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The Dielectric Relaxation of Binary Mixtures of Butyl Alcohol and Water

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Abstract

Dielectric spectra of binary mixtures of Butyl alcohol and water (BTA and WAT) are measured by TDR (time domain reflectometry). The least square fit method is used to obtain relaxation parameters. The observed relaxation process shows Debye type behavior. The concentration dependence of the relaxation time suggests that the intermolecular interaction between BTA and WAT is stronger than that of pure alcohols. The bilinear calibration method has been used to obtain dielectric quantities viz., static dielectric constant (ε_0) and relaxation time (τ). Using these fundamental dielectric quantities the parameters like the Bruggemann factor, Kirkwood correlation factor and excess relaxation time were evaluated.

Keywords

Dielectric relaxation, Time Domain Reflectometry, Bruggemann factor, Kirkwood correlation factor.

1. Introduction

Butyl Alcohol is an organic liquid used as a dielectric material in certain electrical and electronic applications because it has moderate insulating properties. Butyl alcohol is used as a moderate dielectric liquid because of its insulating nature and ability to polarize in an electric field. However, due to flammability and moisture absorption, it is mainly limited to laboratory and specialized industrial applications. Water is an excellent dielectric material in terms of dielectric constant and polarization ability. However, because impure water conducts electricity, its practical use as an insulating dielectric material is limited mainly to scientific and laboratory applications.

There are many studies of the dielectric behavior of alcohol mixtures with structure breaking and structure making [1–6]. The studies of Kirkwood correlation factor provide valuable information regarding the solute–solvent interactions in binary mixtures especially when one of the components has anti parallel orientation of dipoles [7].The dielectric relaxation study of solute–solvent or solute–solute mixtures in the microwave frequency range gives information about the molecular polarization of the system. This is related to formation of multimers in dipoles and their rotations. The earliest studies on the dielectric relaxation processes on mono alcohols [8–10] established that the magnitude of the primary dispersion is much greater than that of higher dispersion and has linear relaxation time which is attributed to the linear bond chain multimers [11]. The formation of a linear hydrogen bonded chain changes according to the amount of shielding of the hydroxyl group or to the steric hindrance of the alkyl groups. Addition of electron donating molecules would modify the structure packing and volume of the relaxing systems.

The present paper reports the dielectric relaxation studies of BTA with WAT mixtures using Time Domain Reflectometry technique in reflection mode at 15°C.

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 BTA 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 $\varepsilon^*(\omega)$ using non linear least square fit method [12, 13].

Frequency dependent complex permittivity spectra for Butyl alcohol-water mixture obtained 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 [14] 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 [15] (β=1), Cole-Davidson [16] (α=0) and Debye [17] (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.

Results and discussion

2.1.Dielectric constant and relaxation time

The static dielectric constants and the relaxation time obtained by fitting the experimental data by the Debye equation for the liquid mixtures studied are shown in figure 1. The decrease in the dielectric constant of the solution with increasing BTA concentration and the systematic change in the relaxation time of the solution can be explained on the basis of molecular interactions. In an ideal mixture of polar liquids, if the molecules are interacting, a nonlinear variation in dielectric constant and relaxation time with concentration is expected, and the same is inferred from these figures. This confirms that the intermolecular association is taking place in the system [18].

