirmation of strong intermolecular interactions between ethanol-water and methanol-water binary solutions. The estimated values of f_B are shown in Figure 5. The Bruggemann factor f_B shows a negative deviation around 30% of water volume fraction, from the ideal line. This indicates that intermolecular interaction is taking place in the mixture.

Conclusion

The dielectric complex spectra of water in Butyl alcohol solutions have been studied in the frequency range of 10 MHz to 30 GHz using the time domain reflectometry method at 20°C. The static dielectric constant of the Butyl alcohol-water system decreases with increase in volume fraction of water. The excess permittivity of the Butyl alcohol-water binary system is negative due to anti-parallel alignment of dipoles in water and Butyl alcohol mixture molecules. Butyl alcohol-water mixtures have negative $\left(\frac{1}{\tau}\right)^E$ values for water content, due to slower rotation of the effective dipoles. In the mixture, the dipole pairs are formed and orient in the antiparallel direction in Butyl alcohol rich region. The Bruggemann factor study shows the deviation from the linear relation which gives the strong evidence of molecular interactions in binary solutions.

Acknowledgment

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References

[1] N.E. Hill, W.E. Vaughan, A.H. Price, M. Davies, Dielectric Properties and Molecular Behaviour, Reinhold, London, 1969

[2] Crossley, J__, L. Glasser, and C. P. Smyth. "Microwave Absorption and Molecular Structure in Liquids. LXXVIII. Dielectric and Association Behavior of Six Isomeric Octyl Alcohols in n-Heptane Solution." *The Journal of Chemical Physics* 55.5 (1971): 2197-2206.

[3] Glasser, L., J. Crossley, and C. P. Smyth. "Microwave Absorption and Molecular Structure in Liquids. LXXIX. Dielectric Behavior and Association of Some Normal Alcohols in n-Heptane Solution." *The Journal of Chemical Physics* 57.9 (1972): 3977-3986.

[4] Minami, Ryuichi, et al. "A theoretical approach to the dielectric relaxation of alcohol solutions." *Bulletin of the Chemical Society of Japan* 54.5 (1981): 1320-1323.

[5] Purohit, Hari Dutt, and Ram Jeewan Sengwa. "Dielectric relaxation studies of oligether of ethylene glycol at microwave frequencies." *Bulletin of the Chemical Society of Japan* 64.6 (1991): 2030-2031.

[6] Purohit, H. D., H. S. Sharma, and A. D. Vyas. "Dielectric dispersion and relaxation mechanism in some trifluoro compounds at microwave frequencies." *Bulletin of the Chemical Society of Japan* 48.1 (1975): 327-329.

[7] Higasi, K., and C. P. Smyth. "Microwave Absorption and Molecular Structure. XXXIII. Change of Mesomeric Moment as a Mechanism of Dielectric Relaxation1." *Journal of the American Chemical Society* 82.18 (1960): 4759-4762.

[8] Vaughan, Worth E., and Charles P. Smyth. "Microwave Absorption and Molecular Structure in Liquids. XXXV. Absorption by Pure Polar Liquids at 4.3 MM. Wave LENGTH1, 2." *The Journal of Physical Chemistry* 65.1 (1961): 98-101.

[9] Reddy, R. R., et al. "Correlations between Moelwyn–Hughes parameter, available volume and intermolecular free-lengths in liquid systems." *Journal of Molecular Liquids* 140.1-3 (2008): 48-53.

[10] Hiejima, Yusuke, and Makoto Yao. "Dielectric relaxation of lower alcohols in the whole fluid phase." *The Journal of chemical physics* 119.15 (2003): 7931-7942.

[11] Cole, R. H., et al. "Time domain reflection methods for dielectric measurements to 10 GHz." *Journal of applied physics* 66.2 (1989): 793-802.

[12] Havriliak, S., and S. Negami. "A complex plane analysis of α-dispersions in some polymer systems." *Journal of Polymer Science Part C: Polymer Symposia*. Vol. 14. No. 1. New York: Wiley Subscription Services, Inc., A Wiley Company, 1966.

[13] Kaatze, Udo. "Microwave dielectric properties of liquids." *Radiation Physics and Chemistry* 45.4 (1995): 549-566.

[14] Cole, Kenneth S., and Robert H. Cole. "Dispersion and absorption in dielectrics I. Alternating current characteristics." *The Journal of chemical physics* 9.4 (1941): 341-351.

[15] Davidson, D. W., and Robert H. Cole. "Dielectric relaxation in glycerine." *The Journal of Chemical Physics* 18.10 (1950): 1417-1417.

[16] Navarkhele, V.V., Bhanarkar, M.K.: Microwave dielectric response of binary mixture of N,N,-dimethylformamide with propylene glycol using TDR method. Mol. Phys. 107, 1823–1830 (2009)

[17] Rana, V.A., Chaube, H., Gadani, D.H.: Dielectric permittivity, density, viscosity and refractive index of binary mixtures of anisole with methanol and 1-propanol at different temperatures. J. Mol. Liq. 164, 191–196 (2011)

[18] Pathan, Abdulrahman W., and Ashok C. Kumbharkhane. "Temperature dependent dielectric relaxation study of 2-butanol-water mixtures from 10 MHz to 30 GHz." *Indian Journal of Pure & Applied Physics* 57.7 (2019).

[19] Deshmukh, S. D., et al. "Investigation of intermolecular interactions between amide-amine binary mixtures through dielectric relaxation study." *Ferroelectrics* 519.1 (2017): 23-32.

[20] Frolhich H. Theory of Dielectrics. London: Oxford University Press; 1949.

[21] Fattepur, R. H., et al. "Dielectric relaxation and structural study of aniline–methanol mixture using picosecond time domain reflectometry." *The Journal of chemical physics* 101.11 (1994): 9956-9960.

[22] Kumbharkhane, A. C., S. M. Puranik, and S. C. Mehrotra. "Structural study of amide-water mixtures using dielectric relaxation technique." *Journal of molecular liquids* 51.3-4 (1992): 261-277.

[23] Kumbharkhane, A. C., S. M. Puranik, and S. C. Mehrotra. "Dielectric relaxation studies of aqueous N, N-dimethylformamide using a picosecond time domain technique." *Journal of solution chemistry* 22.3 (1993): 219-229.

[24] Bruggemann, D. A. G. "Effective medium approximation." *Ann. Phys.(Leipzig)* 24 (1965): 636.

[25] Pathan, Abdulrahman W., and Ashok C. Kumbharkhane. "Temperature-dependent relaxation study of tertiary butyl alcohol–water mixtures using TDR technique." *Physics and Chemistry of Liquids* 55.2 (2017): 179-185.