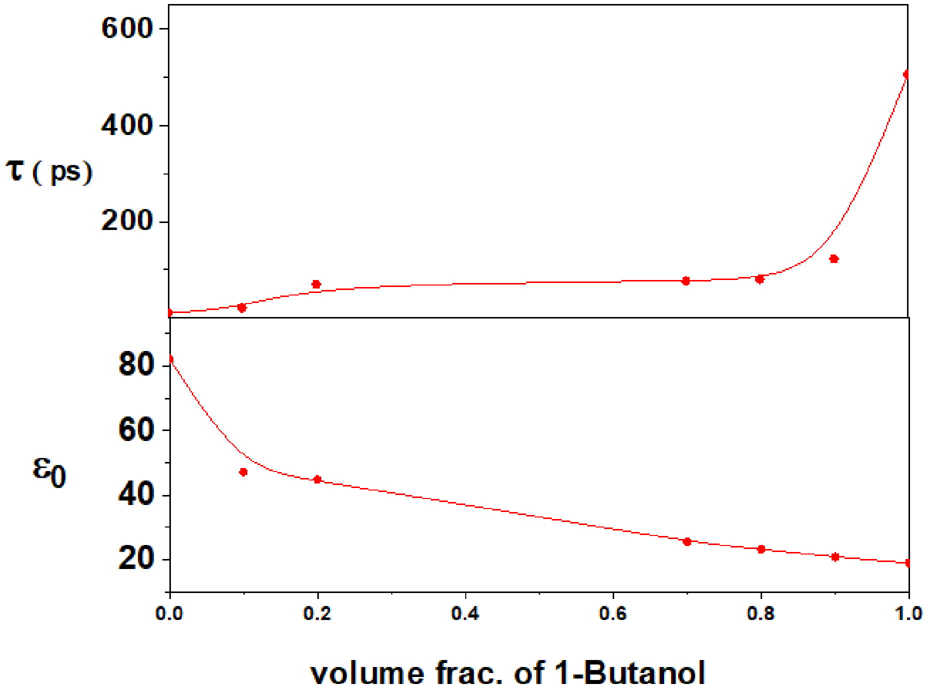


Figure 1: Dielectric parameters for BTA and water binary mixture at 15°C.

2.2.Excess properties

2.2.1. Excess permittivity

The values of excess permittivity has been figured out using equation [19]

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

Where X_E represents the volume fraction of water. Subscripts m, E and A represents Mixture, water and solute 1-Butanolrespectively.

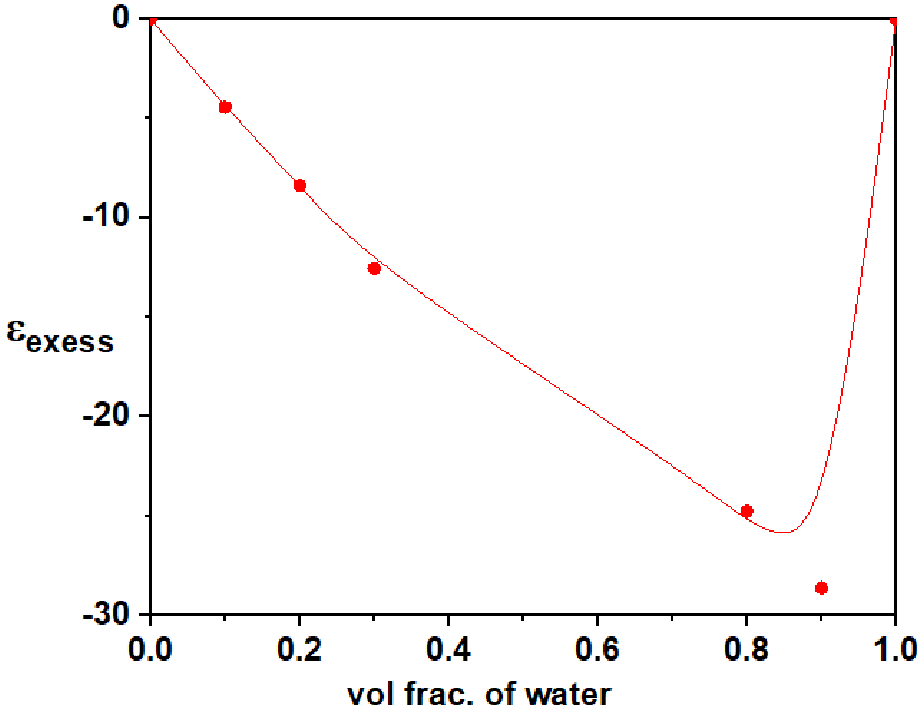


Figure 1: Excess permittivity (ε^E) vs volume fraction of water for BTA-WAT binary mixtures at 15°C

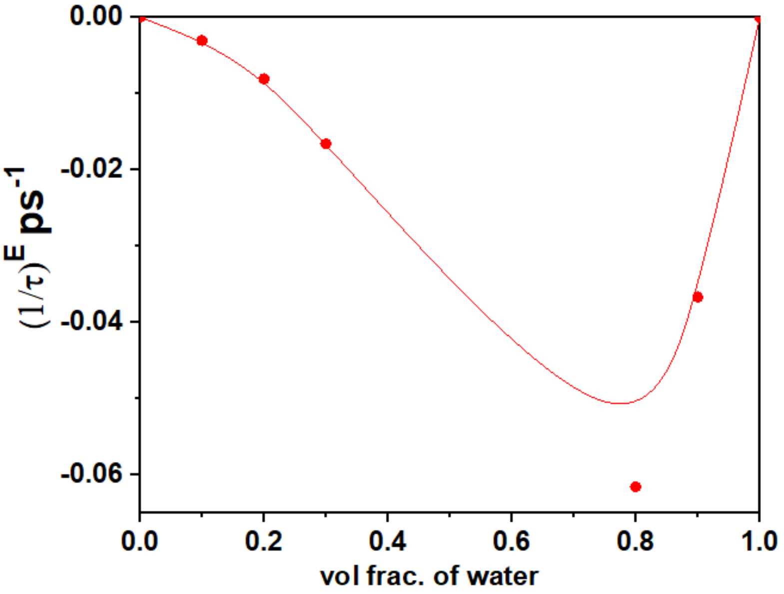
The crucial data regarding the formation of multimeric structures in binary liquid mixtures can be figured out by utilizing excess permittivity (ε^E) [20]. From the figure it is observed that ε^E is negative entire concentration of BTA and WAT mixtures. Negative ε^E indicates that molecules of the mixtures may form multimer structures via hydrogen bonding in such a way that the effective dipole gets reduced. This means that there is an association of BTA and WAT hydrogen bonding with the formation of multimer like structures.

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 [21]. Excess inverse relaxation time is plotted as a function of volume fraction of WAT as shown in figure 3.



This indicates that the addition of BTA to WAT has created a hindering field such that the effective dipole rotates slowly. From figure it can be observed that there is maximum deviation from ideality $(1/\tau)^E = 0$ at 0.8 volume fraction of BTA and WAT binary mixture.

2.3. Kirkwood correlation factor

Static dielectric constant for the mixture can be explained using Kirkwood Frohlich equation as follows [22, 23].

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

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[24, 25] with the assumption that *g* for the binary mixture is expressed by an effective average correlation factor g^{eff} such that

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

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

The dielectric non-ideality of mixtures suggests a random spatial distribution and orientation. In pure alcohols, a self correlation of orientation with strong parallel dipolar alignment exists with *g* values substantially greater than 1. where as in pure BTA the correlation is more likely due to a combination of both parallel and anti parallel orientation. On mixing, we find that (g^{eff}) is composition dependant and greater than unity for all the mixtures studied. Hence it appears that, in the mixtures, there arises a need to assign each molecular species a cavity of its own specific volume which in turn determines the molar orientational polarizability [26]. For all concentration range indicating that in BTA and WAT mixture dipole pairs have been formed in such a way that their orientation is parallel for all volume fractions of BTA in the binary system.

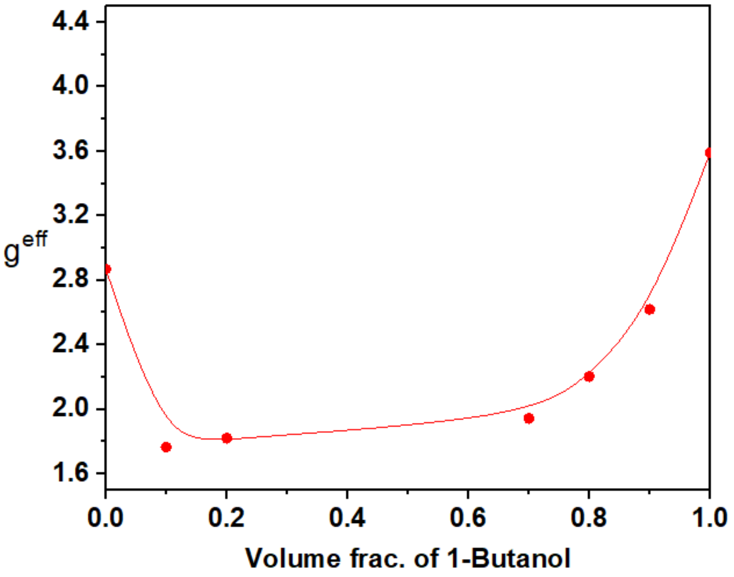


Figure 4: g^{eff} vs volume fraction of water for BTA-WAT binary mixtures at 15°C

2.4.Bruggemann factor

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

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 [28],

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

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

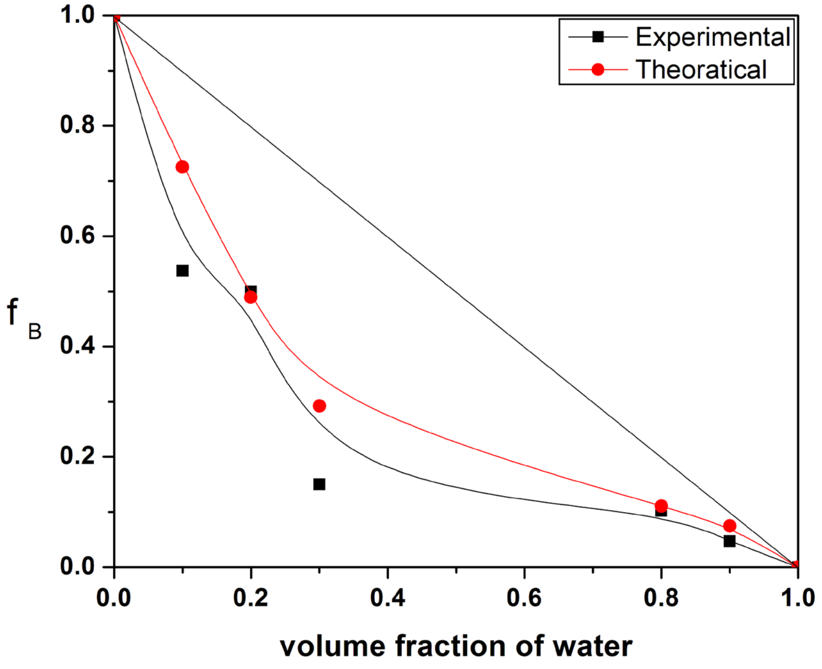


Figure 5: f_B vs volume fraction of water for BTA-WAT binary mixtures at 15°C

The estimated values of f_B are shown in Fig. 5, which shows the nonlinear relation between f_B and WAT. The Bruggemann factor f_B shows a negative deviation around 30% of WAT volume fraction, from the ideal line. This indicates that intermolecular interaction is taking place in the mixture.

The values of ε_0 decreases with addition of BTA in WAT. The τ increases with addition of BTA in WAT, indicates, the intermolecular rotation is the predominant mechanism in the relaxation process, due to the increasing molecular size (carbon chain). Negative ε^E in WAT rich region, indicates, formation of multimers. The $(1/\tau)^E$ values are negative at all temperatures studied, confirms that dipoles rotates slowly in the BTA-WAT binary system. Both BTA and WAT have large intermolecular hydrogen bonding with parallel alignments confirmed by g^{eff} values, but the intermolecular association in BTA molecules is stronger. f_B shows a deviation for all concentrations at 15 ºC, confirms the strong interaction between the molecules of BTA and WAT in the mixtures.

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